During operation at high temperatures, technical alloys inevitably react with the surrounding atmosphere. Therefore, the detailed understanding of oxidation processes is essential for the design of new materials. In the course of the present thesis, oxide scale formation on single-crystalline, $\gamma'$-strengthened Co- and Ni-base model alloys was investigated. Results derived by classical thermogravimetry and sequential exposure to $^{16}\text{O}_2$ were supplemented by various sophisticated, surface analytical techniques. The impact of the two-phase microstructure during the early stages of scale formation could be demonstrated by high-resolution transmission electron microscopy for the ternary Co-Al-W system. Kinetic processes during high-temperature oxidation of ternary model alloys were investigated depending on the W content between 800 and 900 °C. Furthermore, the role of base elements (Co or Ni) was elucidated with the help of another single-crystalline model alloy series. Using the obtained results, the development of diffusion-limiting barrier layers as well as the formation of unwanted phases could be directly correlated to the Co/Ni ratio in the alloy.

Two-stage tracer exchange experiments in $^{16}\text{O}_2$-containing atmospheres were conducted to investigate the transport of reactants through growing oxide scales. Besides counter-current transport of cations and anions along different paths also the development of pores and microchannels was confirmed by the selected experimental approach.
Martin Weiser

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Elementary Mechanisms During the Early Stages of Scale Formation on Single Crystalline Co- and Ni-base Superalloys at High Temperatures

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**M. Weiser,** S. Virtanen, Influence of W content on the oxidation behaviour of ternary $\gamma'$-strengthened Co-base model alloys between 800 and 900 °C, *Submitted to Oxidation of Metals*

**M. Weiser,** R. J. Chater, B. S. Shollock, S. Virtanen, Material transport and microstructural oxide scale evolution during the high-temperature oxidation of Co-base model alloys with alternating $\gamma'$ volume fraction, *Ready for submission*
Abstract

Strengthening of Co-base Superalloys by precipitation of a $\gamma'$ phase in the ternary Co-Al-W system was experimentally confirmed in 2006. Despite notable improvement of mechanical properties due to the addition of alloying elements, the oxidation resistance remained particularly poor above 800 °C.

In the course of the present study, elementary mechanisms during oxide scale formation on single-crystalline, $\gamma'$-strengthened model alloys were investigated. Results derived by classical thermogravimetry were supplemented by various sophisticated, surface analytical techniques. Using the example of a ternary model system, the role of two-phase microstructure during the early stages of scale formation could be characterized with high-resolution. The development and composition of multilayered oxide scales was an important aspect for the understanding of prevailing mechanisms. Kinetic processes during high-temperature oxidation of ternary Co-base model alloys were investigated depending on the W content between 800 and 900 °C. The growth of three individually distinguished layers was approximated with sufficient accuracy using a parabolic rate law for oxidation times longer than 12 h. The low tendency of lateral $\text{Al}_2\text{O}_3$ layer growth in the investigated temperature range remains a factor that limits the oxidation resistance. The transition to slower oxidation rates as a consequence of protective scale growth was only observed in a small number of experiments during the first 100 h of exposure. Reasons for this include the high nucleation rate of alumina precipitates and the rapid progress of internal oxidation in Co-base model alloys.
The transport properties of alloying elements, especially in the region of the alloy/scale-interface comprises another relevant process in understanding the oxidation behavior of alloys. Due to the narrow two-phase region, the availability of Al is further limited. With the help of high-resolution energy dispersive X-ray spectroscopy, depletion of Al along $\gamma$ channels was visualized.

The role of base elements (Co or Ni) was elucidated with the help of another single-crystalline model alloy series. Addition of Cr generally increases the oxidation resistance. Using the obtained results, the development of diffusion-limiting barrier layers as well as the formation of unwanted phases could be directly correlated to the Co/Ni ratio in the alloy. Despite the slower progress of oxidation due to the formation of a Cr-containing diffusion barrier above the internal precipitation region, repeated cracking and subsequent healing of the relatively protective scale section lead to insufficient oxidation properties.

Furthermore, the transport of reactants through growing oxide scales was investigated by means of two-stage tracer exchange experiments in $^{16/18}$O$_2$-containing atmospheres. Counter-current transport of cations and anions along different paths was identified in the outer oxide layer. The development of pores and microchannels between the outer oxide interface and the former alloy surface was confirmed by the selected experimental approach. These pore networks were demonstrated to be a crucial factor for the penetration of internal oxidation fronts into the alloy. After combination of all obtained experimental results, the poor oxidation behavior of Co-base Superalloys can be explained. With the help of the widely understood model systems, useful strategies for the investigation of instantaneous reaction kinetics were discussed. Concluding remarks on detrimental experimental factors, that might reduce the significance of the presented data were provided at the end of the study.
Zusammenfassung


Außerdem wurde der Materialtransport durch Oxidschichten, mit dezierten Oxidationsexperimenten, in sequenzieller 16/18 O₂-Atmosphäre untersucht. Entgegengesetzter Transport von Kationen und Anionen durch die äußeren Oxidschicht entlang unterschiedlicher Pfade konnte belegt werden.

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Symbols

A overall surface area of specimen
B_i mobility of species i
C_i concentration of species i
D diffusion coefficient
\bar{d}_x mean thickness of layer x
e elementary charge
G total/molar Gibbs free energy of reaction
g_t volume fraction of isotope during stage t
\bar{G} partial (molar) free energy
H_f formation enthalpy
if_{18}^{18}O isotopic fraction
j_i flux of particle i
K equilibrium constants
k_B Boltzmann’s constant
k_{i/\gamma/\gamma'} partitioning coefficient between \gamma and \gamma'
k_{inst} instantaneous rate constant
k_p parabolic rate constant (scale thickening)
k_{pqr} parabolic growth rates (estimated from X-\sqrt{t} plots)
k_r rational rate constant
k_w parabolic rate constant (weight gain)
\Delta m weight gain of specimen
Symbols

\( \frac{\Delta m}{A} \) mean value of mass gain per sample area
\( \mu_i \) chemical potential of species \( i \)
n time exponent in power rate law
\( N \) number of columns in SIMS map or experiments per data set
\( n_i \) number of moles
\( n^{\text{inst}} \) instantaneous time exponent
\( N_i \) Mole fraction of \( i \)
\( p_{O_2} \) oxygen partial pressure
\( \phi \) electrical potential
q charge
R general gas constant
S entropy
\( sd(x) \) standard deviation of measurement
T absolute temperature
t time
X layer thickness
\( z_i \) number of component \( i \)
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ADF</td>
<td>annular dark field</td>
</tr>
<tr>
<td>BSE</td>
<td>backscattered electron</td>
</tr>
<tr>
<td>EBSD</td>
<td>electron backscattered diffraction</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EPMA</td>
<td>electron probe micro analysis</td>
</tr>
<tr>
<td>fcc</td>
<td>face centered cubic</td>
</tr>
<tr>
<td>FIB</td>
<td>focused ion beam</td>
</tr>
<tr>
<td>HAADF</td>
<td>high angle angular dark field</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>IF</td>
<td>isotopic fraction</td>
</tr>
<tr>
<td>IOF</td>
<td>internal oxidation front</td>
</tr>
<tr>
<td>IPF</td>
<td>inverse pole figure</td>
</tr>
<tr>
<td>OSI</td>
<td>outer scale interface</td>
</tr>
<tr>
<td>SDD</td>
<td>silicon drift detector</td>
</tr>
<tr>
<td>SE</td>
<td>secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SI</td>
<td>secondary ion</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>SNMS</td>
<td>secondary neutral mass spectroscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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1 Introduction

Increasing the efficiency of gas turbines remains one key challenge in today’s world with the goal of reducing CO$_2$ emission by advancing renewable energy sources while simultaneously sustaining unprecedented high demand for long-distance mobility. Due to their good mechanical performance at high temperatures, especially under creep conditions, Ni-base Superalloys were unchallenged for decades as material for turbine blades in the section of a gas turbine subject to high temperatures. Ni-base Superalloys consist of ten or more elements. Among these elements, Al is of pivotal importance, since it is not only needed for the precipitation of the ordered Ni$_3$Al ($\gamma'$) strengthening phase but also contributes to the high oxidation resistance. Despite all favorable properties, the temperature capability of this class of materials is limited by the solidus temperature of Ni and expected to be close to its maximum [1–3]. Therefore, the need for new alloys that are suitable at even higher temperatures in the harsh environment of a gas turbine is still apparent.

In 2006 the discovery of a hardening phase with L1$_2$ structure in the ternary Co-Al-W system by Sato et al. [4] revived interest in Co-base alloys for high temperature applications abruptly. An exactly 50 °C higher melting point of Co in comparison to Ni as well as promising mechanical properties at elevated temperatures fueled the expectations to reach considerable higher service temperatures in near future. Figure 1.1 shows the crystal structure of pure Co and Ni at elevated temperatures in comparison to the two intermetallic compounds essential for Ni- and Co-base Superalloys, respectively.

Alloys based on Fe and/or Ni are widely used for various application at elevated temperatures since they are capable of bearing high mechanical loads. To properly design these high-temperature alloys, metal consumption and successive phase transformation due to depletion of
elements in regions below the oxide scale have to be considered. The most common strategy to minimize such diffusion-driven processes is to choose alloy compositions able to form protective scales. For this goal, the addition of Al and Cr is known to be most effective. Influential studies that systematically address these phenomena were already published between 1955 and 1965 [5–7]. Alloys with addition of Al and Cr in sufficient amounts were found to show high resistance against oxidation in various environments. Co-base alloys are of minor interest for usage in industry. In certain aggressive environments, where Ni-alloys are prone to form low-melting eutectics, Co-Cr alloys with high amounts of Cr are used [8]. In Figure 1.2 a section of the periodic table mostly displaying transition metals is shown.

Elements that are included in the investigated model alloys are highlighted with an additional entry indicating their stable oxides above 800 °C. As stated above, the rate of metal consumption or its ability to form slow growing oxide scales, is significant for its resistance against oxidation. A summary of oxidation rates for the major oxides formed by the elements contained in the considered model alloys are shown in Figure 1.2. The heaviest element is W, which is needed to stabilize the $\gamma'$ phase in the ternary Co-Al-W system. Despite its high melting point, W can hardly be used in oxygen-containing environments at temperatures above 800 °C. Due to its poor oxidation resistance binary Ni- and Co-W alloys were only rarely addressed in literature.

After over ten years of extensive research, it has to be acknowledged, that the ambitious aim to reach or even exceed the service temperatures of a gas turbine by using Co as base element is still a long way off in the future. Despite higher solidus temperatures [9, 10] and
Figure 1.2: (a) Section of a periodic table highlighting the elements included in the model alloys. (b) Summary of parabolic oxidation rate constants for the pure model alloys constituents Co, Ni, Al, Cr [8].

promising improvement of mechanical properties up to 900 °C [4, 11, 12], the oxidation resistance of these alloys during exposure in air at temperatures over 800 °C remained relatively poor.

The present study aims at providing an essential contribution in understanding the elementary oxidation mechanisms of single- and polycrystalline superalloys at temperatures between 800 and 900 °C. Compared to, for example, mechanical properties and phase stability, oxidation behavior of Co-base Superalloys has only been investigated to a minor extent to date. Significantly inferior resistance against oxidation compared to conventional Ni-base alloys was reported, however reasons for this behavior have rarely been discussed in detail. Understanding the relevant processes leading to drawbacks during exposure can help to exactly overcome these issues, for example, by precise selection of further alloying elements. This in turn may help to minimize the empirical tests of oxidation behavior needed to design more resistant, complex alloy systems.

Relevant elementary mechanisms elucidated by this study include the inability of ternary and quaternary Co-base alloys to form a protective oxide layer especially at temperatures higher than 800 °C, as well as transport processes of oxygen and alloying elements through the oxide scale and in the substrate respectively. The role of the two-phase microstructure of ternary Co-base system, in particular during
the onset of scale formation and the following hours was considered in
detail. Based on its distinct segregation behavior towards the $\gamma'$ phase
in Co-base Superalloys, the role of W in the oxidation behavior was
specifically addressed.

Two dedicated experimental techniques were chosen to provide
insight into the elementary processes during scale formation of a
rather new and unexplored two-phase alloy system. In addition to
thermogravimetric analysis, isotopic tracer experiments was carried
out. The two utilized methods have a comparably long tradition
in high-temperature oxidation research. Even though the particular
strengths of each approach are widely known, they are rarely applied
to the same alloy systems. Results from all experiments are merged
to establish model predictions targeted to describe and explain the
addressed mechanisms.
2 Literature Review

2.1 Fundamentals of high-temperature oxidation

2.1.1 Thermodynamics

Most metals exposed to elevated temperatures in an oxygen-containing environment react with the surrounding gas phase by forming oxides. The observed chemical reaction can be written as \([\text{Me}_{x} \text{O}_{y}]\):

\[
x \text{Me} + \frac{y}{2} \text{O}_2 \rightarrow \text{Me}_x \text{O}_y
\]

(2.1)

A basic concept to determine whether a chemical reaction takes place is to verify if the Gibbs free energy \(\Delta G\) in the given direction reaches negative values. Depending on pressure and temperature, \(\Delta G\) for an isobaric and isothermal reaction (2.1) can be calculated as follows [14]:

\[
\Delta G_{\text{Me}_x \text{O}_y} = H_{\text{Me}_x \text{O}_y} - T \Delta S_{\text{Me}_x \text{O}_y}
\]

(2.2)

where \(H_f\) is the formation enthalpy and \(S\) the entropy of the reaction. Another way to express the change in free energy of formation implies the knowledge of the \(\Delta G^0\), which is the Gibbs free energy of formation at standard conditions. To calculate the change of Gibbs free energy of a chemical reaction, \(\Delta G\) is commonly related directly to the equilibrium constant \(K\) of the very reaction [13, 15]:

\[
\Delta G = \Delta G^0 - RT \ln(K)
\]

(2.3)

with \(\Delta G^0\) expressing the change of Gibbs free energy for all constituents being in its standard condition. The overall change in free energy of a chemical reaction, consisting of at least two components can be
also determined by correlation of all partial (molar) free energies. At isobaric and isothermal conditions, the partial free energy of each component of the system can also be expressed with the chemical potential $\mu_i$ \cite{16}:

$$
\mu_i = \Delta \bar{G} = \left( \frac{\partial G_i}{\partial n_i} \right)_{p,T,n_j \neq i}
$$

(2.4)

where $n_i$ is the number of moles for the respective element. In a chemical equilibrium ($\Delta G = 0$), Equation 2.3 can simplified by transferring the standard free energy to the left side. To calculate the equilibrium constant, the activities of solids are commonly taken as unity. For a gaseous species $i$, activity is replaced by the partial pressure $p_i$. Coming back to the oxidation reaction (compare Equ. 2.1), it is now possible to calculate an oxygen partial pressure at which the metal and oxide are in equilibrium \cite{14}:

$$
\Delta G^0 = -RT \ln \left( \frac{1}{(p_{O_2})^{1/2}} \right)
$$

(2.5)

The oxygen partial pressure at equilibrium between solid and oxide or two oxides is commonly denoted by dissociation pressure. No oxides will form on metals exposed in environments with oxygen partial pressures below the dissociation pressure. For scales composed of more than one oxide, the dissociation pressure is another convenient value to compare thermodynamic stabilities of the involved oxide phases. Since the dissociation pressure is directly connected to the (standard) free energy of an oxidation reaction, the most stable oxide also needs to have the lowest dissociation pressure. In other words, in a multilayered scale on pure metal, the oxide formed directly above the metal will be the thermodynamically more favorable oxide. As indicated in Figure 1.2a, two stable oxides can form on Co during exposure at high temperatures. At 800 °C, due to significantly lower thermodynamic stability, only a relatively thin layer of Co$_3$O$_4$ forms at the outer interface \cite{17}.

Various collections exist, which summarize Gibbs free energies of formations and further relevant thermodynamic data of phases formed at elevated temperatures in diverse environments. For thermodynamic consideration of oxidation reactions on metals and to a limited extend also alloys, the so-called Ellingham/Richardson diagram provides a clear graphic compilation of oxide stabilities over a broad temperature range. In such diagrams, the standard free energies of formation
for oxides, are plotted as function of temperature. Compared to the original representation [14], oxygen partial pressures as well as ratios of CO/CO$_2$ and H$_2$/H$_2$O mixtures are supplemented on additional scales. A presentation of the $\Delta G$ values for selected oxidations, extended by two nitrations are displayed in Figure 2.1.

![Normalized standard free energies of formation for oxides and nitrides (taken from [18, 19]) as function of temperature. Right axis displays equilibrium $p_{O_2}/p_{N_2}$.

Figure 2.1: Normalized standard free energies of formation for oxides and nitrides (taken from [18, 19]) as function of temperature. Right axis displays equilibrium $p_{O_2}/p_{N_2}$.

The choice of presented standard free energies of formation is based on relevance for the following chapters of the present study. In addition to oxides, nitrides are also included since a substantial part of experiments was performed in synthetic air, which contains both gases. $\Delta G$ values were taken from literature [18, 19] and normalized to one mole of gas. With the help of the additional axis on the right side, it is possible to determine dissociation pressures for a given temperature by extending a line connecting the zero point of the
ordinate ($\Delta G = 0$) on the upper left corner and the corresponding $\Delta G_{M_e/M_{e+O_y}}$ value until it reaches the right axis. Despite this helpful information, such common diagrams are generally used to qualitatively compare stabilities of oxides grown on alloys. Furthermore, there are situations, where nitrides form below a closed $\text{Al}_2\text{O}_3$ or $\text{Cr}_2\text{O}_3$ layer [20–23]. These examples precisely illustrate the limitation of exclusive thermodynamic elucidation of high-temperature oxidation processes in air.

### 2.1.2 Oxidation kinetics and material transport

As already indicated above, thermodynamic considerations are not sufficient to understand the complex interplay of metals and more importantly alloys with an oxidizing environment at high temperatures, especially in gas mixtures. For comprehensibility reasons, the following literature review will solely describe processes originating from uptake, transport and reaction of oxygen. These introduced basic concepts are universally applicable to other gaseous species and to complex mixtures of gases.

A blank metallic surface exposed to oxygen-containing atmospheres at elevated temperatures will be instantly covered by a layer of oxygen adsorbed on the surface. Kofstad distinguished the following three stages during the initiation of oxide layer formation [16], ultimately leading to growth of a substantial scale on the metal/alloy surface:

i) oxygen adsorption

ii) formation and lateral growth of nuclei

iii) outward expansion of continuous oxide film

At atmospheric pressures, the first two stages take place within a very narrow time interval. After a closed oxide layer is formed on the surface, transport of reactants through this layer is needed to sustain scale thickening. Compared to the reaction of metal and oxygen, these transport processes are significantly slower and therefore become the rate-determining steps for the overall scale growth.
The most recognized description of oxidation rates at elevated temperatures considering transport processes through a growing scale was postulated by Carl Wagner in 1933 [24]. Besides further assumptions, independent movements of only ions and electrons through a compact, adherent oxide layer, as well as neglectable differences from the perfect oxide stoichiometry are conditions originating his theoretical analysis. Although such conditions are rarely found, Wagner’s theory of oxidation is still widely used to characterize diffusion-driven oxidation processes on metals and alloys [15].

Figure 2.2: a) Diffusion controlled transport through a dense single-phase oxide scale [16]. b) Interfacial processes during scale growth [15, 24].

Figure 2.2a shows relevant transport processes through a single-phase oxide layer $Me_{x}O_{y}$ with instantaneous thickness $\Delta x$. Thermodynamic equilibrium for oxidation and reduction reaction on the interfaces between metal and oxide layer, as well as oxide layer and atmosphere (compare Fig. 2.2b) is assumed. Additionally, gradients of activity established between the metal/oxide and the oxide/gas interface are schematically shown. Movement of particles along an activity gradient proceeds in the direction of the chemical potential gradient. Due to charge separation, a gradient in electrical potential also has to be taken into account. The net driving force for migration of charged particles through a volume increment (with basal plane $q$) of the oxide lattice, is therefore an electrochemical potential gradient [16, 24]. The electrochemical potential is the sum of chemical potential $\mu$ and the electrical potential $\phi$. Consequently, the flux of particles $i$ can be written as:

$$j_i = \frac{dn_i}{dt} = -q c_i B_i \left( \frac{1}{N} \frac{d\mu_i}{dx} + z_i e \frac{d\phi}{dx} \right) \quad (2.6)$$
with $z_i$ number of electrons. For a given temperature, the mobility $B_i$ can be directly transferred into the diffusion coefficient $D_i$ by using the Nernst-Einstein equation [16].

Furthermore, the rate of scale growth for an oxidation reaction as given in Equation 2.1 can be calculated as the quantity of $Me_{x}O_y$ - equivalents per area [16, 24].

$$\frac{dn_{equiv}}{dt} = k_r \frac{1}{\Delta x} \quad (2.7)$$

Based on Equation 2.7, another valid expression for the oxidation rate is the increase of scale thickness $dx$ per time interval $dt$. For this description, the rational rate constant $k_r$ has to be replaced by the parabolic rate constant $k_p'$. Integration ultimately leads to the well-known parabolic dependence of scale thickness $x$ on exposure time $t$:

$$(x)^2 = 2k_p' t + C = k_p t + C \quad (2.8)$$

For exposure of a blank metal ($x = 0$) starting at $t = 0$, the integration constant $C$ is set to zero. A more convenient way to confirm parabolic oxidation rate is to measure the mass gain of a sample with defined surface area over the course of exposure. This experimental approach will later be described in more detail.

### 2.1.3 Oxidation of alloys

To understand the oxidation of alloys, the same basic concepts introduced in the study so far can be used. Due to the higher number of elements that, have to be taken into account, the situation becomes more complex. Still, material transport is a key issue, both in the alloy as well as through the complex oxide scale. Early descriptions of essential differences between the oxidation of metals and alloys were published by Wagner [25]. In the majority of cases, scales grown on alloys are multilayered with two or more oxide phases in the same layer of the scale [26].

To cover the full range of high-temperature oxidation theory is beyond the scope of this study. Instead, selected aspects, helpful to properly interpret the results from the experimental sections are introduced in the following.
2.1 Fundamentals of high-temperature oxidation

2.1.3.1 Multilayered scales and elemental depletion

For the description of scales, the terms *external* and *internal oxide layer* are widely used. Only in a very limited number of cases, the scale during steady-state oxide growth consists of one internal or external oxide layer. In the following, a two-phase multicomponent alloy A-B-X, oxidizing in near atmospheric conditions, is assumed. The minor element B has the highest oxygen affinity. During external scale growth, at least one element of the alloy forms an oxide layer above the original alloy surface. To sustain the growth of this layer, the relevant elements have to be transported towards and, in most cases, through the expanding external scale. By contrast for the formation of internal oxides, oxygen must reach the alloy/scale interface and subsequently dissolve in the alloy first \[13\]. As consequence, minor, alloy components with high oxygen affinity selectively react with the oxygen to form discrete oxide precipitates. The narrow zone including the interface between the deepest formed oxide species and alloy is generally referred to as precipitation \[27\] or internal oxidation front (IOF) \[13, 28\]. In an alloy system containing three and more elements, the appearance of two oxidation fronts by coupled internal oxidation \[29\] could be quantitatively described with help of numerical calculations. Progress of oxidation fronts normal to the original alloy surface are also commonly described by a parabolic rate law. Critical quantities for such theoretical description of internal oxidation are the Diffusion coefficient \(D_O\) and solubility \(N_O\) of oxygen in the alloy \[23, 28–31\]. Various oxidation studies elucidating possible scale morphologies during high-temperature oxidation of multicomponent two-phase alloys can be found in literature \[32–35\]. A summary of different oxidation mechanisms observed for two-phase alloys with exclusive external scale formation are provided in Figure 2.3 \[36\].

In this theoretical treatment, all components of the alloy, A and B being the most reactive components, are included in both phases. Depending on various factors, different oxidation behaviors can be expected. As shown, both phases can participate on the scale growth by either forming a nonuniform scale consisting of the two oxides \(A_nO\) and \(B_mO\) next to each other (Fig. 2.3a) or cooperative formation of a single phase oxide \((AB)_lO\) (Fig. 2.3b). In the last case (Fig. 2.3c), exclusive formation of \(B_mO\) is expected. According to Maak, the amount of B reaching the surface by diffusion has to be the equivalent needed to form \(B_mO\) \[3\]. At a given diffusion coefficient \(D_B\), a critical concentration of
2 Literature Review

Figure 2.3: Schematic representation of oxidation behavior of two-phase alloys with exclusive external scale formation. (a) Independent oxidation of the two phases. (b) Formation of a uniform scale of compound (AB),O. (c) The minor element that is enriched in the second phase acts a reservoir for continuous BO scale \[36\].

B \(N''_B\) can be defined. Due to ongoing diffusion of B to the alloy/scale interface the region below this interface will successively deplete in B \[25\]. For a hypothetical two-phase alloy, where the minor element is particularly enriched in the second phase, depletion in B can lead to dissolution of precipitates in the scale/interface adjoining region of the alloy \[37\]. Evolution of such precipitation free zones are known from studies on the oxidation behavior of conventional single-crystalline Ni-base Superalloys. Following onset of substantial scale growth, the formation of an \(Al_2O_3\) layer leads to depletion in \(\gamma'\) in the region adjoining the scale/alloy interface \[38, 39\].

2.1.3.2 Transition from internal to external scale growth

As mentioned above, transport to the metal/scale interface has been the subject of numerous publications for over 70 years now. Change in the ration diffusion/material fluxes at exactly this interface can lead to a transition from internal to external scale growth \[25, 27, 28, 40, 41\]. This term describes the change from initial, discrete precipitation of an oxide phase towards the formation of a layer, which successively spreads and cover a growing area fraction of the alloy. Despite the slightly misleading name, the external oxide layer is located at the metal/oxide interface.

Most quantities needed for an accurate description of material transports especially in alloys composed of more than two components, are difficult to measure or even predict. This is particularly true
since depletion in alloying elements dynamically alters the composition in regions below the IOF. Therefore, a more qualitative overview of relevant mechanisms is presented in the following.

![Diagram](Image)

**Figure 2.4:** Schematic representation of transport processes and mole fractions of relevant elements close to the IOF [26, 28].

Figure 2.4 shows a representation of diffusion processes in a hypothetical dilute AB alloy forming internal mixed oxides below an external \( A_nO \) scale. In the considered alloy the concentration of the more reactive element \( B \) is too low to instantly form an external scale \( (N^0_B < N'_B) \) as proposed in Figure 2.3c. Nevertheless, the concentration of \( B \) is high enough to sustain a continuous flux of \( B \) at the IOF, needed for the lateral growth of a \( B_mO \) layer. In the course of this study, the lowest concentration of \( B \) at a given temperature that is needed for a transition from internal to external scale growth before reaching steady-state conditions is referred to as \( N'_B \). In Wagner’s classical description, the formation of an external oxide \( B_mO \) is mainly determined by the availability of both species, \( O \) and \( B \) on the IOF. More specifically, the balance between the quantities of \( O \) (\( N_O \)) and \( B \) (\( N_B \)) per given time increment has to ultimately reach the ratio determined by the stoichiometry (\( m \)) of the oxide:

\[
\frac{N_B}{N_O} = m
\]  

(2.9)

Other more recent studies used elemental fluxes \( J \) to describe the same boundary condition for the formation of oxide phases [28]. In addition to the concentrations \( N^0_B \) and \( N^0_O \) diffusion coefficients of the species in the alloy are of crucial importance to estimate the diffusion fluxes
towards the IOF. For the diffusion of \( O \) through the internal oxidation zone, a so-called "blocking-effect" by the already formed \( B_mO \) precipitates, decreasing the diffusion coefficient to \( D^\text{eff}_O \). Suggestions for how to estimate this effective diffusion coefficient can be found in literature \[26, 40, 42\]. Since the progress of internal oxidation follows a parabolic rate law, it has to be noted, that the movement \( dx \) of the IOF per time interval \( dt \) continually decreases. Furthermore, Wagner estimated the oxygen permeability to significantly lower than the diffusion of \( B \) towards the IOF. If this assumption is true, the volume fraction of \( B_mO \) formed per \( dt \) consequently has to increase \[23, 28\]. As recently stated \[28\], another important process is the nucleation of \( B_mO \) precipitates within the alloy. High nucleation rates will definitely lead to the formation of a large number of small particles within the considered time interval. As a consequence, the amount of \( B \) arriving at the IOF during \( dt \) is already consumed before lateral growth of individual \( B_mO \) precipitates can be established.

### 2.1.3.3 Formation of protective scales

As shown in the previous parts, transport processes through the scale are the rate-determining step during oxidation of metals and alloys at elevated temperatures. Among others, applying diffusion-limiting coating-systems, which also act as thermal barriers is a state-of-the-art strategy to minimize the consumption of metal by formation of oxide phases during exposure of structural components at harsh conditions. To ensure the longevity of materials also during potential coating failure in service above 500 °C \[43\], systematic addition of alloying elements is still most commonly used to sustain the properties of the material at least until the next routine maintenance.

In the temperature regime considered in this study, \( Al_2O_3 \) and/or \( Cr_2O_3 \) have been demonstrated to fulfill the basic requirements on a protective scale. Growth rates of both oxides are significantly slower with respect to the majority of base elements used for high-temperature applications (compare Fig. 1.2). Characterized by very high thermodynamic stability, both oxides reveal high melting points \[44\]. However, due to the possible formation of volatile \( CrO_3 \) in near-atmospheric conditions above 1000 °C, usage of chromia-forming alloys is restricted. In the case of \( Al_2O_3 \), spallation and cracking of the protective layer, especially during thermal cycling narrows the field of applications \[44\]. The high thermodynamic stabilities of both
Fundamentals of high-temperature oxidation

Oxides leads to only small deviation from stoichiometry. Above, a low mobility of these defects, even at high temperatures, is assumed [16, 44, 45]. Although numerous studies have proved low diffusivity of various species in protective oxides layers, the exact mechanisms explaining these properties are still subject of extensive discussions (e.g. [46–48]). For the exclusive development of one external Al$_2$O$_3$ or Cr$_2$O$_3$ layer, a sufficiently high amount of the relevant element has to be included in the alloy. Nevertheless, also transition from internal to external scale formation can deliver an acceptable resistance against high-temperature oxidation. With regards to the example of dilute binary Ni-Al and ternary Ni-Cr-Al systems, important mechanisms are discussed.

In his classical highly-acknowledged investigation on the exact scale morphologies and mechanisms Ni-Al during exposure between 900 and 1300 °C, Pettit distinguished between three behaviors [49]. Part of this study is an oxidation map, which summarizes the results of his extensive empirical studies. The oxidation map is demonstrated in Figure 2.5a. Alloy compositions of Group III form one protective Al$_2$O$_3$ layer immediately after exposure, whereas in Group I, no protective layer was observed at all. In the intermediate region a certain amount time is needed before the protective layer at the scale/alloy interface is fully established and protects the alloy.

![Figure 2.5](image)

Figure 2.5: (a) Oxidation map indicating dependency of scale morphologies of dilute Ni-Al alloys from temperature and Al concentration [49]. (b) Schematic view of multilayered oxide scales observed on Group II alloys at 1000 °C during steady-state growth [13].

In the relative broad, crosshatched transition regions, further factors such as surface preparation do not allow for a clear assignment. It can
be seen that the transition between Group I and II is highly dependent upon temperature. For low Al concentrations, higher temperatures are beneficial for the transition from internal to external Al$_2$O$_3$.

In Figure 2.5b schematic cross-sections of a scale grown at 1000 °C can be seen. After steady-state growth is reached, three clearly separated oxide layers are assumed. Oxygen partial pressures for each interface are given [13]. Among others, Hindam and Smeltzer elucidated the transition between oxidation mechanisms during scale formation of Group II alloys in more detail [27, 41]. The consecutive stages ultimately leading to a protective Al$_2$O$_3$ layer can be seen in Figure 2.6.

Figure 2.6: Transient oxidation and subsequent development of a protective Al$_2$O$_3$ layer in dilute Ni-Al alloys [27, 44, 50].

After initiation of scale formation, the stable oxide phases Al$_2$O$_3$ and NiO form at the original alloy surface. Since the amount of Al near the surface is insufficient, NiO starts to overgrow regions, where the slower growing Al$_2$O$_3$ was formed. An external layer of NiO rapidly develops. Transport of oxygen through the scale leads to the formation of discrete Al$_2$O$_3$ precipitates in the alloy. Due to further availability of oxygen, Al$_2$O$_3$ and NiO can form the spinel phase NiAl$_2$O$_4$ in the inner oxidation zone. After a certain time, Al$_2$O$_3$ precipitate impinges, spreading laterally. The availability of Al from the alloy remains rather constant, whereas the availability of oxygen on the IOF successively decreases. Over time, Al$_2$O$_3$ islands initiating from various impingement sites ultimately close to form an Al$_2$O$_3$ layer.
2.1 Fundamentals of high-temperature oxidation

across the whole surface. From this point on, the $\text{Al}_2\text{O}_3$ at the IOF thickness expands by consuming Al from increasingly lower regions of the alloy. The reaction of $\text{Al}_2\text{O}_3$ and NiO to form NiAl$_2$O$_4$ progresses, establishing the scale morphologies, shown in Figure 2.5b is established. At intermediate temperatures, transport processes inside the alloy have a huge impact on the formation of the so-called impingement sites. Since diffusion of light elements, such as Al, is faster along grain boundaries or dislocations [51], alloy grain structure or sample pre-treatment can have a beneficial influence of the formation of protective oxide layers in this temperature range.

Critical amounts of Al needed to sustain protective oxidation properties of an alloy can also be further decreased by adding other elements. The so-called third-element effect was already known before Wagner’s highly-acclaimed explanation from 1965 [7]. Even though the exact elementary processes occurring during the formation of protective scales in Ni-Cr-Al alloys are not fully clarified, the high resistance against corrosion is undisputed. Classical theories attribute oxygen gettering by Cr on the IOF a key role [7, 52, 53]. After reaching steady-state conditions, the multilayered scale of the Ni-Cr-Al model system reveals a Cr-rich layer above the continuous $\text{Al}_2\text{O}_3$ layer on the alloy/scale interface [52, 53]. Another important finding was, that during the transient oxidation of Ni-Cr-Al alloys with intermediate Cr/Al contents, highly irregular growth of protective alumina was observed [52]. Depending on the investigated area of the sample, the progress of $\alpha$-$\text{Al}_2\text{O}_3$ growth was reported to vary considerably.

2.1.4 Oxidation behavior of Co and Co alloys

Scale growth on pure Co is mostly reported to follow a parabolic rate law at high temperatures [7]. Generally CoO, grown at 900 °C, reveals large, columnar grains [54]. At lower temperatures, pure Co is widely known to form a two-layered oxide composed of CoO with a layer of Co$_3$O$_4$ on top [55]. External growth of CoO was shown to be sustained by self-diffusion of Co$^{2+}$ via vacancies for elevated temperatures [7, 54, 56, 57]. A nearly constant grain size of CoO and Co$_3$O$_4$ was reported for the oxidation of pure Co at 800°C [58].

Between 800 and 900 °C, comparable characteristic morphological features are observed in the outer cobalt oxides on binary Co-Al or Co-Cr [5, 59, 60]. Unlike dilute Ni-Al systems, Co-Al alloys were investigated only to a lower extent. Adjacent to a pure CoO layer, the
growth of an inner oxide layer composed of CoO, CoAl$_2$O$_4$ and Al$_2$O$_3$ was reported. A concentration of 13 wt.% (26.4 at.%) stabilized an external Al$_2$O$_3$ layer growth between 800 and 1000 °C [60]. Even though the study only included a comparably narrow range of compositions, it became apparent, that less Al was required to form an external layer at lower temperatures. After addition of 7 wt.% Al, a considerable fraction of the exposed sample surface was already covered by Al$_2$O$_3$-islands. For specimen oxidized at 900 °C, 10 wt.% was needed to form Al$_2$O$_3$ over a comparable fraction of the surface. This behavior is opposite to that of Ni-Al alloys, where higher temperatures decrease the critical Al concentration for a transition from internal to external Al$_2$O$_3$ growth (compare Fig. 2.5). A relatively high degree of porosity in the outer oxide layer as well as spallation of large fractions of the complete oxide scales, revealing a continuous Al$_2$O$_3$, was reported without closer consideration or discussion.

Oxidation resistance of Co-alloys for high-temperature applications is commonly ensured by the addition of relatively large quantities of Cr as alloying element [8]. Kofstad investigated scale growth on Co-Cr alloys between 800 and 1300 °C. The multilayered scales grown in this temperature regime consist of an outer CoO layer, followed by a mixture of CoO, CoCr$_2$O$_4$ and Cr$_2$O$_3$ in the inner oxidation zone. The second Co-containing alloy Co$_3$O$_4$ is only stable below 970 °C and grows on the outer oxide surface as a thin layer. In both layers, a considerable amount of porosity, more pronounced in the outer layer, was reported. The addition of 30 wt.% Cr is needed to exclusively form a stable protective Cr$_2$O$_3$ scale [16, 59, 61–63].

To a smaller extent, the effect of W in ternary, two-phase Co-Cr-W alloys was also investigated [64–66]. The chosen alloy systems for these studies in general already showed initially protective oxidation behavior due to the formation of Cr$_2$O$_3$. In particular for medium Cr contents, a beneficial influence on the oxidation resistance was found between 800 and 1200 °C [64]. The observed trend was opposite of the results obtained for Ni-Cr-W alloys in a comparable temperature regime [66, 67]. Availability of Cr in Co-Cr-W alloys was ensured by the dissolution of a Cr-rich precipitation phase right after exposure. Fundamentally deviating oxidation behavior between Co-Cr-W alloys and comparable Ni-base systems was therefore mainly traced back to their alternating microstructures [66].
A detailed study on the oxidation properties of Co-Cr-Al and Ni-Cr-Al alloys between 1000 and 1200 °C, conducted by Stott et al. revealed significant discrepancies in the required amount of alloying elements needed to achieve protective behavior [68]. Schematic weight gain curves of selected compositions are shown in Figure 2.7.

Figure 2.7: Comparison between oxidation rates of selected Co-Cr-Al and Ni-Cr-Al alloys [68].

Formation of solid protective layers required considerably lower levels of Al and Cr in the case of Ni-base alloys. On the contrary, scales consisting of discrete internal Al$_2$O$_3$ and Cr$_2$O$_3$ precipitates only providing poor resistance against oxidation. After a protective scale could be established, the kinetics of further oxidation reaction are dominated by the transport through the protective layer and therefore, the weight gain curves revealed only marginal differences. The authors concluded that huge differences in the interdiffusion coefficients of Cr and Al in the alloys as well as oxygen solubility are the main reason for the differences in scale formation. Possible scale morphologies that were determined during the extensive experimental studies were provided. Most of the described morphologies are predictable when employing the theory presented so far. An important issue in the case of Co-base alloys was the failure of already established protective oxides, leading to breakaway oxidation and poor reproducibility of the weight gain measurements. Breakaway behavior is characterized by an abrupt and significantly higher increase of sample weight since a now unprotected region of the specimen is suddenly exposed to oxygen. Figure 2.8 summarizes seven different scale morphologies that were observed on Co-Cr-Al alloys.
Figure 2.8: Schematic representation of scale morphologies depending on the composition of Co-Cr-Al alloys after oxidation at 1000 and 1200 °C [68].

To facilitate a classification of experimental results presented in later chapters, actual compositions (in wt.%) are provided in the following. A relatively low level of alloying elements (1% Al and 10-15% Cr) leads to the formation of thick non-protective outer layers, followed by a complex mixture of various oxides in the inner oxidation zone (Type 8). During longer exposure, preferably at 1000 °C, a closed Cr$_2$O$_3$ layer stabilizes above Al$_2$O$_3$ precipitates (Type 7). A protective external Cr$_2$O$_3$ layer, as seen in Type 3 formed at higher Cr contents (30%). Eventually, more pronounced at higher temperatures, the protective layer fails, leading to healing as shown in Type 3. Higher Al levels (4.5%) have a beneficial effect on the growth of external protective layers. In the range of intermediate Cr concentrations (10-15%), mostly Type 1 or Type 2 are observed at 1000 °C. With increasing oxidation temperature, the scale morphology shifts back to multilayered scales of Type 7. The most protective scales (Type 1+2) are predominantly formed on alloys with 28% Cr. Nevertheless, breakdown of the initially protective layers, followed by rapid healing (Type 4) is still possible.
2.1 Fundamentals of high-temperature oxidation

Observation of the L12 hardening phase in the ternary Co-Al-W system investigation of thermophysical properties of alloys based on this system significantly increased. Within these recent research projects, oxidation behavior of γ′-strengthened Co-base alloys (mainly between 800 and 900 °C) was addressed. Klein et al. elucidated scale growth of ternary and higher order polycrystalline two-phase Co-base alloys during up to 500 h isothermal exposure in lab air [69]. All investigated oxide scales revealed a multilayered structure with an outer layer consisting of CoO and Co3O4 growing on top of the original alloy surface. Internal oxidation leads to an inner oxidation zone in which various oxide phases coexist. Growth of a substantially complete Al2O3 layer was observed on the interface between alloy and oxide scale for selected conditions of exposure. Beside the composition of the alloys, temperature as well as the duration of exposure could also make a significant impact on the stabilization of the Al2O3 layer growth.

Representative micrographs of cross-sections grown on a Co9Al9W alloy with the addition of 0.12 at.% B are shown in Figure 2.9.

Figure 2.9: Cross sections of Co-Al-W-B alloy after thermal exposure at a) 900 and b) 800 °C. c) Detailed view of Co3W formed in the course of Al depletion in the region below the Al2O3 layer [69].

Comparable to the behavior of Co-Al and Co-Al-Cr, preferential Al2O3 growth was reported for exposure at 800 °C. Furthermore, addition of 8 at.% Cr was reported to trigger the growth of a protective oxide layer on the internal oxidation front. Phase transformation due to extensive Al depletion in the unoxidized region adjacent to the growing Al2O3 layer was discussed in detail by various authors [10, 70, 71]. The formation of Co3W (compare Fig. 2.9c) is expected to be particularly detrimental for mechanical properties of the Co-base Superalloys and therefore undesired. Even though higher Cr contents were reported to further decrease the stability of the γ/γ′ microstructure [69, 72], oxidation resistance of quaternary Co-base
Superalloys, revealing 10 at.% was demonstrated to further improve. A cross section of a polycrystalline Co7Al7.W10Cr alloy after 196h cyclic oxidation at 800 °C still showed an intact Al2O3 layer [71].

Stabilization of the two-phase microstructure in Co-base Superalloys can be achieved by the addition of further alloying elements. To broaden the γ/γ′ phase field, Ni addition proved to be of high efficacy [73]. Based on this finding, several authors elucidated the oxidation behavior of polycrystalline two-phase Co-Ni-Al-W-Cr alloys [74–76]. The individual composition of the alloys differed widely, nevertheless, every study demonstrated a higher Ni to Co ratios to be beneficial for the formation of a continuous Al2O3 layer at the internal oxidation front after a relatively short transient period.

Successful attempts to foster the formation of protective oxide layers in γ′-strengthened Co-base alloys containing 30 at.% Ni, at temperatures above 800 °C and characterized by a Si content of 2 at.% can be found in the literature [77, 78]. Remarkably the beneficial effect of Si on the oxidation resistance was more pronounced with a simultaneous reduction of the overall W content and showed the best results at 1150 °C. The studies observed full development of the protective Al2O3 layer to establish in a significantly shorter time with increasing temperature. Nevertheless, the oxidation resistant Co-base alloys were characterized by remarkably lower γ′ solvus temperature, which would narrow the temperature range for potential usage. This study demonstrates that already 30 at.% Ni in novel γ/γ′ Co-base Superalloys of a given composition can be sufficient to adapt the oxidation behavior to that of Ni-base alloys. Due to higher phase stability and increased oxidation resistance, Ni addition to Co-base alloys seems to be unavoidable.

2.2 Investigation of high-temperature oxidation mechanisms

2.2.1 Processes during metal-oxygen reactions

Elucidation of elementary mechanisms can only be achieved by diligent experimental design consisting of supplementary methods. In the case of high-temperature oxidation, various processes that have a substantial impact on the overall behavior already take place during the very early stages of scale formation. Starting with adsorption of gas molecules,
the sample surface changes its appearance and physical properties for several times during the initial stages. Kofstad provides a summary of the main aspects, that have to be considered during growth of oxide layers at elevated temperatures [16].

![Figure 2.10](image-url)

**Figure 2.10:** Main aspects of oxidation reactions defined by Kofstad [16] and details related to experimental strategies used in the course of this study.

At temperatures above 800 °C, the period in which separated oxides nuclei grow is relatively short. Nevertheless, observations possible by applying *in situ* approaches at low pressures can provide fascinating insights since the growth of oxides at these initial stages is particularly dependent on surface heterogeneities or crystal orientation [79–81]. Nevertheless, a recent publication on the initiation stages of ternary Co-base Superalloys revealed considerable discrepancies between oxide scales grown during *in situ* oxidation experiments and under ambient pressures [82]. Due to these difficulties, in the following, two experimental approaches were chosen to elucidate aspects of metal-oxygen reaction after a continuous oxide film has formed. The compilation, supplemented by characteristics of experimental set-ups, is replicated in Figure 2.10. Indicated by associated time axes, each
of the selected experimental strategies is particular useful at distinct stages of scale formation over a certain time interval in the course of reaction. Furthermore, the considered processes occur on scales of different length. Detailed consideration of the advantages of the experimental approaches are provided below.

2.2.2 Thermogravimetry and kinetic analysis of mass gain data

Thermogravimetry is an established technique to investigate reactions between metal or alloys and various gases over a wide range of pressures. As demonstrated by Wagner, growth kinetics of dense, adherent single oxide layers are directly related to the weight change of the sample [24]. For these reasons, mass gain of a sample with known surface area $A$ at constant temperature can be assumed to follow a parabolic rate law with exposure time:

$$\left(\frac{\Delta m}{A}\right)^2 = 2k_w t + C$$  \hspace{1cm} (2.10)

In this modified version of Wagner’s classical equation, the parabolic rate constant $k_w$ is often referred to as practical rate constant [15, 24]. Even though Wagner’s idealized conditions are rarely fulfilled, continuous thermogravimetry can provide essential insights into elementary processes during multilayered scale growth. A schematic weight gain curve revealing several characteristic features often detected during isothermal scale formation on alloys is shown in Figure 2.11. In the majority of cases, oxidation of alloys starts with a transient stage. Directly after exposure, a high amount of different oxides grows simultaneously. Therefore, the transient stage is characterized by rapid changes in reaction kinetics and can last from a few minutes to several hundred hours [83]. During steady-state kinetics, only minor changes in the individual layers are expected. This is particularly true if one or more protective layers were established and determine the overall growth rate.

Depending on the substrate, layer detachment can be a common process. Due to strains inside the growing oxide scale, parts can spall off, which consequently leads to an instant decrease of detected mass. After minor spallation during isothermal conditions, growth rates remain generally unaltered. The term breakaway describes the
cracking of an initially protective layer, due to accumulation of growth-stresses inside the scale. Alloys protected by Cr$_2$O$_3$ are particularly prone to suffer from breakaway oxidation [68, 85]. Depending on the composition of the newly exposed specimen section, the protective layer may rapidly heal and only relatively small, sudden increases in weight change are detected. In other cases, where re-formation of protective layers does not occur, substantial amounts of material are consumed by fast-growing oxide species. The reliability of results gained by thermogravimetry is strongly dependent on the construction of the experimental set-up. Important aspects realized in state-of-the-art thermogravimetric analyzers are provided at a later section.

The application of balances that are able to automatically record the obtained data offers a main benefit for the description of prevailing reaction mechanisms during the formation of oxide scales. Continuous monitoring of weight change provides the opportunity not only to detect the details schematically introduced in Figure 2.11, but also to track instantaneous changes in the kinetics of oxidations. Several authors used various treatments of continuously measured mass gain data to reveal instantaneous changes in reaction kinetics. In the following, methods are presented that are particularly useful in locating minor alterations in growth rates that might otherwise remain undetected. During the oxidation of pure Ni, changing grain size distribution in the externally grown NiO layer was reported by several authors to considerably slow down the oxidation rates [86–88].
It is widely accepted that in the temperature range between 700 and 1100 °C, a significant portion of mass transport proceeds along the grain boundaries within the polycrystalline NiO. Consequently, by coarsening of the grain structure in NiO, the parabolic rate constant, commonly used to describe the kinetics of oxide scale formation on pure metals (compare Sec. 2.1.2), decreases with increasing exposure time [87]. To take these alterations into account, Caplan and Graham [86, 89] suggested describing the kinetics more accurately by calculation of an instantaneous rate constant:

\[
k_{w}^{inst} = 2 (\Delta m) \frac{d(\Delta m)}{d(t)}
\] (2.11)

This rate constant \(k_{w}^{inst}\) can be plotted over time to reveal the decline of the oxidation rate with exposure time. Another widely acclaimed process that causes a significant transition from initially fast to slow reaction kinetics is the transformation from \(\theta\) to \(\alpha\)-Al\(_2\)O\(_3\) at temperatures above 900 °C [90, 91]. Diffusion of oxygen in \(\alpha\)-Al\(_2\)O\(_3\) is orders of magnitudes slower and therefore the overall growth rate visibly decreases. In addition, this transition is accompanied by a volume expansion inside the alumina layer, which can lead to cracking [92–94]. Naumenko and Quadakkers demonstrated that both processes the cracking of the foremost protective scale as well as subsequent transformation to protective \(\alpha\)-Al\(_2\)O\(_3\) are strongly dependent on the oxidation temperature and can be seen in the plot of \(k_{w}\) over \(t\) [92, 93].

As an example, Figure 2.12 shows three plots of instantaneous rate constants \(k_{w}\) over oxidation time. In their classical study on the deviation of overall growth rates of alumina formers from the parabolic dependency, such as Fe-Cr-Al during oxidation between 875 and 925 °C, the authors calculated instantaneous rate constants in \(g/cm^4\cdot s\). The specific shape of the \(k_{w}\)-t plot is associated with elementary processes during the growth of protective layers. Particularly interesting is the first increase of \(k_{w}\) after a few hours of oxidation. This increase appears to a different extent at all three investigated temperatures and is explained by the cracking of the initially protective scale and the subsequent exposure of unprotected alloy sections [93]. The decline of \(k_{w}\) towards longer oxidation time is associated to the exclusive growth of \(\alpha\)-Al\(_2\)O\(_3\), which determines the overall growth rate of the oxide scale at a later stage of exposure.
2.2 Investigation of high-temperature oxidation mechanisms

Figure 2.12: Instantaneous rate constants for the isothermal oxidation of Fe-Cr-Al alloys at 875, 900 and 925 °C [92].

The appearance of the previously described processes as well as their duration are strongly temperature-dependent. In a derivative study, the same authors correlated the grain structure of thermally grown alumina layers with the overall kinetics of FeCrAlY alloys [95]. Similar to the previously described processes for pure Ni, the grain size in the Al₂O₃-layer coarsens with ongoing exposure times [96] and therefore cannot be accurately described by a classical parabolic rate law. To overcome these problems, the authors suggested to apply a power rate law to describe the dependency of mass gain \( \Delta m \) and exposure time \( t \) during the growth of Al₂O₃ layers on Fe-Cr-Al-Y alloys:

\[
\Delta m = k t^n
\] (2.12)

For complex oxidation kinetics, the time exponent \( n \) alters in the course of the reaction and can be determined as the slope of the double logarithmic m-t plot. For steady-states in the scale growth, \( n \) remains nearly constant in these graphs. Plotting of instantaneous values of \( n \), referred to as \( n_{inst} \), over the exposure time can therefore be advantageous for locating considerable changes of growth kinetics. A similar treatment was recently used as a starting point for a kinetic-based analysis of the metastable to stable phase transformation occurring during the transient oxidation stage of Ni-base Superalloys exposed to temperatures of 1100 °C [83].
2.2.3 Isotopic tracer exchange experiments in $^{16}\text{O}/^{18}\text{O}$-containing atmospheres

Usage of the stable oxygen isotope $^{18}\text{O}$ to elucidate transport mechanisms in growing scales is a classical experimental approach extensively applied for various materials at a wide range of different temperatures \cite{97-100}. With a natural abundance of 0.203%, $^{18}\text{O}$ plays a minor role in the natural mixture of oxygen isotopes. Gases enriched in $^{18}\text{O}$ can be purchased for a reasonable price. During isotopic tracer experiments samples are subsequently exposed to different oxygen atmospheres at elevated temperatures. After the formation of an initial oxide layer during the first stage, the composition of isotopes in the oxidizing environment is changed. To sustain scale growth, oxygen and/or metal has to be transported to the reactions zone.

Therefore, distribution of oxygen isotopes in the scale gives direct information on transport mechanisms during oxidation. The most commonly used techniques to determine oxygen tracer profiles in oxide layers are secondary ion mass spectroscopy (SIMS) and secondary neutral mass spectroscopy (SNMS). Typically, tracer distribution is measured by depth profiling beginning from the former scale/gas interface. Following two-stage experiments with $^{18}\text{O}$ enrichment during the second step, schematic concentration profiles of oxygen isotopes are typically correlated to six combinations of transport mechanisms \cite{101, 102}. Combination of isotopic tracer experiments with subsequent FIB-SIMS analysis of cross-sections additionally provides the opportunity to directly visualize the diffusion paths of oxygen \cite{103-105}. In Figure 2.13, the widely-used, in-depth schematic $^{18}\text{O}$ concentration profiles are expanded by hypothetical mappings of $^{18}\text{O}$ intensities across a polycrystalline, two-layered oxide scale.

For predominant outward diffusion of metal cations, labeled oxide is found at the outer interface. Exclusive transport of oxygen is generally divided into three sub-cases, depending on the transport mechanism. New oxide growth at the IOF, without traces of $^{18}\text{O}$ within the old oxide was most likely sustained by transport of molecular oxygen through microcracks which can develop during extensive oxide layer expansion. For transport of oxygen anions via diffusion, traces of labeled oxide in the scale that developed after the first stage, can be expected. Diffusion-driven transport of $\text{O}^-\text{-ions}$ proceeds either along grain boundaries or through the lattice.
2.2 Investigation of high-temperature oxidation mechanisms

Figure 2.13: Schematic $^{18}\text{O}$ concentrations profiles and related hypothetical $^{18}\text{O}$ intensity mappings of a scale following two-stage tracer experiments. Six typical transport modes are generally distinguished. Significant amounts of $^{18}\text{O}_2$ were present during the second stage [101, 102].

Simultaneous transport of metal and oxygen in opposite direction is mostly indicated by growth of new oxide phases on both interfaces. In the majority of studies, only minor traces of labeled oxide phases are found in the interior of the oxide scale. These observations can be explained by different predominant paths for material transport. For accurate interpretation of two-stage tracer experiments, the usage of
isotopic fractions instead of measured oxygen intensities was proposed in literature [106]. $^{18}$O isotopic fractions ($\textit{if}_{18}$) can be calculated as the $^{18}$O$^-$ intensity divided by the sum of all detected oxygen isotopes:

$$
\textit{if}_{18} = \frac{^{18}\text{O}^-}{[^{16}\text{O}^- + ^{18}\text{O}^-]} 
$$

Due to its extremely low natural abundance of 0.00037, the third stable oxygen isotope $^{17}$O can be disregarded for this calculation. The maximum depth of concentration profiles recorded in common SIMS devices is limited by the appearance of sputter defects to 10 $\mu$m [105]. Mapping the tracer distribution of mechanically prepared cross-sections also offers the advantage of investigating thicker thermally-grown oxides. The previously described in-depth schematic profiles are strongly idealized cases which may have to be adapted and combined for correct interpretation of oxygen isotopic distribution maps.

2.3 Analysis of scales by secondary ion mass spectroscopy

Characterizations of oxidized specimens with state-of-the-art surface analysis techniques are essential for high validity of the previously described experimental strategies. For a broad overview on most available techniques, the reader is referred to further literature [107]. In addition to electron microscopy, which is well-established and therefore does not need detailed explanation, secondary ion mass spectroscopy (SIMS) is another method that was extensively applied during the course of this study.

The large advantages of SIMS are its high sensitivity and depth resolution. Current SIMS workstations are capable of either visualizing spatial distribution of elements or determining depth profiles of elemental compositions. The most recent SIMS devices can therefore also be used for 3-D reconstruction of the surface-near volume.

A schematic representation of a secondary ion mass spectrometer is displayed in Figure 2.14a. The technique is a combination of material removal, commonly known as sputtering, and subsequent mass spectroscopy. For sputtering, a highly energetic primary ion beam is used. The erosion of material is strongly dependent on the energy and nature of ions (e.g. Bi, Au, Ga, Cs) used to generate the primary ion beam. In the course of interaction, momentum is transferred from
the beam to atoms or molecules on the sample surface. This so-called collision cascade, illustrated in Figure 2.14b, results in displacement of many atoms in surface-near regions. Some of these relocated atoms receive enough energy to move away from the surface [105].

![Diagram](image)

Figure 2.14: (a) Schematic diagram of a conventional SIMS system. (b) Processes induced by sputtering of a solid sample during SIMS [105].

Among the removed particles, secondary electrons are also ejected, facilitating imaging of the surface. Fractions of the sputter products are either positively or negatively charged and are therefore called secondary ions. The ionization yield is defined as the effectiveness of generating charged particles and can be strongly dependent on the nature of material that is sputtered. The secondary ions are attracted to the applied detector. A high vacuum is an essential prerequisite for maximizing the yield of detected ions. Various mass spectrometers such as magnetic sector, time-of-flight, electric radio-frequency quadrupole or a combination of more than one detector are nowadays installed in SIMS devices.

The majority of particles ejected from oxide samples are neutral atoms which cannot be detected by SIMS. In addition to mono atomic ions, positive or negative cluster ions can also be included in the secondary ions, which makes a clear identification of oxide phases using this technique rather challenging. Since the removal of particles is a destructive process, changes of the surface mainly roughening also have to be taken into account.
3 Experimental procedures

3.1 Composition and microstructure of investigated materials

Two sets of Co-base model alloy systems were chosen to systematically elucidate influences of alloy composition on their high-temperature oxidation behavior. Since the central questions which are only addressed on the individual set-ups, there is a high potential for cross-references.

Only single-crystalline alloys were investigated. All rod-shaped single-crystals were casted in a Bridgman investment casting facility at the Institute of Metals Science and Technology (WTM, University of Erlangen-Nürnberg (FAU), Germany). Due to the significant gap between the melting points of Al and W, a Co-Al-W pre-alloy was used as raw material. With the exception of one alloy, addition of unalloyed W to the raw material was not necessary to reach the desired levels of alloy constituents. The diameter of the rods is approximately 11 mm.

After heat treatment consisting of homogenization above the $\gamma'$-solvus temperature and subsequent aging at 900 $^\circ$C for up to 200 h in a vacuum furnace, all samples revealed a two-phase microstructure. Depending on the physical properties of each composition, the heat treatment had to be slightly adjusted. The conducted heat treatments are summarized in Table 3.1.

Table 3.1: Individual heat treatments conducted prior to oxidation experiments.

<table>
<thead>
<tr>
<th>Treatment designation</th>
<th>Homogenization</th>
<th>Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT1a</td>
<td>12 h at 1300 $^\circ$C</td>
<td>200 h at 900 $^\circ$C</td>
</tr>
<tr>
<td>HT1b</td>
<td>24 h at 1300 $^\circ$C</td>
<td>200 h at 900 $^\circ$C</td>
</tr>
<tr>
<td>HT2</td>
<td>12 h at 1250 $^\circ$C</td>
<td>100 h at 900 $^\circ$C</td>
</tr>
</tbody>
</table>
To understand the influence and role of W as an alloying element during scale formation, the ternary Co-Al-W system was cast in three different variations. The composition originally introduced by Sato et al. [4] is used as reference system. Two more compositions, revealing different W contents, with unaltered Al concentration were casted. Deviations from the nominal composition after heat treatment were verified by inductively coupled plasma optical emission spectrometry (ICP-OES). Before measuring, the samples were dissolved. The results are provided in Table 3.2.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Nominal composition</th>
<th>Composition</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7Wsx</td>
<td>Co9Al7W</td>
<td>83.2 9.6 7.2</td>
<td>HT1a</td>
</tr>
<tr>
<td>9Wsx</td>
<td>Co9Al9W</td>
<td>81.3 9.7 9.0</td>
<td>HT1a</td>
</tr>
<tr>
<td>10Wsx</td>
<td>Co9Al10W</td>
<td>80.2 9.7 10.1</td>
<td>HT1b</td>
</tr>
</tbody>
</table>

The heat treatments for the individual model alloy series were chosen according to literature and experience gained at the Institute of General Material Properties (University of Erlangen-Nürnberg (FAU)). The main intention of the heat treatment was to achieve a two-phase microstructure with comparable size of precipitates. In ternary Co-Al-W alloys, W preferentially segregates to the $\gamma'$ cubes. Based on the higher average mass due to the segregation of the heavier alloying element, the precipitates appear bright, whereas the lighter matrix phase is darker in backscattered electron (BSE) micrographs. The lighter element Al was demonstrated to distribute homogeneously across ternary or quaternary Co-base model alloys [10]. Also induced by preferential segregation of W, the volume fraction of $\gamma'$ phase in a ternary Co-Al-W system directly depends on the overall W content. A nearly linear increase from $\gamma'$ volume fraction over W content was reported in literature [109, 110].

Figure 3.1 shows BSE micrographs of the three investigated compositions of the ternary alloy system. The size of $\gamma'$ cubes apparently increases with higher W content. The high W content in 10Wsx makes a homogeneous distribution of all elements extremely difficult. Despite the long homogenization step at 1300 °C, W could not be completely dissolved in the alloy. After heat treatment, the ternary Co-base model alloys with the highest W levels, still exhibits W-rich regions. On the
3.1 Composition and microstructure of investigated materials

Figure 3.1: Microstructure of investigated ternary Co-base model alloys after heat treatment (HT1a).

surface, the shape altered between round to sustained ovals with high aspect ratios. To gain a better impression of distribution and impact on the surrounding microstructure, W-rich precipitates were subject to closer investigation. Figure 3.2a-c shows the BSE micrographs and corresponding EDX measurements of an unoxidized 10Wsx cross-section. EDX analysis indicates an increased W content in the bright phase. The precipitate is surrounded by a volume segment exclusively consisting of $\gamma'$. The adjacent two-phase microstructure appears unaltered from the growth of the unwanted phase. Elemental compositions of the regions marked in the cross-section are summarized in Table 3.3.

Figure 3.2: BSE micrograph showing the microstructure in the surrounding region of a W-rich precipitate (a) and EDX spectra of the points (b-c) marked in (a). (d) Isothermal section of the ternary phase diagram at 1173 K.

The displayed phase revealed a W content of nearly 40 at.%. Referring to the isothermal section of the Co-Al-W ternary phase diagram at 1173 K (Fig. 3.2d), which was published along with the discovery of the $\text{L1}_2$ in the considered system, the precipitate can only be the so-called $\mu$ phase. The surrounding alloy region revealed the expected composition. Since it was not possible to quantify or predict the appearance of these inhomogeneities, their influence on the conducted experiments will be qualitatively discussed in Section 5.3.2.
### Experimental procedures

Table 3.3: Composition (in at.%) acquired from EDX point analysis of precipitate and two-phase microstructure (marked in Fig. 3.2a) found in 10Wsx after heat treatment.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Co</th>
<th>Al</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point b</td>
<td>48.16</td>
<td>11.97</td>
<td>39.87</td>
</tr>
<tr>
<td>Point c</td>
<td>75.60</td>
<td>13.93</td>
<td>10.47</td>
</tr>
</tbody>
</table>

In order to understand the significant differences in oxidation behavior between Co- and Ni-base alloys, another series of model alloys were casted. The samples of the second set of investigated alloys consist of up to five elements. The basis is a quaternary Co-Al-W-Cr alloy, which can be assumed to reveal better resistance against scale formation due to the addition of Cr. To systematically address the role of the respective base element, Co was replaced by Ni in a stepwise manner until a pure Ni-Al-W-Cr alloy was reached. Three intermediate compositions with Co to Ni ratios of 1.5, 1.0 and 0.5 were produced.

For better allocation, the Co fraction with regard to overall content of base element (c(Co)+c(Ni)) is included in the designation used for this alloy series. Again, the actual composition of each alloy was determined by ICP-OES and is provided with all other relevant information in Table 3.4. Alteration of important material properties can already be seen in BSE micrographs of polished samples shown in Figure 3.3.

Table 3.4: Chemical composition in atom percent of the investigated ternary Co/Ni-base model alloys after heat treatment (HT2).

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Nominal composition</th>
<th>Composition Co</th>
<th>Composition Ni</th>
<th>Composition Al</th>
<th>Composition W</th>
<th>Composition Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC100sx</td>
<td>Co9Al8W8Cr</td>
<td>76.7</td>
<td>0</td>
<td>8.6</td>
<td>7.6</td>
<td>7.1</td>
</tr>
<tr>
<td>NC75sx</td>
<td>Co18.75Ni9Al8W8Cr</td>
<td>57.5</td>
<td>19.8</td>
<td>8.5</td>
<td>7.2</td>
<td>7.1</td>
</tr>
<tr>
<td>NC50sx</td>
<td>Co37.5Ni9Al8W8Cr</td>
<td>37.9</td>
<td>38.9</td>
<td>8.5</td>
<td>8.0</td>
<td>6.9</td>
</tr>
<tr>
<td>NC25sx</td>
<td>Co56.25Ni9Al8W8Cr</td>
<td>18.8</td>
<td>58.1</td>
<td>8.4</td>
<td>7.6</td>
<td>7.3</td>
</tr>
<tr>
<td>NC00sx</td>
<td>Ni9Al8W8Cr</td>
<td>0</td>
<td>77.0</td>
<td>8.3</td>
<td>7.7</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The segregation behavior of alloying elements is strongly dependent on the nature of base material. Unlike in pure Co-base alloys, W preferentially segregates in the matrix phase for Ni-base alloys, changing the contrast of the individual phases. In addition the partitioning behavior of W, which inverts due to subsequential replacement of Co by Ni, Al and Cr distributions are also altered between the individual model systems. For all compositions, Al is enriched in the precipitate whereas Cr
3.2 Oxidation experiments in oxygen-containing atmospheres

partitions to the matrix. For this set of alloys, the degree of enrichment increases with higher Co/Ni ratios. Furthermore, the shape of the precipitates change in appearance depending on the Co/Ni ratio. The $\gamma'$ morphology changes from cubic on the Co-rich side to spherical for a Co/Ni ratio of 1 back to cubic in the alloys Ncoosx.

![Microstructure of investigated ternary Co/Ni-base model alloys after heat treatment (HT2).](image)

**Figure 3.3**: Microstructure of investigated ternary Co/Ni-base model alloys after heat treatment (HT2).

### 3.2 Oxidation experiments in oxygen-containing atmospheres

#### 3.2.1 Isothermal oxidation in synthetic air

Isothermal thermogravimetric analyses were conducted using a Setaram Evolution 1650 instrument. The used device is a state-of-the-art assembly of a high-resolution balance with a compact high temperature furnace. A schematic representation of the experimental set-up is shown in Figure 3.4.

Detailed considerations on the interplay between several important factors, which are of exceptional importance for successful mechanistic studies using thermogravimetry, can be found in literature [111]. Besides the selection of atmosphere inside the device, also specimen condition is of crucial importance. Prior to oxidation in the thermogravimetric analyzer, the two head areas of the samples were mechanically ground.
and polished down to 1 µm surface finish. For practical reasons, the edges of the samples were only ground with emery paper (1200 grit size). Following metallographic preparation, the thickness of each sample was measured, and a photo of the nearly circular main area was taken. From these images, the overall sample surface could be determined by measuring the area and perimeter with the image analysis software imageJ.

During the thermogravimetric experiments, the samples are suspended from a high-resolution compensation balance by a cascade of several wires. The lowest wire, directly connected to the sample, is made of Pt. Specimen are positioned in a zone of constant temperature with a height of nearly 3 cm. Directly below the sample, the actual temperature of this zone is continuously measured by a type S thermocouple. During operation, external gas supply ensures a reproducible composition of the atmosphere inside the device. Dry synthetic
3.2 Oxidation experiments in oxygen-containing atmospheres

Air (80% N$_2$ + 20% O$_2$) and Ar are connected via mass flow controller. Rapid alteration of the atmosphere inside the measurement chamber is achieved using a connected rotary vane pump. Evacuation of the whole device, including also the balance measurement head, takes around 10 min. Following this step, the device is purged with one or more of the connected gases at a high flow rate. All described parts are controlled externally by software, which is also used to continuously record the weight change of the sample.

Unless stated otherwise, heating of samples was performed in Ar. In order to ensure only (inevitable) traces of remaining O$_2$ inside the furnace, the atmosphere is repeatedly pumped and refilled with Ar. After reaching the target temperature, the atmosphere inside the chamber is switched to synthetic air. The starting point of the isothermal oxidation is set to correspond to the initiation of air flow. After the atmosphere surrounding the surface reached atmospheric pressure, a constant flow rate of 20 mL/min was used to renew the air continuously.

3.2.2 Two-stage oxidation experiments in $^{16}$O$_2$/$^{18}$O$_2$

Usage of different stable isotopes to trace the position of oxygen in a material system, not only an oxide scale, is a commonly employed technique. Nevertheless, the details of the actual set-up can vary. The experimental rig used for the two-stage oxidation experiments in this study is characterized by the unique capability of recovering the gas-mixture, highly-enriched in $^{18}$O$_2$. For this purpose, sorption pumps based on zeolithe constitute a reservoir able to pump and permanently store the oxygen used during the second stage of oxidation. Details are given in Figure 3.5.

To preserve a high $^{18}$O$_2$ content in the enriched gas, tightness of all vacuum connections is ensured by usage of ConFlat flanges where possible. The inside of the reaction tube is attached via a gate valve to a turbo molecular pump. Besides the $^{18}$O$_2$-containing gas, the quartz tube can be filled with research grade O$_2$ or N$_2$ respectively. N$_2$ mainly serves for purging of the reaction chamber prior and in between the different steps of the oxidation experiments. Samples are placed on a weighing boat in the quartz tube. The temperature inside the constant zone of the tube is directly measured by a thermocouple. Prior to the experiment, the system is evacuated to a pressure below 10$^{-6}$ mbar. The tube is filled with high-purity normal oxygen (>99.995%). The furnace
Figure 3.5: Experimental arrangement used for two-stage tracer exchange experiments.

is heated at constant rate to the target temperature and rolled on the quartz tube. As soon as the target temperature is reached, the first, $^{16}\text{O}$ step starts. The exposure time $t_{^{16}\text{O}}$ considerably exceeded the duration of the second step for all conducted experiments. Between the two steps, the reaction chamber is purged with $\text{N}_2$ and subsequently re-evacuated. Since some oxides tend to spall, the furnace is not moved during the change of atmosphere. The reaction chamber was filled with the $^{18}\text{O}$-containing gas and the second oxidation step proceeded for a time $t_{^{18}\text{O}}$. After the second step and subsequent cooling, the gas from the quartz tube was recovered and permanently trapped by the sorption pumps. To verify the actual amount of $^{18}\text{O}_2$ in the gas mixture, a Si wafer was oxidized in the system and afterwards the $^{16}\text{O}$ to $^{18}\text{O}$ ratio of the grown SiO$_2$ layer was measured by ToF-SIMS. Detailed oxidation times for all two-stage experiments performed during this study are provided in Table 3.5.
Table 3.5: Detailed exposure times of two-stage oxidation experiments between 800 and 900 °C.

<table>
<thead>
<tr>
<th>Designation</th>
<th>( t_{16O} )</th>
<th>( t_{18O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C-24h</td>
<td>18 h</td>
<td>6 h</td>
</tr>
<tr>
<td>850°C-24h</td>
<td>18 h</td>
<td>6 h</td>
</tr>
<tr>
<td>900°C-5h</td>
<td>200 min</td>
<td>100 min</td>
</tr>
<tr>
<td>900°C-24h</td>
<td>18 h</td>
<td>6 h</td>
</tr>
<tr>
<td>900°C-48h</td>
<td>32 h</td>
<td>16 h</td>
</tr>
</tbody>
</table>

3.2.3 Characterization of oxidized specimens

3.2.3.1 Preparation of cross-sections

To provide information on the morphology of oxide scales in the sub-micrometer range, high surface quality prior to analysis is essential. The classical metallographic preparation consisting of mechanical grinding and polishing was only applied to a very limited extent for FIB-SIMS analysis following two-stage tracer experiments. Instead, ion-milling was used for surface finishing of cross-sections. Figure 3.6 illustrates individual steps conducted during the preparation of ion milled cross-sections.

Figure 3.6: Procedure of sample preparation.
The brittle oxide scales were protected by a Ni layer during mechanical preparation. An oversaturated Ni solution was used to deposit the Ni-layers galvanostatically. Pure Ni was connected as anode in a two-electrode set-up. Details on the electrolyte and utilized parameters of the deposition are provided in Figure 3.6. Depending on the selected milling method, different surface grades are required. Cross-sectional milling removes large quantities of surface atoms via perpendicular interaction of the generated Ar ion beam and the edge of the sample. Using a slow speed saw and cutting the specimen in the middle is therefore sufficient to expose a statistical arbitrary region of the grown oxide scale. A drawback of cross-sectional ion milling is the relatively narrow region prepared with the necessary quality for ensuing SEM analysis.

In order to obtain more information on statistics of measured layer thicknesses, a complete cross-section could be prepared with (ion) flat milling. For this mode, a mostly flat surface is needed to minimize the time of irradiation of the specimen by the ion beam. Surface roughening due to alternating sputter rates for individual phases in course of surface-beam interaction can thereby be reduced. Specimens were embedded in epoxy resin and pre-polished to a 1 µm surface finish. The epoxy resin was removed using a strong solvent to exclude evaporation of residual organic species during subsequently applied analysis which would deteriorate the necessary vacuum of the devices. Considerably lower acceleration voltage was used for flat-milling. The irradiation angle between beam and rotating sample surface was kept below 30°. Details of this procedure are summarized in Figure 3.6.

Providing samples with electron transparency, required for TEM investigation, is a complex and time-consuming process. Due to the brittleness of oxide scales, careful handling is even more important. Firstly, two small pieces of the oxidized bulk sample were extracted along the <100> direction using a wire saw. On the external scale surface, a slice of superalloy base material was glued to protect the oxide during the mechanical preparation. The whole stack was clamped into a Titanium TEM sample plate carrier for subsequent one-sided grinding and polishing. After reaching a common height with the plate carrier, a wedge grinding and polishing method (wedge angle of 5-7 °) was applied to the opposite side. The final thinning was performed in different steps by ion milling. In the last step, an acceleration voltage of 1 kV at 5 ° was used for 30 min to reach electron transparency.
3.2 Oxidation experiments in oxygen-containing atmospheres

3.2.3.2 Details of characterization techniques

**Scanning electron microscopy (SEM)**

Morphologies of cross-sections were investigated using a scanning electron microscope (Hitachi FE-SEM S-4800) with cold field emission electron source. An acceleration voltage of 8 keV in combination with an external backscattered electron detector was used. Distances were directly determined from the backscattered SEM micrographs with the imaging software *imageJ*.

**Analytical scanning transmission electron microscopy (STEM)**

Annular Dark Field Scanning TEM (ADF-STEM) was performed on a double-aberration-corrected Titan Themis³ 300 operating at an acceleration voltage of 300 kV. To reveal the different oxides and phases, ADF-STEM was performed under conditions of Z-contrast using a small camera length of 115 mm. The high-resolution STEM-EDX mappings at 300 kV were performed using a Super-X detector incorporating the Bruker ChemiSTEM™ system. The Super-X detector comprises four silicon drift detectors (SDD) symmetrically placed around the optical axis, close to the sample area. All four signals are combined into one spectrum to improve the collection efficiency. More details explaining this system can be found in the literature [112–114].

Part of the EDX results are shown as color coded element distribution maps. For each investigated sample, mappings of the four relevant elements (Co, Al, W and O) are combined into one figure. Due to varying maximum concentrations, the color coding is individually adjusted, with dark blue representing a low and red a high amount (at.%) of the corresponding element.

**FIB-SIMS analysis**

A FEI-FIB200-SIMS instrument was used for the majority of SIMS investigation on cross-sections following two-stage tracer experiments. The device worked at pressures below 1·10⁻⁷ mbar. The FEI quadrupole-based SIMS detector is setup to detect the negative oxygen secondary ions. A gridded channeltron detector was used for gallium beam generated secondary electron (SE) and total positive secondary ion (SI) images of the analyzed sample regions. Prior to the detection of the $^{16}\text{O}^-$ map, the image of the site was recorded as an SI image at the current and pixel resolution used for the subsequent SIMS maps with
3 Experimental procedures

a beam dose of approximately $4 \cdot 10^{14}$ cm$^{-2}$. The $^{16}$O$^-$ SIMS map was always recorded prior to the $^{18}$O$^-$ SIMS map. A 8 times higher dwell time for the acquisition of $^{18}$O$^-$ SIMS maps was necessary to enable comparable intensity levels for the detected oxygen isotopes. Details on the data processing are provided during the presentation results in Section 4.2.1. At the end of each analysis, a third SIMS map was recorded at M/e value of 17.5 amu in order to estimate background signal levels in the detector system associated with stray secondary electrons.

Unless stated otherwise, all presented data were generated from mechanically prepared cross-sections. For two samples, the polished cross-sections were not suitable since the brittle oxide scales suffered severe cracking leading to localized dropout and delamination during the two-stage tracer experiments. For these samples, fresh cross-section surfaces were produced in situ using the gallium FIB beam at a slight angle to the mechanically polished cross-section surface.
4 Results

The intention of all investigations presented in this chapter is to contribute to a fundamental understanding of elementary mechanisms during oxide scale growth on Co- and Ni-base model alloys in way that is as comprehensive as possible. Therefore, a clear distinction between the individual findings is difficult. Experimental design was deliberately chosen to elucidate the overarching mechanistic questions already defined in the introduction of this thesis.

A first reasonable categorization of the presented results is made with regards to the surrounding atmosphere to which the samples were exposed. The majority of experiments were performed in synthetic air. Complementary investigations in pure oxygen with either varying isotopic composition were conducted. The two series of model alloys are considered separately for both experimental approaches. Although the results will be compiled to model predictions in the discussion, occasional cross-references between the investigated two series are already made in this chapter.

4.1 Isothermal oxidation in synthetic air

Based on the available literature covering elucidation of the oxidation behavior of novel γ′-strengthened Co-base Superalloys, the temperature regime for the performed experiments was set between 800 and 900 °C. Reaching acceptable resistance against oxide scale growth at high service temperatures is not the aim of the present study. Furthermore, remarkable and mostly unexplained changes in the oxidation mechanisms of these novel alloys which were reported in literature [69, 70, 115], will be addressed in the necessary detail. The ternary Co-Al-W system, which was originally introduced by Sato et al. [4], revealed particularly poor resistance at 900 °C. This original Sato composition,
including 9 at.% Al and W, was chosen for an initial assessment of prevailing kinetics during individual stages of scale growth at 900 °C. Supervening changes due to varying W content, the addition of Cr and Ni in this temperature window are subjects of the following subsections.

4.1.1 Multilayered oxide scale growth of a ternary Co-base model alloy at 900 °C

The following detailed considerations on the development of multilayered scales on 9Wsx at 900 °C were already published in a separate study that also included TEM-EDX (compare Sec. 4.1.2.4) analysis and model predictions (compare Sec. 5.1). Mass gain data of the ternary 9Wsx during 100 h isothermal oxidation in synthetic air at 900 °C are given in Figure 4.1a. The kinetics of scale formation are subjected to a first examination. Growth rates of initially rapidly oxidizing samples are known to undergo several changes during the so-called transient stages of scale growth. Therefore, a simple parabolic rate law is incapable of accurately describing the time dependence of the weight change. To overcome these limitations, several authors suggested using a power rate law (compare Fig. 2.2.2) for the whole duration of the oxidation experiment as a first approximation of growth kinetics [83, 92, 95, 96].

\[ \Delta m = kt^n \] (4.1)

Mass gain per surface area (\(\Delta m\)) was measured in \(\frac{mg}{cm^2}\). During this study, the exposure time is mostly given in \(h\). With this treatment, it is possible to locate sections of uniform growth rates over the whole range of measured data. As soon as uniform kinetics are obeyed for a considerable period during exposure, the exponent \(n\) is assumed to approach a constant value. The instantaneous values of the exponent (\(n^{inst}\)), depending from the exposure time can be calculated as the deviation of the double-logarithmic plot of mass gain over time. With ongoing duration of oxidation, the measured values decrease successively. Therefore, increments between the considered data points are increased with ongoing progress of oxidation, which decreases the scattering in the \(n^{inst}\)-data.

The instantaneous time exponent is plotted for the whole range of performed oxidation experiments in Figure 4.1b. As noted by several authors, interpretation of instantaneous time exponents is not always straightforward. Nevertheless, this way of treating kinetic data,
4.1 Isothermal oxidation in synthetic air

Figure 4.1: a) Mass gain of 9Wsx during thermal exposure at 900 °C. b) Instantaneous time exponent \( n_{\text{inst}} \) for the duration of exposure [116].

especially supplemented by information on the appearance of cross-sections, can help to locate and isolate changes in the overall kinetics of the scale growth reactions. Expansion of oxide scales at 900 °C is known to be driven by diffusion of reactants. During the first 12 h after the onset of scale formation, the strong decrease of \( n_{\text{inst}} \) reveals a rapid transition to slower oxidation kinetics. Reactants have to diffuse through the scale to sustain growth of the individual oxide layers. Therefore, the overall composition and more specifically, the portion of individually formed oxide phases within the scale are of pivotal importance for the growth kinetics [83]. After this initial period, the change in oxidation kinetics becomes less pronounced. A local maximum around 24 h and a moderate but steady increase of \( n_{\text{inst}} \) after 55 h can be identified. Figure 4.2 shows a series of BSE images documenting the evolution of a multilayered scale grown on the ternary Co-base model alloy 9Wsx.

Figure 4.2: BSE micrographs of multilayered scales on 9Wsx after various durations of exposure at 900 °C in synthetique air [116].
After a sufficiently long duration of exposure, three individual layers can be clearly distinguished. In the following, these layers are referred to as $d_1$, $d_2$ and $d_3$. The outer oxide layer $d_1$ can be assumed to be almost exclusively composed of pure CoO. The overview micrographs (Fig. 4.2) reveal sufficient detail about the size and appearance of this layer. The two layers below exhibit considerably higher complexity and are therefore magnified in Figure 4.3. The three individual distinguished regions are marked as examples on the complete cross section of an oxide scale grown for 100 h. The internal oxidation zone starts below a smooth interface marking the original alloy surface. This zone can be further distinguished into two separate regions $d_2$ and $d_3$. The inner oxide layer ($d_2$) is a fully oxidized section of the scale, where several oxides phases are present alongside each other. This conglomerate of various complex species is followed by $d_3$, which is a region of small precipitates in an unoxidized $\gamma$ matrix. The compositions and nature of each of the mentioned layers are addressed at a later stage of this study. Strictly speaking $d_3$ is present from the onset of internal oxide scale formation. However, it is not possible to clearly distinguish $d_3$ from $d_2$ by SEM before 5 h of oxidation.

![Figure 4.3](image-url): BSE micrographs showing the evolution of internal oxidation zone over the course of exposure at 900 °C in synthetic air [116].

The size of the precipitates is explicitly dependent on the progress of oxidation. The formation of larger precipitates is accompanied by the consumption of alloying elements. As a consequence, the region
4.1 Isothermal oxidation in synthetic air

enclosing the IOF will deplete in these elements. In ternary Co-base Superalloys, the depletion of Al for example was reported to result in the formation of the unfavorable intermetallic DO$_{19}$ phase ($\chi$-Co$_3$W)\cite{10, 70, 71}. Due to their high W content, these phases are easily recognizable in the ternary Co-Al-W system by its bright appearance in BSE micrographs. The first indications of this phase can already be observed after 12 h of oxidation in close proximity of dark precipitates in d$_3$ (compare Fig. 4.3). After sufficiently long oxidation times (>24 h) formation of this new phase can be found further below the IOF. The well-known phase transformation does not contribute to the measured mass gain and presumably has only negligible effect on the diffusion of alloying elements. Therefore, it is not considered to be part of the scale.

Figure 4.4 shows the evolution of the three individual layers over time. The (mean) thickness of each layer was determined from five separated measurements on representative spots of the investigated cross-sections. The results are plotted with the standard deviation as error bars.

![Figure 4.4: Layer thickness as a function of oxidation time at 900 °C. Complete range of considered exposure times with local fits (−−) between [24 h; 100 h]; (b) Evolution of layer thickness at 300 min exposure with local fits (···) between [5 min; 300 min], (c) evolution of layer thickness at 24 h exposure with local fits (−−) between [5 h; 24 h]](116).

As stated, diffusion-controlled growth of each individual oxide layer is assumed. In spite of this assumption, it is not possible to fit the whole range of data points with sufficiently high accuracy for any of the individual layers. Following the suggestions from Hindam and Pieraggi
for oxidation reaction with fast initial kinetics, the classical Wagner was modified in the following way:

\[ X = k_p^{sqr} \cdot \sqrt{t} \]  

(4.2)

The layer thickness \( X \) was measured in \( \mu m \), the time in minutes. To determine \( k_p^{sqr} \) (in \( \mu m \sqrt{\text{min}} \)), \( X - \sqrt{t} \) - data was fitted locally in distinct intervals during scale growth. Three individual local fits, each only taking data from the respective time window into account, were conducted. Following this procedure, significantly less deviation between calculated and measured data could be achieved. The \( k_p^{sqr} \) values are valid in a finite period during exposure. Results along with the chosen time window are summarized in Table 4.1.

Table 4.1: Comparison of estimated parabolic growth rates (\( \frac{\mu m}{\sqrt{\text{min}}} \)) for individual layer growth on 9Wsx at 900 °C from curve fitting (Fig. 4.4).

<table>
<thead>
<tr>
<th>fit interval</th>
<th>( k_p^{sqr} ) (( \frac{\mu m}{\sqrt{\text{min}}} ))</th>
<th>( d_1 )</th>
<th>( d_2 )</th>
<th>( d_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[5 min; 300 min]</td>
<td>0.578</td>
<td>0.466</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[5 h; 24 h]</td>
<td>0.413</td>
<td>0.265</td>
<td>0.366</td>
<td></td>
</tr>
<tr>
<td>[24 h; 100 h]</td>
<td>0.237</td>
<td>0.177</td>
<td>0.240</td>
<td></td>
</tr>
</tbody>
</table>

The determined growth rates were used to recalculate \( X - t \) - curves (dashed lines in Fig. 4.4) for the evolution of layer thickness over time. For reasons of clarity, fits for times smaller than 24 h are shown as separate graphs (Fig. 4.4b and Fig. 4.4c).

It can be seen in Figure 4.4b that the conducted fit is already valid during the first 5 h of oxidation. Therefore, the initial assumption of diffusion-controlled growth during the whole duration of exposure is confirmed by the measured and fitted data of layer thicknesses. The strong decrease of expansion rates \( k_p^{sqr} \) of the distinct layers during the early stages of oxidation coincides well with the substantial decay of \( n^{\text{inst}} \) detected during the first 12 h of scale formation (compare Fig. 4.1b). Calculated growth rates \( k_p^{sqr} \) for all layers decrease with ongoing exposure. The relative decline of \( k_p^{sqr} \) values from each individual layer does not follow one overall dependency. After considerable growth of \( d_3 \) within the internal oxidation zone, the rate constant for the internal precipitation region \( d_3 \) drops by over 40%. Between 5 and 100 h, the \( k_p^{sqr} \) values undergo significantly slower changes. As already mentioned, a zone of oxide precipitates embedded in an unoxidized matrix at the
IOF starts to develop in samples exposed for more than 1 h. At this stage it is difficult to already present an universal explanation for all processes taking place. Mass transport occurs across three differently composed layers, most probably in opposite directions. Therefore, more details about the composition of individually grown layers are needed.

4.1.2 Oxidation behavior of ternary Co-base model alloys with varying W content between 800 and 900 °C

The oxidation behavior of three different ternary Co-base Superalloys was elucidated in detail between 800 and 900 °C. As demonstrated above, the particularly poor resistance at the upper limit of this temperature window against oxidation is an obvious disadvantage for applications of this new class of alloys. As stated during preceding chapters, also the influence of the microstructure of ternary Co-base alloy on the oxide scale growth during isothermal exposure remained relatively unexplored. The already introduced ternary alloy 9Wsx serves as base system for the following studies. Results gained by EPMA investigations are firstly presented to provide an essential understanding of elemental distributions in surface areas affected by oxide film formation. This technique is particularly strong in visualizing enrichment or depletion of elements. One of the most classical experimental approach, thermogravimetry during isothermal exposure and subsequent evaluation of cross-sections is extensively applied to elucidate prevailing kinetics during various stages of scale growth depending on temperature and alloy composition. High-resolution analytical scanning transmission electron microscopy (STEM) was additionally applied to further confirm conclusion drawn by the preceding findings during the elucidation of oxide scale growth. Due to the relatively complex and time-consuming sample preparation, only the introduced base system 9Wsx was selected for this extensive investigations.

4.1.2.1 Oxide scale appearance and elemental distribution after exposure

The multilayered growth of oxide scales demonstrated for 9Wsx exposed at 900 °C in the previous section, was found for the whole range of considered alloy compositions during oxidation between 800 and 900 °C. For better allocation of specific features found in these
complex scales, electron probe microanalysis (EPMA) of representative oxidation-affected regions after 100 h exposure at 900 °C are shown in Figure 4.5.

Figure 4.5: SE micrographs of oxide scales grown on (a) 7Wsx, (b) 9Wsx and (c) 10Wsx during 100 h exposure at 900 °C. Elemental distributions in the marked (–) regions were determined by EPMA.

Additionally, EPMA line scans starting from the outer oxide interface across the entire oxide scales and adjacent oxidation-affected regions, were acquired. Due to the high complexity of the grown scales, especially in the inner oxide layer, the complete set of data for each
Isothermal oxidation in synthetic air

measurement are presented in the appendix of this study (compare Fig. A.1-A.3). The aim of the investigation was to analyze elemental distribution in oxide scales and adjacent regions with high resolution. Therefore, the outer oxide layer $d_1$ was not necessary included to its full extent in each mapping. For all three ternary compositions, only Co and O signal can be seen in $d_1$. The determined Co and O concentrations (compare Fig. A.1-A.3) match the ideally expected value (50 at.%), which can be assigned to CoO. These results are according to literature (compare Sec. 2.1.4) and confirm the assumption made in Section 4.1.1. The complex inner oxide layer was initially defined as conglomerate of various oxides containing all alloying elements could be verified. With EPMA the nature of specific oxide phases in $d_2$ could not be identified. However, it was possible to visualize elemental depletion or segregation over larger regions of the inner oxide layer. The Co which is consumed by the expansion of $d_1$ originates from exactly this layer. For 7Wsx and 9Wsx samples narrow zones with low W signal are observed. The W-depleted zone is clearly recognizable in BSE micrographs by its darker contrast compared to the surrounding scale sections. Below the W-depleted zone follows a region that is enriched in W. For the sample with 7 at.% W alternating zones with enriched and depleted W contents evolved. Oxide phases found in $d_3$ are unequivocal and exclusively $\text{Al}_2\text{O}_3$, confirmed by the O and Al intensity mappings of this layer. Size and appearance of alumina in $d_3$ alter depending on the composition of the substrate. For the alloy revealing the highest W content, larger fractions of the exposed surface are covered by a discontinuous $\text{Al}_2\text{O}_3$ layer. The first indications of considerable alumina growth can be seen approximately 8 $\mu m$ apart from the original alloy surface. Notable below these first, presumably less protective $\text{Al}_2\text{O}_3$ section, broader sample fractions are covered by a still not continuous alumina layer on the $d_2/d_3$ interface. For 9Wsx also the formation of $\text{Al}_2\text{O}_3$ segments is evident, even though to a quite limited extent. After 100 h exposure of 7Wsx at 900 °C, no indications for the onset of $\text{Al}_2\text{O}_3$ growth parallel to the original alloy surface could be found on the investigated cross-sections.

The narrow stability window of the two phase $\gamma/\gamma'$ microstructure was already mentioned several times in the course of this study. Below the IOF, formation of Co$_3$W phases are apparent for the W-rich 10Wsx sample. The regions affected by this undesired phase formation spreads over 15 $\mu m$ into the alloy. Besides these compositional changes, initiated by the diffusion of Al, elemental mappings of this region do not
Results

reveal further considerable depletion of elements. For intermediate W contents of 9 at.%, the formation of larger Co$_3$W islands can be seen is limited to the width of the fractional area covered with alumina segments that are spread perpendicular to the flux of Al. Since in particular this W-rich unwanted phase is easily distinguishable already by bright contrast in BSE micrographs, phase transformation in sub-scale region will be subject to more detailed considerations at a later stage of this study.

Oxide scale cross-sections on ternary Co-base model alloys with varying W content did not reveal apparent differences in the elemental compositions of the individual layers grown during oxidation at 900 °C in synthetic air. Figure 4.6 shows cross-sections and corresponding elemental distributions determined by EPMA of 9Wsx oxidized for 100 h at 800 and 850 °C.

![Figure 4.6: SE micrographs of oxide scales grown on 9Wsx samples during 100 h exposure at (a) 850 and (b) 800 °C. Elemental distributions in the marked (−) regions were determined by EPMA.](image)

In the following the influence of temperature during scale growth is elucidated for 9Wsx samples, revealing the intermediate W content
of the considered ternary Co-base model alloys. The Co/O ratio
determined from individual EPMA point analysis in the outer oxide
layer for oxidation at 800 °C differs from the ideal value of 1 (compare
Fig. A.4) expected for pure CoO. At lower oxidation temperature $d_1$ can
be a mixture of the two stable pure Co oxides (compare Sec. 2.1.4) [55].
Despite considerable differences in the individual layer thicknesses,
also elemental compositions in the inner oxide layer ($d_2$) are highly
comparable to the oxide scale found after 100 h exposure of the same
alloy at 900 °C. The expansion of $d_1$ is sustained by diffusion of
Co originating from the inner oxide layer. This is true for samples
oxidized at 800 and 850 °C. Differences appear in the evolution of
$d_3$. The cross-section displayed in Figure 4.6b is covered over the
full length by a relatively protective Al$_2$O$_3$ layer hindering diffusion of
oxygen further into the alloy. After 100 h oxidation of 9Wsx at 850 °C
(Fig. 4.6a) only part of the sample surface is covered by an alumina
layer. The unprotected regions clearly exhibit an internal precipitation
zone, with simultaneous evolution of a W-depleted region. For both
considered temperatures, the growth of considerable Al$_2$O$_3$ segments
is accompanied by formation of large Co$_3$W islands in the adjacent
regions. Even though, a higher fraction of the sample surface is covered
by alumina after exposure at 800 °C, the region where unwanted W-rich
intermetallic phases grow is less extended into the alloy.

4.1.2.2 Influence of W content on the kinetic of oxide
layer growth

Figure 4.7 shows weight gain data of ternary Co-base alloys continu-
ously recorded during exposure in synthetic air at 900 °C. The increase
in weight is substantial for all samples, even though compositions with
higher W content exhibit significantly lower mass gain over the whole
duration of experiments. All curves revealing comparable underlying
kinetics.

A detailed consideration of changing oxidation rates in the course
of exposure were shown for 9Wsx at the beginning of this chapter
(Sec. 4.1.1). The length of transient oxidation with initially fast weight
gain directly after beginning of scale growth to overall slower oxidation
kinetics strongly depends on the composition of the sample. A long
transient period extending more than 15 h is apparent for 7Wsx. For
higher W contents, the initial period shortens. In the case of 10Wsx,
the slope of mass gain exhibits a first change after approximately 10 h and another considerable alteration of prevailing kinetics after 70 h of oxidation.

Microstructural features associated with elemental distribution of multilayered oxide scales on ternary Co-base alloys after 100 h oxidation at 900 °C were discussed in a preceding section (compare Sec. 4.1.2.1) of this study. At this point it is not necessary to repeat all details. A comparison of high-quality micrographs taken in a field-emission SEM is provided in Figure 4.8.

In the following, time-dependent growth of the individual oxide layers depending on the W content in the ternary model alloys is addressed. The morphology of precipitates in d₃, as well as the evolution of d₂ is of particular interest. After formation, Al₂O₃ layers
are known to act as an effective diffusion barrier with strong influence on the overall kinetics of oxidation processes. The onset of considerable $\text{Al}_2\text{O}_3$ growth parallel to the original sample surface is consequently of high relevance for the explanation of observed changes and features in the weight gain data. Figure 4.9 shows BSE micrographs of the internal oxidation zone of scales formed on ternary Co-base model alloys after 5, 12, 24, 72 and 100 h exposure at 900 °C in synthetic air.

**Figure 4.9:** Development of the internal oxidation zone ($d_2+d_3$) on ternary Co-base model alloys with varying W content during exposure at 900 °C.
The outer oxide layers are only partly included in the topmost part of the micrographs to reveal as much detail on the complex morphology of $d_2$ and $d_3$ as possible. For all investigated compositions, the two layers in the internal oxidation zone are fully developed and recognizable in cross-sections after 5 h exposure at 900 °C. In samples with the highest W content, first indications of Al$_2$O$_3$ sections that cover considerable fractions of the sample can be observed following 5 h exposure at 900 °C. The micrograph taken from the cross-section of 10Wsx after 12 h oxidation at 900 °C exhibits a considerably larger extent of dark-appearing, separated alumina segments. Formation of considerable alumina in $d_3$ is accompanied by the decay of the $\gamma/\gamma'$ structure and growth of bright Co$_3$W needles. Following longer exposure, the extent of alumina segments in the micrographs increases, even though partly uncovered regions can still be seen after 100 h oxidation. For alloys with 7 at.%, no continuous Al$_2$O$_3$ layer was found in any of the investigated cross-sections. The shape of Al$_2$O$_3$ precipitates growing in $d_3$ depends firstly on the duration of exposure and to a certain extent also on the W content in the alloy. The size of the dark appearing precipitates increases with longer times. The needle-shaped phases follow a preferential growth direction, even though a possible correlation to the microstructure was not systematically investigated. The thickness of the precipitates decreases slightly towards the internal oxidation front. The diameter of the precipitates is mostly independent of the composition in the alloy. However, the length of internal alumina phases increases towards higher W contents in the ternary alloys. All findings regarding the morphology of Al$_2$O$_3$ precipitates in $d_3$ can be associated with slower transport of Al and O towards the IOF.

The advantage of data gained by thermogravimetry is the continuous monitoring of changes occurring during parallel growth of the three distinguished sections of the scale. For 9Wsx, it could be demonstrated that the expansion of each individual layer can reasonably be assumed to exhibit a parabolic relationship with increasing duration of exposure. In Figure 4.10, the measured thicknesses for $d_1$, $d_2$ and $d_3$ are plotted against oxidation time.

For scale growth on all investigated ternary Co-base alloy almost steady-state conditions were reached following 12 h of oxidation. Rates of individual layer growth $k_{\text{par}}$ were determined for individual layer thickening between 12 and 100 h exposure depending on the W content in the alloys. The results are summarized in Table 4.2. Using the
4.1 Isothermal oxidation in synthetic air

**Figure 4.10:** Increase in individual layer thickness on ternary Co-base model alloys at 900 °C in synthetic air as a function of exposure time. Results for the prediction of layer thicknesses (Equ. 4.2) are shown as dashed lines. The individual layers (a) \(d_1\), (b) \(d_2\) and (c) \(d_3\) are plotted separately.

determined values, the expected layer thicknesses for parabolic growth, which depended on the sample composition, were calculated according to Equation 4.2 for the whole duration of exposure. Predicted layer thicknesses time are added as (dashed) lines to the experimentally determined data in Figure 4.10.

**Table 4.2:** Comparison of growth rates \((\mu m/\sqrt{min})\) for individual layer growth on ternary Co-base model alloys at 900 °C from curve fitting (Fig. 4.10).

<table>
<thead>
<tr>
<th>specimen</th>
<th>fit interval</th>
<th>(k_{sp}^{sqr}) ((\mu m/\sqrt{min}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(d_1)</td>
</tr>
<tr>
<td>7Wsx</td>
<td>[12 h; 100 h]</td>
<td>0.89</td>
</tr>
<tr>
<td>9Wsx</td>
<td>[12 h; 100 h]</td>
<td>0.24</td>
</tr>
<tr>
<td>10sx</td>
<td>[12 h; 100 h]</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The calculated fits correspond to a high degree with the dimensions of the outer oxide layers for all compositions. Deviation from the measured values increases for \(d_2\) and \(d_3\) in particular with increasing W content. Unlike the insights provided by thermogravimetry data, these estimated parabolic expansion rates for the increase of layer thickness include mainly information on the protective properties of each sample composition at the investigated temperature. Transition from internal to external \(Al_2O_3\) layer growth was not completed for any of the tested samples after 100 h oxidation at 900 °C. However, a considerable fraction of the surface was covered by isolated alumina segments. These inhomogeneities mainly explain deviation from an ideal kinetic description and are partly reflected in the rather large error bars, especially for longer times. Additionally, scattering increases
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for layers in the internal oxidation zone, since a direct and immediate influence of Al$_2$O$_3$ sections on the thickness of d$_2$ or d$_3$ can be expected. Low W content not only leads to faster overall growth kinetics, but also favors the growth of the inner oxide layer d$_2$, whereas even after 100 h oxidation, the internal precipitation region is developed to a minor extent. An initial interpretation might be an either higher susceptibility of 7Wsx for the formation of all kinds of internal oxides or the presence of considerably larger extents of oxygen at the d$_2$/d$_3$ interface. Nevertheless, the rate constants for each individual layer decreases with increasing W content. For model alloys containing 9 and 10 at.% W, the d$_3$ growth is faster than that of d$_2$. Comparing the estimated k$_{p}^{sqr}$ values between the investigated compositions, the growth kinetics of outer oxide layers reflects the same trend already seen in the thermogravimetric data. Expansion of this layer has to be correlated with an outward flux of Co, which evidently depends on the W level in the alloy. The impact of W content on the expansion of d$_3$ is less pronounced. However, the penetration of oxygen into the alloy has to be attributed to the growth of d$_2$ and d$_3$, which then leads to a comparable dependency of the W content as seen in the expansion of the outer oxide layer. For 7 at.% W, the thickness of the inner oxide layer increases considerably faster than the internal precipitation region. For higher W contents, a reverse trend can be found.

A considerable impact of oxidation temperature on the extent of transverse Al$_2$O$_3$ segments was demonstrated by EPMA measurements (compare Sec. [4.1.2.1]). Continuous monitoring of mass gain can indicate deviation from the rapid initial rate of scale formation to significantly slower kinetics due to the partial blocking of reactant transport. The extent of transverse Al$_2$O$_3$ segments covering the exposed specimen surface and the expansion of this scale parallel to the original sample surface can exhibit drastic variation depending on exposure temperature and alloy composition. The reasons for this phenomenon were discussed using the example of binary alumina formers in Section [2.1.3.2]. The mass gain of ternary Co-base model alloys at 850 °C are shown in Figure [4.11].

Due to evident scattering in the data recorded for 10Wsx, the measurements for the maximum duration of exposure were repeated 3 times. Standard deviations between the available data are indicated by error bars. For sake of clarity, three durations, namely 12, 68 and 100 h were selected to develop a general impression of how these deviations
4.1 Isothermal oxidation in synthetic air

Figure 4.11: Mass gain of ternary Co-base model alloys during 100 h oxidation at 850 °C in synthetic air. For 10Wsx, the average of 3 measurements, including standard deviation as error bars (3 selected values) of exposure is displayed.

evolve over the oxidation process. Independent of relative variance in the measured weight change, samples including 10 at.% W exhibit the lowest mass gain of the three tested alloys. For this composition the slope of the average curve shows a considerable decrease already during the early stage, before 10 h of exposure. Beyond 70 h of oxidation, the rate of mass gain increases evidently. At 850 °C, alloys with lower W levels reveal significant higher mass gain over the course of experiment.

The deviation between 9Wsx and 10Wsx is more pronounced at this temperature. For lower W contents, oxidation proceeds almost unaltered during the 100 h experiments. The sample reaches a maximum mass gain of approximately \(10 \frac{mg}{cm^2}\). Similar to the findings at 900 °C, the evident transitions in weight gain rates might be associated to the development of transverse Al\(_2\)O\(_3\) segments at the IOF. Cross-sections of oxidized ternary Co-base model alloys after 100 h exposure are shown in Figure 4.12.

For all compositions, the displayed multilayered scales reveal the same features already visible after oxidation at 900 °C. The overall thickness of the scales decreases. A different extent of transverse alumina can be seen on the IOF. The micrographs are representative sections of the oxide scales seen after thermogravimetry. At 850 °C, scale morphologies exhibit less dependency on the W content in the alloy. Formation of transverse Al\(_2\)O\(_3\) sections within the internal oxidation zone can be found on all samples. The specimen with 7 and
9 at.% W exhibit a wide inner oxide layer. After 100 h exposure at 900 °C, only minor parts of the specimen surface were covered by alumina. As already indicated by the scattering in the mass gain data and during the investigation of cross-sections, inconsistent oxidation behavior was observed. Even though selected samples exhibited significantly higher number of transverse alumina section, only representative cross-sections are displayed in the Figure 4.12 and 4.13. Since the samples without a wide Al₂O₃ sections in the oxide scale also revealed significantly slower scale growth, this deviant behavior is discussed in detail at a later section of this study. The dimensions of the multilayered scales demonstrate the same trend already observed in the thermogravimetric data for exposure at 850 °C. However it has to be conceded, that lower W content considerably facilitates the internal oxidation.

Figure 4.13 shows cross-sections at different stages of scale growth, supporting the conclusions determined by continuous thermogravimetry. For better comparability, the same durations of exposure are considered as for 900 °C. Micrographs taken from 7Wsx and 9Wsx exhibit a narrow W-depleted region, which was also apparent at higher oxidation temperatures. For specimens with 10 at.% W, occasional indications of considerable alumina segments could already be observed after 5 and 12 h exposure. Larger parts of the sample are covered by Al₂O₃ at 72 h oxidation. For lower W contents, considerable Al₂O₃ sections were only recognized after the maximum duration of scale growth. Additionally, the IOF for 7Wsx after 100 h oxidation reveals a rather irregular course which is not apparent at higher W levels. Furthermore, oxide scales grown on 7Wsx were increasingly vulnerable to cracking. Higher porosity might be the cause of this brittleness. However, it is not possible to state at which stage these cracks develop. The most probable
Figure 4.13: Development of the internal oxidation zone \((d_2+d_3)\) on ternary Co-base model alloys with varying W content during exposure at 850 °C.

causes are strains during cooling or metallographic preparation of cross-sections. Since samples with low W contents were especially prone to spallation or at least crack formation after cooling, mechanistic reasons for this behavior cannot be excluded. The impact of exposure temperature on the oxidation mechanisms of multinary alloys is highly complex. In addition to overall growth kinetics, the ratio between the flux of reactants also alters. An estimate of this flux is again based on rate
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constants of individual layer growth determined from the micrographs of cross-section.

Figure 4.14 displays the increase in the individual layer thickness with oxidation time. For all compositions, nearly steady state conditions were assumed after 12 h of exposure. Values for $k_p$ were determined by linear fits of the layer thickness over $\sqrt{t}$. Using Equation 2.8, layer thicknesses were estimated for a continuous growth progress over the complete duration of oxidation. Originating $k_{sqr}$ values for the calculation are summarized in Table 4.3.

![Figure 4.14](image)

**Figure 4.14:** Increase in individual layer thickness on ternary Co-base model alloys at 850 °C in synthetic air as a function of exposure time. The individual layers (a) $d_1$, (b) $d_2$ and (c) $d_3$ are plotted separately.

For specimen oxidized at 850 °C the deviation between the calculated, expected layer thicknesses and the measured values slightly increases compared to the exposures at 900 °C. Most likely, this lower accuracy can be explained by a change in transport mechanism towards longer oxidation times, already apparent in the continuous recorded mass gain data for all compositions. Interestingly, the measured values for 7Wsx and 9Wsx after 72 h oxidation considerably deviate from the approximated continuous increase of layer thicknesses.

**Table 4.3:** Comparison of growth rates ($\mu m \sqrt{min}$) for individual layer growth on ternary Co-base model alloys at 850 °C from curve fitting (Fig. 4.14).

<table>
<thead>
<tr>
<th>specimen</th>
<th>fit interval</th>
<th>$k_{sqr}$ ($\mu m \sqrt{min}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_1$</td>
<td>$d_2$</td>
</tr>
<tr>
<td>7Wsx</td>
<td>[12 h; 100 h]</td>
<td>0.68</td>
</tr>
<tr>
<td>9Wsx</td>
<td>[12 h; 100 h]</td>
<td>0.32</td>
</tr>
<tr>
<td>10sx</td>
<td>[12 h; 100 h]</td>
<td>0.16</td>
</tr>
</tbody>
</table>
4.1 Isothermal oxidation in synthetic air

Again, the expansion of layers reflects a similar dependency on the W content in the alloy as the weight gain data already revealed. One reason explaining the particularly low $k_{p}^{sqr}$ value for $d_3$ growth is the significant amount of Al$_2$O$_3$ segments found on the $d_2/d_3$ interface. The micrographs as well as the kinetic data confirm that the transition from internal to external alumina growth on ternary Co-base alloys is not complete after 100 h exposure. However, the onset of the desired mechanistic change is found at a considerably earlier stage for all investigated alloys. Thermogravimetric data of ternary Co-base model alloys during exposure in synthetic air at 800 °C are displayed in Figure 4.15. Samples with high W content revealed slight differences in mass gain, especially between 12 and 80 h oxidation. Average weight gain data, originating from 2 measurements including error bars for the standard deviation after chosen exposure times are displayed. For this limited number of experiments, no statistically sound evaluation can be conducted. Nevertheless, they provide additional information that would go unnoticed by just showing one representative measurement.

![Figure 4.15: Mass gain of ternary Co-base model alloys during 100 h oxidation at 800 °C in synthetic air. For 10Wsx, the average of 3 measurements, including standard deviation as error bars (3 selected values) of exposure is displayed.](image)

After 100 h oxidation at 800 °C, overall mass gain of 7Wsx and 9Wsx is considerably lower than at 850 °C. For samples with 10 at.% W, the total increase in weight per area after the maximum duration of the experiment reaches almost the same value for the two temperatures. The initially fast oxidation rates, which undergo an apparent decline
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observed at 850 °C during the early exposure periods, are not evident at 800 °C. In contrast, a rather moderate increase of weight over a period of more than 30 h can be observed at the lowest investigated temperature. However, the data for 9Wsx and 10Wsx exhibit an evident transition towards slower oxidation kinetics. In the case of 7Wsx, the mass significantly increases during the first 2 h. After this short initiation period, no further considerable decline is visible over the course of exposure. On the contrary, the slope of the weight gain curve seems to slightly increase between approximately 80 h until the end of the experiment. Cross-sections of ternary Co-base alloys oxidized at 800 °C for 100 h are displayed in Figure 4.16.

As already indicated by the EPMA investigations, continuous Al₂O₃ is formed after 100 h exposure on samples containing 9 at.% W. For lower W levels, the IOF is also completely covered by a continuous diffusion-limiting alumina layer. The surface of 10Wsx is only partly by transverse Al₂O₃ sections. Considerable alumina formation is accompanied by the growth of W-rich secondary phases. In the case of 7Wsx and 9Wsx, the curved interface between oxide scale and alloy indicates a comparably long duration between initiation and completion of a continuous diffusion-limiting barrier layer.

Confirmatory evidence for an early development of an Al₂O₃ layer at the d₂/d₃ interface can be depicted by reviewing the evolution of the internal oxidation zone after intermediate durations of thermal exposure. Electron micrographs for all ternary Co-base model alloys after 5, 12, 24, 72 and 100h are summarized in Figure 4.16.

After 5 h oxidation, the appearance of the inner oxide layer for low and intermediate W levels seems to depict the initial two-phase microstructure still visible in the unoxidized regions, also included in the micrographs. For all compositions, Al₂O₃ precipitates are

Figure 4.16: BSE micrographs of oxide scales on all ternary Co-base model alloys after 100 h exposure at 800 °C.
considerable shorter than at higher temperatures. The expansion of d₃ for 9 and 10 at.% W after 5 h oxidation reaches 350 nm and is therefore difficult to even recognize within the displayed micrographs of the scales. Larger internal alumina precipitates developed for longer times in the sample containing the highest W content. The IOF of 7Wsx and 9Wsx reveal unaltered morphology of Al₂O₃ precipitates until a continuous layer spreads over the d₂/d₃ interface. After 12 h exposure, all distinguished layers of the scale are developed to a larger
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extent. For 9Wsx, a short section of transverse Al\(_2\)O\(_3\) is displayed in the lower-left corner of the micrograph. Even though not included at the shown scale after 24 h oxidation, isolated sections were also found for this duration of exposure at 800 °C. For oxidized 7Wsx and 9Wsx samples, considerable spreading of Al\(_2\)O\(_3\) can be observed following longer oxidation. In the course of exposure Al-containing precipitates grow together and form larger, transverse alumina sections. After 72 h exposure at 800 °C, discontinuous Al\(_2\)O\(_3\) sections covers the sample surface to a considerable amount for these compositions. Only significantly shorter sections of alumina were found on samples revealing the highest W content. After 100 h exposure, the cross-sections for low and intermediate W levels are covered by a nearly-continuous alumina layer. Due to the barrier properties, no internal precipitate region formed.

Due to the limited number of data points, as a consequence of considerable formation of alumina, layer growth kinetics of d\(_3\) are not estimated for 7Wsx and 9Wsx at 800 °C. All measured layer thicknesses and the conducted fittings of growth kinetics are presented in Figure 4.18.

![Figure 4.18](image)

**Figure 4.18:** Increase in individual layer thickness on ternary Co-base model alloys at 800 °C in synthetic air as function of exposure time. The individual layers (a) d\(_1\), (b) d\(_2\) and (c) d\(_3\) are plotted separately.

Growth rates for the outer and inner oxide layer as well as the internal precipitation region developed on 10Wsx alloys were determined by the previously described procedure. For 7Wsx, another oxidation experiment over a duration of 84 h was conducted at 800 °C. The cross-section of this sample showed an almost fully developed Al\(_2\)O\(_3\) layer on the IOF. The values for individual layer expansion after 84 h were added to the analysis, since it will definitely increase the accuracy of the conducted fits. Internal oxidation zones for samples on which
a continuous alumina layer develop over a comparably long duration of exposure are naturally quite uneven. Growth rates significantly decrease on regions covered by Al₂O₃ sections, whereas the expansion of d₂ and d₃ proceeds at unaltered rates in the remaining samples. These processes are reflected in a curved interface and high scattering in the determined d₂ and d₃ values for longer durations of exposure. The calculated rate constants for individual layer growth are more than two times higher for 7Wsx than for the alloys with higher W levels. Standard deviations for the measured d₂ values for 7Wsx and 9Wsx reflect a long transition period between internal and external alumina growth. Astonishingly, it was still possible to achieve a reasonable fit quality using the d₂/d₃-mean thicknesses grown on samples with low and intermediate W content. The rather accurate fits suggest that this transformation may be completed shortly before reaching the maximum duration of exposure. Furthermore, this could also be the reason for the absence of an evident decline in the weight gain curve of 7Wsx, whereas the transition is clearly visible for samples with 9 at.% W. At 800 °C, expansion of outer and inner oxide layers reaches comparable values. Although also the growth of d₃ has to be considered for the accurate description of oxygen penetration through the scale, it demonstrates a fundamental difference between growth kinetics of external and internal oxidation from the exposure temperature. A huge variety of processes directly influences the oxidation kinetics of each individual layer. An unequivocal explanation for this evident change in temperature dependence is therefore rather difficult.

Table 4.4: Comparison of growth rates (µm/√min) for individual layer growth on ternary Co-base model alloys at 800 °C from curve fitting (Fig. 4.18).

<table>
<thead>
<tr>
<th>specimen</th>
<th>fit interval</th>
<th>k²</th>
<th>d₁</th>
<th>d₂</th>
<th>d₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>7Wsx</td>
<td>[12 h; 100 h]</td>
<td>0.37</td>
<td>0.34</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>9Wsx</td>
<td>[12 h; 100 h]</td>
<td>0.15</td>
<td>0.13</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>10sx</td>
<td>[12 h; 100 h]</td>
<td>0.12</td>
<td>0.11</td>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>
4.1.2.3 Evolution of grain structure in the outer oxide layer

For pure Ni, the instantaneous growth kinetics could be correlated to the evolution of grain structure in the externally grown oxide [86–89]. The coarsening of grains generally results in a decrease of oxidation rate. At 900 °C, the evident decay of the initially rapid reaction kinetics to moderate almost steady-state conditions occurred for 9Wsx during the first 12 h of exposure (compare Fig. 4.1b). The rapid expansion of the outer oxide layer of all ternary Co-base model alloys can be one reason for this pronounced changes. The grain structure of the outer oxide layer, that developed on 9Wsx during exposure between 800 and 900 °C is documented by electron backscattered diffraction (EBSD) measurements of the relevant scale sections. Inverse pole figure (IPF) maps of the CoO layer after 30 min and 5 h of oxidation are provided in Figure 4.19.

![IPF map of externally grown CoO layers on 9Wsx during (a) 30 min and (b) 5 h exposure at 900 °C in synthetic air. (c) Stereographic triangle for CoO.](image)

Following 30 min oxidation, the outer oxide layer consist of many grains with a maximum diameter of approximately 5 μm. Directly above the original alloy surface, a comparably thin (< 2 μm) layer of equally oriented small grains can be observed. Above this layer, significant porosity impedes the assignment of measurement spots to grain orientations. The size of grains that developed closer to the outer scale interface decreases. Already after 5 h of exposure, the displayed oxide scale section is dominated by a few large grains. Above the original alloy surface, an approximately 5 μm thick layer
composed of equiaxed grains was observed. The following layer of coarse columnar grains is separated from the inner fine-grained region by evident porosity. At the outer scale interface, the nucleation of new, relatively small grains could be observed.

In Figure 4.20, IPF maps of d1 after 12 and 100 h exposure are displayed. The investigated regions exhibit a comparable sequences of a (fine) inner layer, that is followed by a columnar outer layer. In the outer oxide layer, considerable porosity is found along grain boundaries after 12 h oxidation. Following the maximum duration of exposure, small grains at the outer interface of the columnar layer are no longer visible. Individual grains in the columnar section of the outer oxide layer revealed larger width, whereas the diameter of grains after 5 and 12 h reached comparable values. However, the height of the inner, fine-grained layer remained constant between 5 and 100 h exposure. As pointed out by Atkinson and co-workers, the equiaxial nature of this inner layer is strongly influenced by the substrate [118].

![Figure 4.20: IPF map of externally grown CoO layers on 9Wsx during (a) 12 h and (b) 100 h exposure at 900 °C in synthetic air. (c) Stereographic triangle for CoO.](image)

The characteristic grain structure in the outer oxide layer on 9Wsx, that is found after 5 h oxidation at 900 °C and beyond is generally referred to as duplex oxide scale. As pointed out in literature, rapid expansion of oxide layers favor the evolution of duplex scales on pure metal and alloys [119]. Furthermore, theoretical predictions as well as various experimental proofs correlate the evolution of duplex structures to fast outward diffusion of metal cations during the external growth of
scales [88, 120, 21]. During early stages of scale growth, a higher number of cations are available on the outer interface. Consequently, formation of new oxide sections proceeds rapidly. During this stage, the high nucleation rate leads to new grains without preferential orientation at the outer oxide interface. For longer times, the nucleation rate subsequently decreases since the extension of existing oxide lattice is energetically favorable. Evolution of duplex scales is also related to the formation of microchannels between individual grains [120, 122]. These microchannels can be of vital importance for the transport of reactants and are discussed separately in Section 5.1.3 after the presentation of all results.

As demonstrated in Section 4.1.2.2, expansion kinetics of outer oxide layers proceeds significantly slower at temperatures below 900 °C. To verify, whether growth of duplex scales can still be observed on ternary Co-base model alloys after 100 h exposure, EBSD mappings from samples after oxidation at 800 and 850 °C were recorded. IPF maps that were determined from the EBSD data of the investigated oxide scales are displayed in Figure 4.21.

Figure 4.21: IPF map of externally grown CoO layers on 9Wsx during 100 h exposure at (a) 800 and (b) 850 °C in synthetic air. (c) Stereographic triangle for CoO.

At temperatures below 900 °C, the outer oxide layers are not characterized by a duplex structure. Following 100 h exposure, the observed grain sizes are widely comparable in the two elucidated oxide scales. Neither a considerable equiaxial inner zone nor any preferred
orientation are evident after exposure at lower temperatures. Generally, all grains are more extended into the growth direction, which indicates minor differences between the activation energies of nucleation and lattice expansion during grain growth.

4.1.2.4 Role of microstructure during early stages of oxidation

The transport of material was repeatedly highlighted to be highly relevant for the overall kinetics of oxidation reactions in previous sections. As long as the depletion of alloying elements in regions adjacent to the scale remains comparably narrow, the two-phase microstructure could influence the nature and shape of formed oxide phases inside the scale. To verify whether such an impact is likely, scales grown on ternary Co-base alloys need to be compared in detail after short-time oxidation experiments. In Figure 4.22, BSE micrographs of the IOF of ternary Co-base alloys after 30 min exposure at 900 °C are displayed.

![BSE micrographs of the observed morphology on the IOF of all ternary Co-base model alloys after 30 min exposure at 900 °C.](image)

After 30 min of oxidation, the IOF is not yet clearly separated from the $d_2/d_3$ interface for all compositions. However, a clear tendency for the initiation of oxide growth to take place along the $\gamma$ channels is evident. Further oxide phases, which appear less dark in the BSE contrast, surround Al-rich precipitates. From the results gained via EPMA, the presence of all alloying elements inside the inner oxide layer was determined. Identification of individual oxide phases grown inside this complex layer was not possible due to the low spatial resolution of the technique. High-resolution analytical scanning transmission electron microscopy (STEM) is not characterized by these limitations and was therefore applied for clarify the nature of oxides present in the
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inner oxide layer. Differences between the investigated ternary alloys are not expected. Figure 4.23 shows a HAADF STEM overview image of a section covering the greater part of d_2 after 30 min oxidation.

Figure 4.23: HAADF STEM micrograph of the inner oxide layer observed after 30 min oxidation of 9Wsx. The two magnified areas were analyzed by STEM-EDX. Table 4.5 provides the compositions of the numbered regions [116].

Notwithstanding the high complexity of this area, different oxides can already be clearly distinguished by the Z-contrast of the image. To locate different oxide phases within d_2, compositions were extracted from STEM-EDX maps of five representative regions within the inner oxide layer (see Figure 4.23). The results are summarized in Table 4.5.

Table 4.5: Composition (in at.%) extracted from STEM-EDX maps of representative regions included in d_2 (compare Fig. 4.23).

<table>
<thead>
<tr>
<th>Map</th>
<th>Co</th>
<th>Al</th>
<th>W</th>
<th>O</th>
<th>Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>47.93</td>
<td>0.95</td>
<td>0.08</td>
<td>51.04</td>
<td>CoO</td>
</tr>
<tr>
<td>2</td>
<td>17.76</td>
<td>0.93</td>
<td>18.24</td>
<td>63.07</td>
<td>CoWO_4</td>
</tr>
<tr>
<td>3</td>
<td>18.34</td>
<td>21.09</td>
<td>3.68</td>
<td>56.90</td>
<td>CoAl_2O_4</td>
</tr>
<tr>
<td>4</td>
<td>1.38</td>
<td>37.23</td>
<td>0.32</td>
<td>61.06</td>
<td>Al_2O_3</td>
</tr>
<tr>
<td>5</td>
<td>18.12</td>
<td>2.74</td>
<td>18.31</td>
<td>60.83</td>
<td>CoWO_4</td>
</tr>
</tbody>
</table>

In Figure 4.23, a change of morphology within d_2 is clearly apparent. Two regions, from the top including fine, lamellar structures and one close to the IOF including newly formed oxides were selected for closer
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analysis. The upper magnified region in Figure 4.23 shows lamellar CoAl$_2$O$_4$ spinels (map 3). The presence of CoAl$_2$O$_4$ in internal scales grown during cyclic oxidation at 800 °C on ternary Co-base Superalloys has already been reported in the literature [71]. CoWO$_4$ (map 2) and CoO (map 1) are found located adjacent to the Al containing spinel. The combination of these three oxides throughout the upper section of d$_2$ and the characteristic morphology can be encountered repeatedly. Closer to the IOF, CoAl$_2$O$_4$ has not been formed at that stage. Two additional analyses of oxides grown in a γ channel (map 4 and 5 in Fig. 4.23) at the IOF were performed. The analyzed precipitates were identified as Al$_2$O$_3$ and CoWO$_4$, respectively. An elemental mapping across d$_2$ reveals the exact location of the identified oxides. Both, the HAADF STEM micrograph (Fig. 4.23) as well as the elemental mapping (Fig. 4.24) indicated that the morphology of d$_2$ from top to bottom becomes coarser. A closer look at the elemental map reveals that this coarsening is particularly pronounced for Al containing phases. This finding provides useful insight into the ratio of counter current diffusion fluxes, which are addressed at a later section of this study.

**Figure 4.24:** STEM-EDX analysis of element distribution across the inner oxide layer (compare Fig. 4.23) after 30 min and of exposure at 900 °C. Color-coded maps (at.%) for Co, Al, W and O, (left to right) are displayed [116].

Changes appearing on the IOF during the early stages of oxidation are of particular interest for revealing significant differences in the prevailing scale growth mechanisms. As shown at the beginning of this chapter, during the first 5 h of exposure, the initially rapid oxidation kinetics of the alloy 9Wsx can already be approximated by parabolic growth rates with sufficiently high accuracy (compare Fig. 4.4c). In his
influential study, Wagner considered mass balances in the IOF for the most essential processes to explain the morphology and appearance of internally-formed oxide layers in multi-element alloys \[7, 26\]. Despite the relative high rate of oxygen penetration through the scale, the amount of available oxygen per time interval $\Delta t$ decreases steadily with ongoing duration of exposure. At the same time, the availability of Al from the unoxidized region below the IOF can be assumed to be widely constant. The $\gamma'$ phase is only stable in a narrow compositional range. Therefore, the two-phase microstructure close to the IOF offers the unique opportunity to draw qualitative conclusions on relative diffusion velocities of both alloying elements. For this purpose, further element distribution maps from the region enclosing the IOF were acquired using quantitative STEM-EDX. To obtain an impression whether visible changes already appear during the very early stages of oxide phase formation, the samples were analyzed after 5, 30 and 300 min oxidation.

Figure 4.25 displays elemental distribution in corresponding regions.

Figure 4.25: STEM-EDX analysis of element distribution across the oxidation-affected region surrounding the IOF after a) 5 min, b) 30 min and c) 5 h of exposure at 900 °C. Color-coded maps (at.%) for Co, Al, W and O, (left to right) are displayed [116].

In ternary Co-base alloys, W partitioning is highly evident in the $\gamma'$ phase whereas the distribution of Al occurs homogeneously across...
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the alloy [108]. These findings help to assign the observed changes in element distribution to transport processes in the course of oxidation time. In case where the two-phase microstructure is evident in the Al map, significant diffusion/depletion of Al in one of the two phases took place. The contrary applies for comparable findings in the W distribution maps.

In Figure 4.25a, most of the image displays one unoxidized γ channel surrounded by γ′ cubes. The IOF is located at the top of the map. After 5 min oxidation, Al₂O₃ and CoWO₄ grow adjacently on the interface between scale and alloy. Precipitation of Al₂O₃ appears first in the γ channel (compare white arrow in Fig. 4.25a). The region surrounding the newly-formed small precipitate is evidently depleted in Al. A minor Al gradient (marked in Fig. 4.25a) extends in the direction of the alloy along the γ channel, whereas the γ′ precipitates reveal unaltered Al concentration.

The element distribution map in Figure 4.25b cover a larger area of the internal oxidation zone above the IOF. After 30 min of exposure, the distribution of elements is mostly comparable to the situation after 5 min. Due to the progress of the oxidation front, the Al gradient inside the γ channels is more pronounced. Compared to 5 min of scale growth, a substantial change in the ratio of elemental fluxes occurred after 30 min. The diffusion velocity of Al can be expected to be nearly constant, while the progress of the oxidation front slows down continuously, since the diffusion path for oxygen steadily increases. Insular growth of Al₂O₃ and CoWO₄ (compare arrows in the Al and W map of Fig. 4.25b) can be seen in the inner oxide layer. An accumulation of Al is visible the γ channels. Particularly noteworthy are the several traces of Al₂O₃ found in close proximity. This could be an indication for a high precipitation rate of Al₂O₃ within the matrix phase.

In Figure 4.25c, the elemental distribution across the IOF after 5 h is displayed. In contrast to the expansion of the internal precipitation region after shorter periods of time, d₃ is already developed to a considerable extent. The Al₂O₃ precipitates are characterized by a rod-like shape with a length of up to 200 nm. The diameter of the needle-shaped precipitates remains relatively constant. In the Al map, depletion along γ channels is clearly visible in the bottom-left and right region of the image. The outline of a γ′ cube below the IOF, marked with a white ellipse, is still recognizable in the W distribution map. In the corresponding regions of the Co and Al maps, the measured
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concentrations are lower than in unaltered $\gamma'$ cubes. This finding indicates that after 5 h, the depletion of Al expands from exclusively along the $\gamma$ channels (5 and 30 min) to both phases. The top of the W map shows the first indications of W-depletion, which were also apparent during EPMA analysis of 9Wsx alloys after 100 h exposure at 850 and 900 °C (compare Fig. 4.5b and 4.6b).

4.1.2.5 Phase stability in sub-scale regions

The formation of unwanted intermetallic, Co$_3$W species is not necessarily connected to the growth of a considerable Al$_2$O$_3$ layer on the d$_2$/d$_3$ interface of the oxide scale. As already briefly mentioned at the beginning of this chapter (compare Sec. 4.1.1), the dissolution of the $\gamma'$ phase already occurred in close vicinity of the relatively short needle-shaped alumina precipitates after 12 h oxidation of 9Wsx. Depending on the W content in the ternary alloy, the duration until the first W-rich faces are evident on the IOF vary. Figure 4.26 displays the IOF of ternary Co-base model after different exposure times at 900 °C.

Figure 4.26: BSE micrographs documenting Co$_3$W formation on the IOF in ternary Co-base model alloys depending on W content and exposure time at 900 °C: a) 7Wsx after 72 h oxidation; b) 9Wsx after 12 h oxidation; c) 10Wsx after 5 h oxidation;

Due to the alternating oxidation times, the dimensions of Al$_2$O$_3$ precipitates are hardly comparable. For samples with 7 at.% W, the first traces of thin Co$_3$W needles become apparent in micrographs taken after 12 h oxidation, whereas a high density of unwanted phases can already be seen on 10Wsx samples exposed for 5h at the same temperature. Increasing W content reduces the distance between the bright needles growing next to alumina precipitates. In contrast to the appearance of alumina precipitates, the aspect ratio of Co$_3$W remains widely unaffected from the W level in the specimen. Furthermore, W-rich intermetallic phases grow along two preferred orientations.
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independent of sample composition. Oxidation temperature also influences the initiation and extent of intermetallic phase formation on the IOF. At 85 °C, the onset of Co$_3$W growth for 10Wsx could be estimated to initiate shortly before 5 h exposure. For 9 at.% W, sub-scale phase transformation is evident after 12 h oxidation at 850 °C, however confined to a narrow region, expanding between 1 to 2 μm. In the samples revealing the lowest W content, the first indication of precipitation of intermetallic phases are observed after 72 h. Representative micrographs of Co$_3$W formation on the IOF during exposure at 850 °C are displayed in Figure 4.27. The onset of intermetallic sub-scale dissolution of the former two-phase microstructure is further retarded by reducing the oxidation to 800 °C. However, oxidized samples still demonstrate Co$_3$W growth in adjacent to isolated Al$_2$O$_3$ precipitates.

Figure 4.27: BSE micrographs documenting Co$_3$W formation on the IOF after exposure for a) 72 h, b) 24 h, c) 5 h at 850 °C.

After 100 h exposure, the initially needle-like W-rich precipitates can be observed as islands spread over several μm. As already pointed out by several authors, the occurrence of these large Co$_3$W-γ regions are normally directly related to considerable diffusion of Al towards a growing Al$_2$O$_3$ layer [70, 71]. To compare the degree depletion in sub-scale regions depending on the W content of the alloys, concentration profiles below the IOF are extracted from EPMA line scans. Figure 4.28 indicates Co, W and Al concentrations (in at.%) depending on the distance from the IOF in ternary alloys after 100 h oxidation at 900 °C.

For samples containing 9 and 10 at.% W, the concentration profiles were measured below an already formed Al$_2$O$_3$ segment (compare Fig. 4.5 b and c). Due to the rapidly advancing IOF during the oxidation of 7Wsx at 900 °C, no considerable enrichment or depletion for any element is apparent in the measured concentrations profiles. For 9Wsx, the Al concentration starts at almost 0 at.% and steadily increases
Figure 4.28: Concentration profiles of alloying elements below the IOF of (a) 7Wsx, (b) 9Wsx and (c) 10Wsx measured by EPMA after 100 exposure at 900 °C.

until the initial alloy concentration is reached at approximately 11 µm below the IOF. The local maximum 3 µm below the IOF can be assigned to the formation of AlN in the ternary alloys. Only minor differences are apparent in the W concentration profile. Relatively low W contents are measured for the γ phase surrounding the Co₃W, which is recognizable as sharp peaks (6 and 9 µm below the IOF). Comparable findings are made for the sample that contains the highest amount of W. Larger Co₃W islands are indicated by a local increase in the W concentration, accompanied by a simultaneous decrease of Co. Compared to measurements on 9Wsx, the Al concentration directly below the IOF is higher. This finding and the considerably longer expansion of the Al-depleted zone can be an indication for an earlier onset of Al₂O₃ expansion parallel to the original sample surface compared to the investigated region of the 9Wsx alloy.

4.1.3 Oxidation behavior of Cr-containing Co/Ni-base model alloys

As previously indicated, the intermediate Al content in ternary Co-Al-W systems is a core issue limiting oxidation resistance of all Co-base model alloys. It is not possible to overcome these limitations by increasing or decreasing the W content. These findings mainly reflect and confirm results regarding the oxidation behavior of binary Co-Al and ternary Co-Al-Cr alloys from studies conducted several decades ago. As the details on the role of the two-phase microstructure are to date unknown, especially during the early stages of scale growth, extension of the range of considered alloying elements is unavoidable. The narrow two-phase field can considerably widened with the addition
of Ni [73]. Furthermore, the important role of Cr in increasing the oxidation resistant of Co alloys has been known since the early 70s and was recently approved for polycrystalline quaternary Co-base alloys [69]. Another study on polycrystalline Co/Ni base model alloys with a constant Cr level of 8 at.% demonstrated intriguing dependency of thermophysical properties on the Co/Ni ratio in the respective alloy [74]. In addition to phase stability, oxidation resistance was also demonstrated to drastically decrease towards higher Co contents for this set of alloys. In the following, a detailed elucidation of oxidation mechanisms of single-crystalline Co/Ni-base model alloys between 800 and 900 °C is presented. The work was performed in close cooperation with Christopher Zenk from the Institute I: General Materials Properties in Erlangen. Part of the results that are presented in Section 4.1.3.1 and 4.1.3.2 are already included in a publication [123].

4.1.3.1 Influence of the Co/Ni ratio on the kinetic of scale growth

Figure 4.29 indicates the weight gain of Co/Ni-base model alloys during 100 h exposure at 900 °C. The thermogravimetric data acquired for the pure Co-base alloy NC100sx, demonstrated only a low degree of reproducibility. The deviation of the data between individual measurements was particular pronounced during the first 50 h of isothermal exposure. In the graph, a mean value of three experiments is displayed, with error bars indicating the standard deviation of the mass gain values after selected duration of oxidation in addition to the average curve.

For all other compositions, the reproducibility was sufficiently high. Therefore, only representative data originating from one measurement are displayed for model alloys containing Ni. The reason for the scattering in mass gain is explained in more detail at a later stage of this section. Replacing Co by Ni involves a clear decrease in mass gain. Differences in the overall behavior are already visible after 2 h of oxidation. All tested compositions revealed a period of initially rapid increase in sample weight during the first 20 h of oxidation. Depending on the alloy composition, the prevailing kinetics of scale growth demonstrate remarkable differences. The pure Co-base alloy NC100sx, reveals by far the highest mass gain after 100 h exposure. The average mass gain curve for NC100sx exhibits several sudden declines followed by subsequent moderate increases. In the end, the overall mass gain corresponds to a factor of nearly two higher than for
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Figure 4.29: Mass gain of Co/Ni-base model alloys during 100 h oxidation at 900 °C in synthetic air [123].

NC75sx and NC50sx. In the case of NC75sx and NC50sx, the reaction kinetics, particularly after the period of initially rapid kinetics, are highly comparable. The mass gain of the pure Ni-base sample, NC00sx, reached 1.25 mg cm$^{-2}$ after 100 h oxidation. The sample weight of NC00sx increases only by 10% between 30 and 100 h of exposure. Weight change of NC25sx is between the pure Ni-base alloy and NC50sx during the whole duration of the isothermal experiment.

Backscattered electron (BSE) micrographs of all compositions after 100 h thermogravimetric analysis are shown in Figure 4.30. In the case of NC100sx, the oxidation behavior did not only alter between individual specimen, but also demonstrated remarkable changes across the same sample. The two displayed micrographs for NC100sx were taken from different locations of scale grown on the same specimen.

The oxide scales observed on Co/Ni-base model alloys exhibited multilayered morphologies highly comparable to the previously presented results from ternary Co-base alloys following thermal exposure. Considering the overall thickness of the grown oxide scales, the trend is consistent with the data obtained from thermogravimetric analysis. In other words, the oxide scale observed on NC100sx exhibited the greatest thickness, and the scale on NC00sx, the smallest thickness. Despite the high number of possible different oxide species developed on each individual sample, every scale can be divided into three individual layers. The outer oxide layer ($d_1$) formed on top of the original alloy surface. Below $d_1$, a mixture of various oxide phases can be summarized as inner
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Figure 4.30: Backscattered SEM micrographs of multilayered scales on Co/Ni-base model alloys after 100 h exposure at 900 °C in synthetic air \[123\].

oxide layer (d$_2$). Between the unoxidized alloy and d$_2$, a region (d$_3$) can be seen where isolated dark phases precipitated in the unaffected (γ) matrix phase. Not only the size but also the appearance of oxide scales alter considerably when Co is successively replaced by Ni. The overall thicknesses increase towards higher Co contents. Furthermore, a higher fractional area of this interface is covered by a layer appearing dark in the backscatter electron micrographs. The dark layers in the majority of cases found on the d$_2$/d$_3$ interfaces are most probably segments of a barrier layer, which appear to only cover part of the exposed surface area of alloys NC100sx and NC75sx after 100 h oxidation. For Ni contents exceeding the amount of Co, the entire surface is covered by these transversely spread layers. The shape of internal precipitates in d$_3$ found after 100 h oxidation evidently depends on the Co/Ni ratio. In the pure Co-base sample these phases are thin and needle-like, whereas their appearance is mostly globular in the alloy characterized by equal Co and Ni contents. Following the subsequently addition of Ni, a pear-shaped internal precipitates are observed. The originally polished sample surface forms the border between outer oxide layer and internal oxidation zone. As can be seen in Fig. 4.30, the outer oxide can be prone to detachment. Even though only the outer oxide layer of NCoosx and NC50sx spalled in the displayed micrographs, no clear dependency of scale detachment on the Co/Ni ratio of the specimen could be determined. A relatively homogeneous outer oxide layer can be observed on the pure Ni alloy. Compared to the other scales, smaller grains in d$_1$ are recognizable in the electron micrograph.
The outer oxide layer \( d_1 \) on all Co-containing samples is characterized by a curved outer interface and furthermore exhibits a certain degree of porosity. In the presented mass gain data and corresponding cross-sections, the most evident differences could be observed between NC100sx, NC50sx and NC00sx. The alloy compositions with a Co to Ni ratio of 3:1 and 1:3 respectively demonstrating the merge of fundamentally divergent processes responsible for the appearance of oxide scales grown on the selected samples. For a more complete picture, data from NC75sx and NC25sx are taken into consideration, but nevertheless, the primary focus of this study is set on the fundamental differences between the pure Co- and Ni-base alloys and the intermediate composition with equal Co and Ni contents.

During the exposure of the pure Co-base alloy NC100sx, the overall oxidation kinetics undergo persistent transitions indicating repeated cracking and subsequent healing of oxide layers within the scale. Due to the initially high increase in mass, during the first 20 h of exposure, they are less pronounced in the plot after 50 h, but still evident. All alloys containing Ni do not exhibit these characteristic features over the course of the experiment. Information on elemental distribution are needed to unravel relevant elementary mechanisms that can explain evident differences during the oxidation of Co/Ni-base alloys. Figure 4.31 shows elemental mappings of regions in the samples NC100sx, NC50sx and NC00sx that are affected by the formation of oxide scales during 100 h exposure. The intention of the displayed mappings is to highlight relevant changes in high resolution. Since \( d_1 \), especially for pure Co- or Ni-base alloys is not expected to exhibit measurable deviations from the stoichiometry of the pure Co and Ni oxides which are stable at the investigated temperature, the outer oxide layer is not necessarily included to its full extent for all specimens.

For NC100sx, two regions of the prepared sample cross-section are shown in Fig. 4.31a and 4.31b. The outer oxide layer contains in both cases solely O and Co. Due to the high oxidation temperature, the majority of \( d_1 \) is expected to consist of pure CoO. In the inner oxide layer, all alloying elements are included. This layer is a conglomerate of several oxide phases which was already evident in the BSE micrographs (Fig. 4.30). At the interface between \( d_2 \) and \( d_3 \) at location I (Fig. 4.31a), a substantial enrichment of Cr indicates the formation of a Cr-containing barrier layer. At location II enrichment of Cr in \( d_2 \) is evident along the interface to \( d_3 \), but also in higher regions. Considering the different
Figure 4.31: SE micrographs of oxide scales grown on (a/b) NC100sx, (c) NC50sx and (d) NC00sx during 100 h exposure at 900 °C. Elemental distribution in the marked (–) regions was determined by EPMA [123].
extent of diffusion-limiting, Cr-containing layer growth, the abrupt changes in the mass gain curve can be explained (compare Fig. 4.29). The initially formed barrier layer, could not sustain its properties over the entire duration of exposure. Furthermore, the Cr-containing layer along the interface between \( d_2 \) and \( d_3 \) is not continuous, which exposes part of the alloy for internal oxidation attack. The distribution of W in \( d_2 \) does not exhibit a clear tendency. EPMA line scans, that are provided in the appendix of this study exhibit also considerable Co levels at the \( d_2/d_3 \) interface. For binary Co-Cr alloys, that exhibit a Cr content below 20 at.\%, the formation of CoCr\(_2\)O\(_4\) spinel phases were reported in literature [61, 124, 125]. Only for higher Cr contents (20-30 at.\%), the formation of a thin Cr\(_2\)O\(_3\) layer below the spinel layer was observed [124]. Due to the intermediate Cr content of 8 at.\% in the investigated alloy, the Cr-rich layer can be expected to consist primarily of CoCr\(_2\)O\(_4\). A considerable blocking effect of continuous spinel layers was observed in binary Co-Cr alloys in earlier studies [126].

The oxide scale on NC75sx (shown in the supplementary material) exhibit comparable layering. Particularly notable is that on the investigated cross-section no indication of a continuous and barrier layer could be found.

The oxide scale on NC50sx after 100 h, displayed in Figure 4.31c, contains more phases due to the addition of Ni as second base element. In addition to O, both Co and Ni can be found in the outer oxide layer. Even though the Co intensity is higher, it is not possible to make conclusions on the nature of the prevailing oxide in this layer. In \( d_2 \), all elements are included. However, the intensity values for Ni remain relatively low. The distribution of W in NC50sx is mostly unaffected by oxidation during exposure in air. Minor increases in
measured intensities are evident in d\textsubscript{2} and the adjacent section of d\textsubscript{3}. This increase is a consequence of Co and Ni diffusion towards the outer interface. A continuous Cr-containing barrier layer is evident on the interface between d\textsubscript{2} and d\textsubscript{3}. The EPMA line scan reveal a significant content of Co and Ni in the Cr-enriched lower section of d\textsubscript{2} (compare Fig. A.7). A further stable, Cr-containing spinel phase that was reported to grow in Ni-Cr alloys during high-temperature exposure is NiCr\textsubscript{2}O\textsubscript{4} \cite{127}. Due to the limited resolution of EPMA, it is not possible to identify the exact composition or layering of the barrier layer. Similar to the Co-Cr-spinel, diffusion was observed to be effectively reduced by the formation of a continuous NiCr\textsubscript{2}O\textsubscript{4} layer \cite{53, 126, 128}. The depletion of Co accompanied by an apparent increase in Ni, is visible in the uppermost region of d\textsubscript{3}. Even though the alloy contains equal Co and Ni contents, these findings indicate that the flux of Co, compared to Ni, originates from regions located deeper into the unoxidized alloy. In d\textsubscript{3}, Al-rich phases can be determined. Similar to the pure Co-base alloy, the internal precipitate region is partly composed of AlN.

Oxide scales that are observed on alloys with higher Ni content (NC25sx and NCoosx) are comparable in terms of oxide layer morphology. In Figure 4.31d, intensity mappings of all relevant elements in the scale and adjacent regions of NCoosx after 100 h oxidation are displayed. The outer oxide layer developed at 900 °C is assumed to be NiO, since it is the only stable oxide that Ni and O can form. Considerable amounts of all elements are found in d\textsubscript{2}. The formation of a continuous Cr-rich layer barrier layer started only a few microns below the original alloy surface and represents the transition from the inner oxide layer to the internal precipitation regions. Several studies pointed out the solid state reaction between NiO and Cr\textsubscript{2}O\textsubscript{3}, that can lead to the formation of NiCr\textsubscript{2}O\textsubscript{4} spinel phases \cite{53, 127}. Ni depletion is only noticeable in d\textsubscript{2}. For the pure Ni-base alloys, nearly all Al precipitates in d\textsubscript{3} also exhibits high O intensities and can therefore be identified as Al\textsubscript{2}O\textsubscript{3}. Two impingement sites of Al\textsubscript{2}O\textsubscript{3} precipitates can be observed in the Al and O mapping. Commonly, these stages are attributed to the onset of transverse spreading of Al\textsubscript{2}O\textsubscript{3} sections \cite{27}.

Considerable depletion of Al coincides with the growth of an unwanted intermetallic Co\textsubscript{3}W phase. The narrow compositional window in which the desired γ/γ′ microstructure can be sustained is a major drawback that limits the usability of Co-base alloys. The addition of Ni is known to widen the γ/γ′ two-phase region \cite{73}. Therefore,
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a higher tolerance of the unoxidized substrate towards Al depletion can also be expected with increasing Ni content. To examine the validity of this assumption, BSE micrographs of representative regions surrounding the IOF after exposure in air at 900 °C are shown in Figure 4.32. All BSE micrographs were taken after 100 h oxidation and include the interface between $d_2$ and $d_3$ in the uppermost region along with unaltered $\gamma'/\gamma''$ microstructure. Unwanted $Co_3W$ phases as well as considerable depletion of $\gamma'$ are highlighted in the figure.

![Figure 4.32: Appearance of internal oxidation front (IOF) after 100 h exposure at 900 °C in synthetic air.](image)

Due to the partitioning of W in the $\gamma'$ phase, the precipitation phase appears bright for the Co-rich samples NC100sx and NC75sx. In Ni-rich model alloys, W is enriched in the matrix phase, which is reflected by the darker $\gamma'$ cubes in the BSE micrograph. For equal Co and Ni content, W does not partition to a significant extent in either of the two phases. Therefore, additional ion flat milling was used to visualize the $\gamma'$ phase in the cross sections of oxidized NC50sx samples by preferential sputtering of the matrix. In both Co-rich alloys, $Co_3W$ was found contiguous to Al-rich precipitates in $d_3$. The W-rich intermetallic phases grew to a large extent in the pure Co-base alloys, whereas only very thin isolated needles occurred in NC75sx. For Co/Ni ratios of 0.5 and lower, no additional phases were found in $d_3$. Furthermore, the development of a $\gamma'$-depleted zone can be observed, corresponding to the majority of cases closely linked to the formation of continuous $Al_2O_3$ layers on the IOF [38, 17]. Such zones
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comprise more pronounced alloys with higher Ni contents. Since no continuous alumina layer was found for the investigated range of alloy compositions, the Al content is either too low to sustain the necessary flux of Al towards the IOF or the Al already reacts with N which is evidently present in scales on samples with a high Co content.

For NC100sx, NC50sx and NCoosx, the development of the identified sections of a diffusion barrier within the internal oxidation zone is documented by micrographs at various durations of thermal exposure. Figure 4.33 documents the changes of specific morphological features of d_2 and d_3 after 5, 12, 24, 72 and 100 h exposure.

For the pure Ni-base alloy, the formation of a γ'-depleted layer is already evident after 5 h oxidation. With ongoing scale growth, this zone spreads further into the alloy. During the first 24 h of exposure, the appearance of Al_2O_3 precipitates in d_3 remains relatively unaltered. The shape of these precipitates considerably coarsened after 72 h oxidation. Consequently, the first indications of impingement events can be observed at isolated locations. After 100 h oxidation, a relatively short segment of transverse Al_2O_3 is evident. The appearance of alumina phases formed in d_3 during the first 5 h of oxidation is generally comparable for all investigated compositions. However, in the specimens with equal Co and Ni contents, the Al-rich precipitates exhibit a considerable rounder shape after 12 h of exposure. Larger amounts of Cr-containing spinel phase are already evident after 12 h oxidation. The sample region of NC50sx after 24 h exposure, displayed in Figure 4.33, exhibits a continuous barrier layer. Observation of the progress of γ'-depletion adjacent to the IOF is not possible, since the two-phase microstructure is not distinguishable in NC50sx (compare 3.1) samples prepared by cross-sectional ion milling. Needle-shaped AlN phases are only visible in the cross-section obtained after the maximum duration of exposure. Due to the high scattering in the thermogravimetric data, only unequivocal features of the internal oxidation zone for pure Co-base alloys are highlighted in the results. The internal precipitation region d_3 consists of a significant amount of W-rich regions already after 5 h exposure at 900 °C. Al-containing phases retain their needle-shape appearance but significantly increase in length with ongoing oxidation time. After 72 h, d_3 already spreads over a zone characterized by a width of more than 12 μm. Due to the similar appearance of the internal precipitation region in samples after 72 and 100 h oxidation, a higher tendency for the formation of
nitrides in the pure Co-base model alloy can be ultimately concluded. In contrast to the internal oxidation zone on ternary Co-base alloys after exposure at 900 °C, Co/Ni-base alloys exhibit a significantly lower degree of porosity. Nevertheless, scale cracking on the original alloy interface can be seen after intermediate oxidation times, especially for NCoosx samples.

The kinetics of scale development are addressed in the same way already applied for ternary Co-base model alloys. Even though, consid-
erable scattering was detected during the thermogravimetric analysis of the pure Co-base sample, layer thicknesses were determined and plotted over exposure time. The results including the calculated linear fits (see dashed lines), are displayed in Figure 4.34. Oxide layers grown on alloys with Co/Ni ratio of 1.5 or 0.5 were only considered in order to facilitate a better categorization, after the maximum duration of isothermal oxidation experiments.

![Figure 4.34](image)

**Figure 4.34:** Increase of individual layer thickness on Co/Ni-base model alloys at 900 °C in synthetic air as a function of exposure time. The individual layers (a) $d_1$, (b) $d_2$ and (c) $d_3$ are plotted separately [123].

Due to the evidently low reproducibility during thermogravimetry, three experiments over the maximum duration of exposure were conducted for the pure Co-base alloy. The oxide scale of one sample spalled completely while cooling. Therefore, only the thicknesses of two samples could be measured. Both investigated oxide scales after 100 h experiments were considered for the calculation of expected scale thicknesses. Over the entire duration of isothermal exposure steady-state kinetics were not reached in the case of the pure Co-base alloys. Scattering in the determined values evidently increases with higher Co contents in the specimens. For NC50sx and NC00sx growth rates approach a steady state between 12 and 24 h exposure. Divergent behavior of NC50sx and the pure Ni-base alloy NC00sx are more evident after longer exposure times. The results coincide with the first conclusions drawn by means of weight gain data (Fig. 4.29). The dimensions of individual layers can only be compared after 100 h exposure for the complete set of considered alloys. Differences between NC00sx and NC25sx are only recognizable for the outward expansion of $d_1$. Equally thick inner oxide layers grew for specimens with Ni contents of more than 50%. Interestingly, the dimensions of $d_2$ and $d_3$ found on NC75sx and NC50sx after 100 h oxidation also follow
this fit curve. However, a considerably thicker outer oxide layer was observed for NC75sx, the sample with higher Co content, perhaps due to varying elemental transport properties depending on the composition of $d_1$. Prevailing kinetics during steady-state scale growth on Co/Ni-base model alloys are approximated by a linear fit of mean thicknesses over $\sqrt{t}$. The growth rates of the individual layers are given in Table 4.6.

Table 4.6: Comparison of estimated individual growth rates ($\mu m/\sqrt{min}$) for individual layer growth on Cr-containing Co/Ni-base model alloys at 900 °C from curve fitting (Fig. 4.34).

<table>
<thead>
<tr>
<th>specimen</th>
<th>fit interval</th>
<th>$k_{sp}^{\text{sqr}}$ ($\mu m/\sqrt{\text{min}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$d_1$</td>
</tr>
<tr>
<td>NC100sx</td>
<td>[12 h; 100 h]</td>
<td>0.20</td>
</tr>
<tr>
<td>NC50sx</td>
<td>[12 h; 100 h]</td>
<td>0.10</td>
</tr>
<tr>
<td>NC00sx</td>
<td>[12 h; 100 h]</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The estimated individual expansion rate ($k_{sp}^{\text{sqr}}$) for the expansion of $d_2$ and $d_3$ are direct measures for the susceptibility to internal oxidation depending on the Co/Ni ratio, due to the occurrence of Cr-containing barrier layers in all specimens. The kinetics of $d_1$ are a result of the transport processes through the outer oxide layer and can therefore be directly correlated to the diffusivity of Ni/Co in the outer oxide layers. The rate constants corresponding to the expansion of all oxide layers on NC100sx significantly exceed the $k_{sp}^{\text{sqr}}$-values determined for specimens containing Ni. As already demonstrated by the preceding results, the pure Co-base alloy exhibits low resistance to scale formation for experiments characterized by a duration of 100 h. On the contrary, the pure Ni-base alloy exhibits reasonable oxidation properties after the first 12 h of exposure. Low O permeability of the Cr-containing barrier layer is indicated by the small rate of $d_2$ expansion. Only minor amounts of O are observed below the diffusion-limiting barrier layer, in the pure Ni-base alloy. This is consequently expressed by the smallest $k_{sp}^{\text{sqr}}$-value for the expansion of $d_3$. Even though the growth rate of $d_3$ determined for NC50sx is higher than the growth rate of the pure Ni-base alloy, $k_{sp}^{\text{sqr}}$ remains significantly below that determined for NC100sx. An intermediate $k_{sp}^{\text{sqr}}$-value for the growth of $d_3$ supports the assumption that in the alloy with equal Co and Ni contents, cracking of the barrier layer also takes place. Since such events are not apparent in the mass gain data, those processes might occur in isolated locations.
and are followed by comparably fast healing. Diffusivity of Co/Ni through $d_1$, sustaining the expansion of the outer oxide layer increases with higher Co contents. This trend is normally assigned to prevailing defect densities in these layers. Detailed studies on cation transport processes through externally growing scales on binary Co/Ni-alloys can be found in the literature \[129, 130\].

The complete set of Co/Ni-base model alloys is oxidized for 100 h in synthetic air at 850 °C to elucidate whether a similar dependency of reaction kinetics on the Co/Ni ratio can be also observed at lower temperatures. The acquired thermogravimetric data are summarized in Figure 4.11.

Figure 4.35: Mass gain of Co/Ni-base model alloys during 100 h oxidation at 850 °C in synthetic air.

The prevailing kinetics undergo evident transitions over the course of 100 h oxidation for alloys containing Co at lower temperatures. In contrast to exposure at 900 °C, the extent of measured mass gain does not directly reflect the Co/Ni ratio in the alloy. The composition characterized by equal Co and Ni contents of 37.75 at.% exhibits the lowest overall increase in weight per surface area. Furthermore, the mass gain data exhibits repeated increases followed by moderate decreases for NC50sx over the course of oxidation at 850 °C. Similar to the Co-containing samples at 900 °C, these discontinuities can be associated with substantial cracking and subsequent healing of the barrier layer in the internal oxidation zone. The total mass gain for NC100sx, NC75sx and NC25sx approach the nearly same value after
100 h exposure at 850 °C. Among these three compositions, the pure Co-base alloy exhibits the most rapid increase in weight during the first 10 h of thermogravimetry. After 50 h of oxidation, the slope of the mass gain data appears to increase. The addition of 18.75 at.% Ni in NC75sx leads to less weight gain during the initiation stage of exposure. Compared to the pure Co-base alloy, the increase in mass is evident after a shorter period of exposure for NC75sx. The curves for NC100sx and NC75sx do not exhibit an apparent decrease in oxidation rates after the slope approaches higher values. Slower initial scale growth kinetics are observed for NC25sx. After a less pronounced increase between 30 and 40 h exposure, the weight gain curve steadily declines for the second 50 h of the experiment. The highest mass gain per sample area is measured for NC00sx. After 100 h oxidation, the total weight gain of $1.33 \text{ mg cm}^{-2}$ even exceeds the maximum value measured during thermogravimetry at 900 °C ($\Delta m_A = 1.24 \text{ mg cm}^{-2}$).

![Figure 4.36](image.png)

**Figure 4.36:** Backscattered SEM micrographs of multilayered scales on Co/Ni-base model alloys after 100 h exposure at 850 °C in synthetic air.

Figure 4.36 shows cross-sections of oxide scale grown on Co/Ni-base alloys during 100 h exposure at 850 °C. The overall appearance of the samples is comparable between experiments conducted at 850 and 900 °C. This is particularly true for the morphology of the internal precipitation region $d_3$. It can therefore be assumed that the alteration of oxidation temperature has the most significant impact on the development and the sustainability of the Cr-containing barrier layer. An apparent irregular outer oxide interface might be the result
of scale cracking, which was already evident in the weight gain data. For NC75sx, two dark appearing regions also indicate poor protective properties of the initially formed barrier layer. The oxide scale grown on NC50sx exhibits a very thin inner oxide layer ($d_2$). The outer interface of $d_1$ exhibits less irregularity than the interface observed on the pure Co-base alloy. The average size of $d_1$ for NC50sx corresponds to the outer oxide layer thickness of NC100sx above the intact section of the Cr-rich layer on the $d_2/d_3$ interface. For all intermediate Co/Ni-base alloys, $d_3$ expands to a comparable extent.

In contrast, the pure Co-base alloy demonstrates substantially deeper penetration by internal precipitates, even below the Cr-enriched scale sections. The thickest inner oxide layer followed by a rather narrow internal precipitation region was observed for NCoosx. Elemental distribution in the scale and adjacent regions of NC100sx after 100 h oxidation at 850 °C is demonstrated in Figure 4.37.

**Figure 4.37**: SE micrographs of oxide scales grown on NC100sx during 100 h exposure at 850 °C. Elemental distribution in the marked (–) regions was determined by EPMA.

The EPMA mapping confirms the first conclusion drawn after the review of thermogravimetric data in combination with corresponding cross-sections. Cr enrichment was observed across the entire $d_2/d_3$ interface. The diffusion-limiting characteristics of this barrier layer did not sustain for the entire duration of exposure. During oxidation at lower temperatures, substantial amount of AlN were observed over the investigated sample surface. Local break-down of O blocking can be seen on the right-hand side of the displayed scale. In this region of the sample, extensive growth of W-rich phases that also exhibit intermediate oxygen intensities can be observed. Even though no EPMA
measurements were acquired for alloys containing Ni, the displayed cross-sections after maximum duration of exposure suggest a lower extent of AlN formation for NC75sx and NC50sx.

The results of the thermogravimetric analysis during 100 h exposure in synthetic air at 800 °C, are summarized in Figure 4.38. At the lowest investigated temperature, the highest mass gain was measured for the pure Ni-base alloy. The increase in weight per sample area is slightly below the values that were observed at 850 °C. The addition of 18.75 at.% Co slightly improves the oxidation behavior. Compared to thermogravimetric analysis at 900 °C, the overall dependency of mass gain on the Co/Ni ratio is completely inverted. The sudden enhancements in the oxidation rate of all Co-containing alloys are indications of temporary distortion of the prevailing oxidation kinetics. Resumption of the diffusion-limiting properties of the scale, which is normally accompanied by a steady decline in oxidation rates, can not be observed in the mass gain data of NC50sx and NC75sx. For intermediate Co/Ni-base alloy NC50sx, the transient period of initially high weight gain converts into a steady-state after approximately 12 h of exposure.

Figure 4.38: Mass gain of Co/Ni-base model alloys during 100 h oxidation at 800 °C in synthetic air.

The relatively slow oxidation rate is not maintained for the whole duration of experiment. For exposures after 50 h, an apparent increase in the sample weight indicates the breakdown of the barrier properties at several locations of the sample surface. NC75sx, the specimen containing more Co than Ni, exhibits a similar behavior. A slightly lower
weight gain is observed for NC75sx than for NC50sx during the initial stage of scale growth. However, the oxidation rate evidently increases as consequence of scale cracking after already approximately 24 h of exposure. The pure Co-base alloy exhibits the lowest mass gain over the entire duration of experiment. After 100 h oxidation, the measured weight gain per surface area of NC50sx exceeds that of NC100sx by a factor of two. Accelerated attack is indicated by moderate increases in sample weight after 50 h oxidation in the data observed for the pure Co-base alloy.

Most likely those cracks are less detrimental to the overall performance of this alloy at the investigated temperature. Due to the overall lower mass gains, changes initiated by cracking of the diffusion-limiting scale section and subsequent healing of the disturbed regions are consequently less pronounced and therefore difficult to detect in this plot.

Representative electron micrographs of multilayered oxide scales formed during thermogravimetric analysis of Co/Ni-base model alloys at 800 °C are demonstrated in Figure 4.39. After 100 h oxidation at 800 °C, the oxide scale observed on NC100sx appears to be relatively uniform in terms of thickness over the displayed region of the sample. The apparent development of a barrier layer within the oxide scales is accompanied by the growth of intermetallic Co3W phases in the adjacent regions of the unoxidized sample.

Figure 4.39: Backscattered SEM micrographs of multilayered scales on Co/Ni-base model alloys after 100 h exposure at 800 °C in synthetic air.
4 Results

In contrast to cross-sections after 100 h exposure at higher temperatures, only a low number of dark precipitates below \( d_2 \) are observed. For higher Ni contents, the dimensions of each distinguished oxide layer as well as the overall layer thickness increase. The Al-rich precipitates in \( d_3 \) are characterized by a needle-like shape, which is different from the round appearance that was observed at 850 and 900 °C, respectively. Furthermore, a relatively uneven outer oxide interface can be most probably assigned to the partial exposure of unoxidized surface during break-down of the barrier layer. At the lowest oxidation temperature, the dimensions of individual layers decrease for NC00sx.

Electron micrographs at a lower magnification along with elemental distribution in the marked region for NC100sx, NC50sx and NC00sx are demonstrated in Figure 4.40. An almost continuously developed barrier layer, which is characterized by high Cr content can be observed at the \( d_2/d_3 \) interface of NC100sx (compare Fig. 4.40a). The Cr-containing layer is interrupted by a short transverse section of \( \text{Al}_3\text{O}_3 \) with evidently higher thermodynamic stability. The outer oxide layer is composed of Co and O. At lower oxidation temperatures, \( d_1 \) may also consist to a certain extent of \( \text{Co}_3\text{O}_4 \) (compare Sec. 4.1.2.1). Extensive formation of \( \text{Co}_3\text{W} \) embedded in the \( \gamma \)-matrix is clearly visible in the Co and W maps. In addition to this phase transition, no obvious depletion can be observed in the region below the oxide scale. A relatively high intensity of Al in precipitates obtained in \( d_3 \), indicates the formation of AlN.

The outer oxide layer of the NC50sx sample that was oxidized for 100 h at 800 °C exhibits Co and Ni signal along with O over a wide range of the displayed specimen. However, this mixed oxide is interrupted by grains that exclusively consist of pure Co oxide. For the intermediate Co/Ni-base alloy, all elements are present in the inner oxide layer. After 100 h exposure, a Cr-containing barrier layer formed below \( d_2 \). At various locations, high Al intensities can most probably be associated with \( \text{Al}_2\text{O}_3 \) formation. Higher W contents are also detected at these locations. Unfortunately, the achieved resolution of the mapping does not allow the formed phases to be further distinguished or identified. The Cr mapping demonstrates considerable depletion in the unoxidized region of the samples. In the Al distribution map, relatively narrow and localized Al depletion can be observed.

Element distribution maps across the oxide scale and the adjacent alloy region of NC0osx after exposure are displayed in Figure 4.40c. The outer oxide layer formed on the pure Ni-base alloy unequivocally consist
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Figure 4.40: SE micrographs of oxide scales grown on (a) NC100sx, (b) NC50sx and (c) NC00sx during 100 h exposure at 900 °C. Elemental distribution in the marked (−) regions was determined by EPMA.

of NiO. In the inner oxide layer, a conglomerate of oxides containing all elements is observed. The insufficient oxidation resistance of the pure Ni-base alloys can be explained by the absence of a barrier layer, that was observed for Co-containing samples. The precipitates in d₃ are characterized by Al and O intensities and can therefore be identified as alumina. No indications of nitrides below d₂ are apparent. Even
though, the entire surface was not covered by a Cr-containing barrier layer, considerable depletion in Cr is evident.

The internal oxidation zone of NC100sx, NC50sx and NC00sx after 5, 24 and 100 h oxidation are demonstrated in Figure 4.41. Due to the relatively slow scale growth in combination with evident repeated break-down of the barrier layers, a detailed analysis of the scale growth kinetics is not imposed for exposure at 800 °C. The goal of the more detailed elucidation of the internal oxidation zone is to verify conclusions, that were drawn using thermogravimetry along with EPMA analysis.

Figure 4.41: Evolution of the internal oxidation zone (d$_2$+d$_3$) on Co/Ni-base model alloys with varying Co/Ni ratio during exposure at 800 °C.

The oxide scales on all investigated compositions are characterized by three layers. The comparably high resistance of the pure Co-base model alloy to scale growth is reflected in an exceptionally low thickness (< 500 nm) of the inner oxide layer. Below d$_2$, a considerable number of Co$_3$W needles are apparent after already 12 h of exposure. Various cracks are observed on the interface between d$_2$ and d$_3$ for the pure Co-base alloys after 12 and 24 h oxidation. The resistance to scale formation evidently decreases with Ni additions. For equal Co and Ni contents,
the demonstrated oxide scales in Figure 4.4 exhibit indications of the formation of a barrier layer after 100 h of oxidation. Since the thickness of the inner oxide layer formed during 24 and 100 h exposure remains nearly unaltered, the development of a barrier layer can be assumed to be effective shortly after 24 h oxidation. The extensive formation of internal precipitates, that was observed after 100 h confirms the insufficient long-term stability of NC50sx. Significant enhancement of the oxidation rate (compare Fig. 4.38) during thermogravimetry was a first indication for the poor oxidation resistance. The displayed internal oxidation zone, that was observed for NC00sx, considerably expanded between 12 and 100 h. During the first 24 h of scale growth, relatively small Al$_2$O$_3$ precipitates were observed on the IOF. After the maximum duration of exposure in synthetic air at 800 and 850 °C, the internal precipitation regions in NC00sx exhibit similar morphologies. The apparent depletion of Cr that could be observed during EPMA investigations (compare Fig. 4.40) in conjunction with an evident dark layer on the d$_2$/d$_3$ interface in the BSE micrographs indicates the formation of transverse scale sections that are able to slow down the diffusion of O. However, EMPA measurements demonstrated the appearance of unprotected parts across the sample surface (compare Fig. 4.40).

4.1.3.2 Phase stability and elemental depletion

The development of unwanted phases and regions significantly depleted in alloying elements in close proximity to the IOF are illustrated by BSE micrographs at different exposure times in Figure 4.42. The low phase stability of γ’ is confirmed by the appearance of Co$_3$W after only 5 h of oxidation. With ongoing durations of exposure the amount of these phases steadily increases. The large number of discrete Al-rich precipitates observed in NC100sx is an indication for high O activity at the IOF. Following rapid progress of internal oxidation, Al is consumed in large quantities. The formation of transverse Al$_2$O$_3$ sections, as well as the development of a γ’-depleted region is suppressed by the high O activity at the reaction front over the entire duration of exposure. Both Ni-containing alloys, NC50sx and NC00sx, are not prone to the growth of unwanted phases. The formation of a clearly visible zone with no precipitation phase in the pure Ni-base alloy, can be
mainly explained by the neglectable amount of N below the Cr-enriched barrier layer. The inward expansion of an Al-depleted region is enabled by the availability of Al, as it was not consumed by the reaction to AlN.

Figure 4.42: Evolution of the IOF on Co/Ni-base model alloys with varying Co/Ni ratio during exposure at 900 °C in synthetic air.

The region surrounding the IOF after oxidation at lower temperature is shown in Figure 4.43. After 100 h exposure at 800 °C, the IOF exhibits different precipitate morphology for the pure Ni-base alloy. Alumina phases exhibit needle-like structures indicating a considerable change in the ratio of O and Al flux reaching the IOF. Nevertheless, a $\gamma'$-depleted zone is still recognizable. Neither NC00sx nor NC50sx show clear indication of the formation of nitrides or $\text{Co}_3\text{W}$ in the depicted region. Furthermore, no considerable depletion of $\gamma'$ in the oxidation-affected region of the intermediate Co-base alloy is recognizable. Despite the low mass gain during exposure at the lowest considered temperature, the pure Co-base alloy exhibits extensive formation of
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W-rich intermetallic phases. The transformation from $\gamma'$ to Co$_3$W is initiated by considerable growth of AlN, which was also evident in EPMA mappings of the oxide scale (compare Fig. 4.40).

**Figure 4.43:** Appearance of the IOF in Co/Ni-base model alloys with varying Co/Ni ratio after 100 h exposure at 800 °C in synthetic air.

EPMA analysis on ternary Co-base alloys after 100 h exposure at 900 °C revealed Al-depletion below sections of spread alumina segments. Due to the substantial formation of AlN in NC50sx and NC100sx, Al concentration measured below the IOF are of less significance. As can be seen by the elemental mappings (Fig. 4.31), Cr is the most essential element to the sustainment of the barrier properties of the investigated Co/Ni-base model alloys and not consumed by the formation of unwanted phases. At this stage, a qualitative comparison of Cr concentration below the IOF is the only measurement that provides meaningful insight into transport processes of alloying elements depending on the Co/Ni-ratio. Ideally, the continuous barrier layer corresponds to the Cr-containing oxide phases that expand the furthest into the alloy. The concentrations of Cr (in at.%) are extracted from EPMA line scans starting from the d$_2$/d$_3$ interface, moving towards the unoxidized alloy. The Cr profiles for NC100sx, NC50sx and NC00sx are plotted over the distance to the d$_2$/d$_3$ interface in Figure 4.44.

A considerable decrease in the Cr content across d$_3$ is evident for all three samples. The formation of a Cr-containing barrier layer is accompanied by a strong decline of the d$_2$ growth rates. This first transition towards significantly slower kinetics is expected to occur between 12 and 24 h (compare Fig. 4.34) for the three considered compositions. Based on these findings, a nearly equal time span between the completion of the barrier layer development and the end of experiment can be assumed. In other words, the measured Cr concentration evolved over a comparable time interval of the conducted oxidation experiment. The plotted Cr concentrations indicate a less pronounced depletion for both pure model alloys. The level of Cr in
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Figure 4.44: Cr concentration over distance from $d_2/d_3$ interface. EPMA line scans were conducted from $d_1$ towards the unaffected alloy. Along the scan, the last measurement point that can conclusively be assigned to the Cr-containing barrier layer was designated as Cr concentration at $x=0$. The nominal Cr concentration (8 at.%) in all alloys is indicated by a horizontal line. 

The depleted zone of NC00sx is between 2 and 3 at.%, whereas the Co-containing alloys exhibit Cr contents below 1 at.% in these regions. For NC100sx and NC50sx, considerably higher amounts of Cr might be consumed during the repeated healing of cracks inside the barrier layer. From a different perspective one can assume that more O is generally average available at the $d_2/d_3$ interface during 100 h exposure at 900 $^\circ$C. From the presented data, the highest diffusivity of Cr can be concluded in the intermediate Co/Ni-base alloy NC50sx at 900 $^\circ$C.

4.1.4 Comparison of the oxidation resistance of investigated alloys

A first classification of the oxidation resistance of each alloy composition at a given temperature in synthetic air, can be made by reviewing the oxide scale thickness after 100 h exposure. The overall thicknesses ($\bar{d}$), along with standard deviations ($sd(d)$) and dimensions for the distinguished three layers ($\bar{d}_x$) after the maximum duration of experiment are summarized in Table 4.7. The listed values are additionally plotted as bar charts in Figure 4.45. For more information on the scattering in the individual oxide layer thicknesses, the reader is referred to the relevant sections that address the scale growth kinetic (Sec. 4.1.2.2 and 4.1.3.1) of the alloy series.
Table 4.7: Mean scale thicknesses after 100 h thermogravimetry at 900 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{d}/\mu m$</th>
<th>$sd (d)/\mu m$</th>
<th>$\bar{d}_1/\mu m$</th>
<th>$\bar{d}_2/\mu m$</th>
<th>$\bar{d}_3/\mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7Wsx</td>
<td>162.0</td>
<td>4.7</td>
<td>74.7</td>
<td>60.7</td>
<td>24.5</td>
</tr>
<tr>
<td>9Wsx</td>
<td>73.9</td>
<td>4.6</td>
<td>30.8</td>
<td>23.0</td>
<td>18.2</td>
</tr>
<tr>
<td>10Wsx</td>
<td>47.3</td>
<td>9.3</td>
<td>20.9</td>
<td>15.0</td>
<td>17.2</td>
</tr>
<tr>
<td>NC100sx</td>
<td>65.0</td>
<td>1.6</td>
<td>23.5</td>
<td>23.0</td>
<td>21.2</td>
</tr>
<tr>
<td>NC75sx</td>
<td>32.9</td>
<td>4.5</td>
<td>12.9</td>
<td>9.3</td>
<td>10.7</td>
</tr>
<tr>
<td>NC50sx</td>
<td>29.1</td>
<td>2.0</td>
<td>10.4</td>
<td>10.0</td>
<td>8.2</td>
</tr>
<tr>
<td>NC25sx</td>
<td>19.9</td>
<td>2.4</td>
<td>7.0</td>
<td>4.9</td>
<td>6.7</td>
</tr>
<tr>
<td>NC00sx</td>
<td>19.3</td>
<td>1.6</td>
<td>6.4</td>
<td>5.2</td>
<td>6.8</td>
</tr>
</tbody>
</table>

Despite slight improvement of the oxidation behavior by higher W contents in ternary model alloys, the oxidation resistance remained low. The overall thickness of the developed scales as well as the expansions of each individual oxide layer decreases to a comparable extent. Kinetic analysis (Sec. 4.1.2.2) supplemented with EPMA mappings revealed differences in the expansion of the individual layers. However, alloys with higher W levels evidently required increasing temperatures for the formation of considerable transverse Al$_2$O$_3$ sections. Therefore, it can be concluded that the W levels in the ternary alloys primarily influence the transport of reactants, such as Co to the outer scale interface and O to the IOF. Apart from isolated sections where lateral alumina provides to some degree a barrier to material transport, external and internal oxidation proceed nearly uninhibited over the entire surface of the exposed specimen during the first 100 h of exposure, for all elucidated ternary model alloys.

Figure 4.45: (a) Determined mean thickness of oxide scales and (b) individual oxide layer thickness for all considered alloys after 100 h exposure at 900 °C in synthetic air.
4 Results

Even though the addition of 8 at.% Cr to 9Wsx further decreases the overall scale thickness, the protective properties of NC100sx remained insufficient. Over the duration of 100 h exposure, neither a continuous Al$_2$O$_3$ nor a Cr$_2$O$_3$ layer develops in the internal oxidation zone. Furthermore, nearly equal mean thicknesses of $d_2$ and $d_3$ in 9Wsx and NC100sx indicate that the penetration of oxygen through the outer oxide layer is mostly unaffected by the addition of Cr. The formation of Cr-containing scale sections, that provide a certain barrier to material transport could be demonstrated to proceed irregularly over the surface of the sample. Furthermore, regions of the scale where these barrier sections formed at an early stage of oxidation could not sustain the protective properties over the complete duration of exposure. Replacement of Co by Ni improves phase stability in the sub-scale region and simultaneously lowers the overall mass gain during oxidation. The evident relationship between the thickness of the outer oxide layer and the Co/Ni ratio, can be directly associated with the transport of cations towards the outer scale interface. The addition of Ni is accompanied by the formation of a Cr-containing barrier layer on the $d_2/d_3$ interface over the whole sample surface. However, for Co/Ni ratios of 1 or higher, substantial formation of AlN remained an issue.

At lower exposure temperatures, an increased tendency to form Al-containing oxide scale sections, which provide a certain degree of protection, were observed for 7Wsx and 9Wsx. The dimensions of oxide scales and individual layer thicknesses observed after 100 h exposure at 800 °C are summarized in Table 4.8 and shown as bar charts in Figure 4.46. Protective Al$_2$O$_3$ covered the IOF of 7Wsx and 9Wsx after the maximum duration of experiment. The overall scale thicknesses follow the same dependency on the W content that was already observed for higher exposure temperatures. However, the growth of alumina sections is evidently hindered by higher W levels.

Co/Ni-base model alloys that were oxidized at 800 °C exhibit an inverse trend compared to the trend observed for 100 °C higher exposure temperatures. The main reason for this behavior is the increased tendency for Co-base alloys to form more protective oxide sections at lower temperatures. Particularly thin inner oxide layers, that were found for NC50sx and NC100sx support this assumption. A relatively complete Cr-containing barrier layer, accompanied by additional sections of Al$_2$O$_3$ on the $d_2/d_3$ interface was observed during EPMA investigations in the oxide scale of NC100sx after 100 h
4.1 Isothermal oxidation in synthetic air

Table 4.8: Mean scale thicknesses after 100 h thermogravimetry at 800 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{d}_{\mu m}$</th>
<th>$sd \ (d)_{\mu m}$</th>
<th>$\bar{d}<em>1</em>{\mu m}$</th>
<th>$\bar{d}<em>2</em>{\mu m}$</th>
<th>$\bar{d}<em>3</em>{\mu m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7Wsx</td>
<td>46.7</td>
<td>6.3</td>
<td>24.3</td>
<td>20.6</td>
<td>-</td>
</tr>
<tr>
<td>9Wsx</td>
<td>24.2</td>
<td>2.3</td>
<td>12.8</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td>10Wsx</td>
<td>20.1</td>
<td>5.0</td>
<td>10.4</td>
<td>8.0</td>
<td>4.8</td>
</tr>
<tr>
<td>NC100sx</td>
<td>6.2</td>
<td>2.7</td>
<td>1.5</td>
<td>1.3</td>
<td>5.8</td>
</tr>
<tr>
<td>NC75sx</td>
<td>7.2</td>
<td>1.5</td>
<td>4.2</td>
<td>1.6</td>
<td>2.5</td>
</tr>
<tr>
<td>NC50sx</td>
<td>6.8</td>
<td>0.8</td>
<td>3.1</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>NC25sx</td>
<td>10.3</td>
<td>1.5</td>
<td>4.3</td>
<td>3.6</td>
<td>2.4</td>
</tr>
<tr>
<td>NCoosx</td>
<td>16.7</td>
<td>0.4</td>
<td>7.2</td>
<td>6.3</td>
<td>3.3</td>
</tr>
</tbody>
</table>

exposure at 800 °C. Nevertheless, the sample still exhibits a relatively thick internal precipitation region at several locations. The repeated cracking of these scale sections can facilitate the formation of these precipitates, which consist to a substantial portion of nitrides. At the lowest oxidation temperature, less AlN was observed for increasing Ni contents (compare Fig. 4.40a).

The oxide scale formed on the pure Ni-base model alloy NCoosx at 800 °C exhibited the highest overall thickness. Nevertheless, the mean $d_3$ value remained considerably smaller than the value measured for the pure Co-base alloy. Despite the suppressed scale formation at 800 °C, long-term stability of barrier layers in alloys that contains high Co contents remained an evident issue.

Figure 4.46: (a) Determined mean thickness of oxide scales and (b) individual oxide layer thickness for all considered alloys after 100 h exposure at 800 °C in synthetic air.
4.2 Oxidation in $^{16/18}$O atmospheres

In the preceding sections, conclusions on transport processes of reactants through the grown scales on Co- and Co/Ni-base model alloys were indirect in nature. Two-stage oxidation experiments using distinguishable stable oxygen isotopes $^{16}$O and $^{18}$O can provide direct evidences of the diffusion paths of oxygen. In the following, the processing of SIMS data obtained after a representative two-stage tracer experiment is introduced as an example for the ternary 9Wsx sample after 24 h duration of experiment at 900 °C. In the subsequent sections, previously processed data is presented for different oxidation times and compositions. The majority of the experiments were conducted at 900 °C. Additional specimen of the ternary Co-base model alloy with intermediate W content were exposed to $^{16/18}$O-containing atmospheres at 800 and 850 °C.

4.2.1 Handling of SIMS data

After two-stage tracer experiments, the distributions of stable oxygen isotopes were determined by FIB-SIMS. The combination of focused ion beam (FIB) and SIMS allows imaging of morphological features of the oxide scale and simultaneous elucidation of tracer distribution in the considered sample region. Due to preceding EPMA investigations, the compositional informations on oxide scales and the adjacent alloy regions are already available. Therefore, all SIMS investigations were limited to the distribution of $^{16}$O$^-$ and $^{18}$O$^-$ in the scale. Prior to the acquisition of SIMS maps, a negative SIMS spectrum was measured to confirm the exact peak positions of the stable oxygen isotopes. Figure 4.47 demonstrates the relevant extract of a representative negative SIMS spectrum that was recorded from the scale observed on 9Wsx after 24 h two-stage experiment.

In addition to the characteristic $^{16}$O$^-$ and $^{18}$O$^-$ peaks, considerable intensity at approximately 17 and 19 amu on the m/z scale was also detected for all oxide scales. Those two peaks can be assigned to $^{17}$(OH)$^-$ and $^{19}F^-$ . The significant amount of F$^-$ observed in the oxide layers are caused by contamination of the samples during the preparation and are consequently not relevant for the analysis of material transport. The recorded intensity at 18.1 amu is over one order of magnitude smaller than for the peak, that can be assigned to $^{16}$O. The stable oxygen isotope $^{18}$O is only present in considerable amounts.
4.2 Oxidation in $^{16/18}O$ atmospheres

Figure 4.47: Mass spectra of 9Wsx, recorded by FIB-SIMS after two-stage oxidation in sequential $^{16/18}O$ atmospheres at 900 °C. The region surrounding the $^{18}O^−$-peak is magnified in the red inlet.

during the second stage of the experiment, when the oxide scales already exhibit substantial thickness. Therefore, a perceptibly lower intensity in the negative mass spectrum can be expected. To separate the $^{18}O^−$ peak from the surrounding background signal (compare inlet Fig. 4.47), dwell times for the acquisition of $^{18}O^−$ distribution maps have to be selected carefully. Since longer interaction of the primary ion beam with the sample surface increases its roughness, different dwell times for the recording of $^{16}O^−$ distribution in the scale was used.

Despite the disadvantageous signal-to-noise level, FIB-SIMS offers the opportunity to simultaneously acquire information on the appearance of the oxide scale and the corresponding tracer distribution. The quality and resolution of SE images are normally higher. Nevertheless, total positive secondary ions were used for imaging since they exhibit the exact resolution that can be reached during the acquisition of the SIMS map. Examples of positive ion images of the oxide scale that formed on 9Wsx during two-stage tracer experiments at 900 °C after a total exposure of 24 h are displayed in Figure 4.48a-c. The demonstrated distribution maps of $^{16}O^−$ and $^{18}O^−$ were recorded between the SI images.

A dwell time with a factor 8 times longer was used during acquisition of $^{18}O^−$ maps in order to account for the comparably low $^{18}O^−$ signal in addition to high noise levels of the detector (compare inlet in Fig. 4.47a). The negative ion intensity signal can be deteriorated by the oxide scale topography or local charging of the sample. Therefore, roughening due to sputtering (compare Fig. 4.48) was minimized as much as possible.
Figure 4.48: (a-c) Total positive secondary ion (SI) images and corresponding (d) $^{16}\text{O}^-$ and (e) $^{18}\text{O}^-$ intensity maps. SI images were taken to demonstrate the roughening in course of SIMS analysis. Oxide scale (a) prior to SIMS analysis, (b) after acquisition of $^{16}\text{O}^-$ and (c) $^{18}\text{O}^-$ intensity map.

through the careful selection of the primary ion beam intensity. The SI images (Fig. 4.48a-c) exhibit a moderate increase of surface roughness during FIB-SIMS investigations. To account for the background signal levels in the FIB-SIMS analyzer, a third mapping at m/e value of 17.5 amu is recorded. Prior to further processing, the background intensity of each measurement point is subtracted from the $^{18}\text{O}^-$ intensity.

Several authors suggested the usage of isotopic fractions (if$_{18}$ compare Equ. 2.13) to eliminate unwanted influences that are caused by localized charging, instrumental factors or sample topography [103, 106]. Since the dwell time was varied during SIMS analysis, a correction factor is needed to reach comparable conditions for accurate pointwise calculation of if$_{18}$. The increase of sputter yield over time can be assumed to be linear. $^{16}\text{O}^-$ intensities were therefore multiplied by a correction factor to account for the different times of acquisition.

The relative tracer enrichment during the second oxidation stage can be determined by correcting the calculated if$_{18}$ values (compare Equ. 2.13) using the actual concentration of $^{18}\text{O}_2$ partial pressures in
the gas that was used during the first stage \((g_1)\) and the second stage \((g_2)\) of the experiment [106]:

\[ \text{ir}_{18} = \frac{i_f_{18} - g_1}{g_2 - g_1} \]  \hspace{1cm} (4.3)

The \(^{18}\text{O}_2\)-partial pressure during the first stage equals the natural abundance of \(^{18}\text{O}\) (0.0024). The actual \(^{18}\text{O}_2\) concentration in the atmosphere of the second stage was determined prior to the conducted experiments (compare Sec. 3.2.2). Unfortunately, the calculation of \(i_{f_{18}}\) directly from oxygen intensity maps that contain relatively high noise levels can lead to misinterpretation. These difficulties are mainly observed for measurement points with both a low \(^{16}\text{O}^-\) and \(^{18}\text{O}^-\) intensity. The calculated \(i_{f_{18}}\) values for such points still correspond to considerably high values for relative tracer enrichment in the oxide scale. The application of Equation 4.3 for measurement points exhibiting \((^{18}\text{O}^-) - (^{16}\text{O}^-)\) value pairs of 3-1 and 6-2 respectively would both lead to the same result. Undoubtedly, the second measurement has higher relevance to the desired conclusions on transport mechanisms in the grown oxide scales. Figure 4.49 depicts the occurrence of value pairs observed during the calculation of relative tracer enrichment from the \(^{16}\text{O}^-\) and \(^{18}\text{O}^-\) intensity maps displayed in Figure 4.48 d-e. The originating maps are arrays of the size 512 x 442.

**Figure 4.49:** Contour plot indicating sum of measured value pairs.

To overcome the above described difficulties for low intensity values, measurement points exhibiting both \(^{18}\text{O}^-\) and \(^{16}\text{O}^-\) intensities below a certain threshold were treated as 0. The thresholds for oxygen ion intensities were individually determined for each experiment by means
of contour-plots that indicate the distribution of measured value pairs (compare Fig. 4.49). The used threshold values are summarized in the appendix of this study (Tab. B.1).

The isotopic enrichment in the displayed oxide scale established on 9Wsx at 900 °C (Fig. 4.48) was calculated by the described procedure and is demonstrated in Figure 4.50. Threshold values for $^{16}\text{O}^-$ and $^{18}\text{O}^-$ intensities in this case were set to 8 and 5. The distribution of the calculated relative isotopic enrichment across the scale is displayed as a color-coded map, where red indicates high and blue low values.

![Figure 4.50: Color-coded map of relative tracer enrichment in the oxide scale grown on 9Wsx during 24 h two-stage experiments at 900 °C. Values were calculated from $^{16}\text{O}^-$ and $^{18}\text{O}^-$ intensities exhibited in Figure 4.48. More details are provided in the text.](image)

Noticeable enrichment of $^{18}\text{O}$ isotopes is evident around pores and cracks. Along the grain boundary located in the left-hand side of the outer oxide scale, diffusion of oxygen is indicated by isotopic enrichment in this region. Interestingly, the apparent diffusion path disappears before reaching the internal oxidation zone. From the intermediate levels of $^{18}\text{O}^-$ signals in the inner oxide layer, diffusion-driven transport through this layer can be inferred. Closer inspection reveals that $d_3$ can be divided into two parts. In the upper regions, no $^{18}\text{O}^-$ signal was detected. The localized high isotopic enrichment towards the IOF corresponds to the width of $\text{Al}_2\text{O}_3$ observed in the internal precipitation region after 24 h exposure at 900 °C.

Foss et al. used $if_{18}$ maps following two-stage oxidation of a commercial Ni-based Superalloy to calculated "pseudo"-depth profiles of $if_{18}$ intensities [13]. The principle idea was adapted in this study. For the calculation of $if_{18}$, depending on the penetration depth $x$ of oxygen...
4.2 Oxidation in $^{16/18}O$ atmospheres

Into the scale, the values from one row were summed and divided by the total number of considered columns $N$:

$$
\bar{f}_{18}(x) = \frac{1}{N} \sum_{i=1}^{n} if_{18}
$$

Due to the irregular outer oxide interface, usage of the average $if_{18}$ across the entire width of the displayed oxide scale overestimates the expansion of $d_1$. The calculation of $if_{18}$ depth profiles from sections where the outer oxide scale is nearly parallel to the initial sample surface can be demonstrated to be considerably more meaningful. To determine effective enrichment of $^{18}O$ in the scale, the computed $if_{18}$ values are also corrected by the initial $^{18}O_2$ concentration in the gas. Isotopic enrichment depth profiles from the two sections marked in Figure 4.50 were calculated using Equation 4.4. The first region of the scale exhibits apparent indications for transport of oxygen along a grain boundary in the outer oxide layer. The isotopic enrichment, starting from the outer oxide interface, along with the average $^{16}O^-$ and $^{18}O^-$ intensity values in the same section of the mapping are included in Figure 4.51. High isotopic enrichment is evident over the first 5 $\mu$m of $d_1$. After this, features of a concentration profile for diffusion in a semi-infinite media are evident. An increased $^{18}O^-$ intensity on the edge of a pore, directly above the original sample surface, caused the sharp peak between 19 and 20 $\mu$m.

**Figure 4.51:** (a) Average tracer enrichment profiles of 9Wsx after 24 h two-stage oxidation experiments at 900 °C, calculated from section 01 (compare Fig. 4.50). Initial average intensities of oxygen isotopes in the same section are demonstrated in (b) $^{16}O^-$ and (c) $^{18}O^-$. 
The average intensity profiles for both oxygen isotopes are at an intermediate level within the inner oxide layer. Towards the internal precipitation region, the increase in the average $^{16}\text{O}^-$ intensity (Fig. 4.51b) can be explained by particularly higher secondary ion yields of Al-containing oxides. At the beginning of the internal precipitation region, the average $^{18}\text{O}^-$ intensity drops to nearly zero over a distance of approximately $3\,\mu m$. This finding is an indication for the existence of a second oxidation front separating the two distinguished regions ($d_2$ and $d_3$) in the internal oxidation zone. The second section for closer elucidation represents a region inside one large grain of the outer oxide layer. Figure 4.52 exhibits comparable features to those of the previously discussed intensity profiles.

**Figure 4.52:** (a) Average tracer enrichment profiles of 9Wsx after 24 h two-stage oxidation experiments at $900\,^\circ\text{C}$, calculated from section 02 (compare Fig. 4.50). Originating average intensities of oxygen isotopes in the same section are demonstrated in (b) $^{16}\text{O}^-$ and (c) $^{18}\text{O}^-$. An increased enrichment of $^{18}\text{O}^-$ indicates the outward transport of oxygen towards the scale/gas interface. A steep decrease of relative isotopic enrichment is evident after the outer region of new oxide formed by outward growth of $d_1$ during the second stage. Contrary to the first profile, no indications of considerable oxygen transport via diffusion are observed. Two sharp peaks of $^{18}\text{O}^-$ can be attributed to newly grown oxide inside the pores of the outer oxide layer. Across $d_2$, both excerpts exhibit comparable $^{18}\text{O}^-$ levels. Separation of two independently progressing oxidation fronts is less obvious but still recognizable in the isotopic intensity profile of section 02.
4.2.2 Tracer distribution in scales grown on ternary Co-base model alloys

The results of the thermogravimetry lead to the assumption that the principal oxidation mechanisms of ternary Co-base model alloys are widely comparable at 900 °C. Variation of the W content, corresponding to different γ’-volume fractions primarily alters the kinetics of individual processes. To confirm this assessment, two-stage oxidation experiments at 90 °C were conducted with 7Wsx and 10Wsx for 24 h. In the following, the results of one isotopic tracer experiment are summarized in one figure containing intensity maps $^{16}$O$^-$ and $^{18}$O$^-$ along with the computed isotopic enrichment in the investigated part of the scale. For better comparison of absolute dimensions, pseudo depth profiles from marked sections (white rectangles) of the scale are displayed as well.

![Image](image_url)

**Figure 4.53**: Total positive secondary ion images and corresponding for (a) 7Wsx, (b) 9Wsx and (c) 10Wsx after 24 h tracer experiments at 900 °C. All images were taken prior to the acquisition of SIMS maps.

Total positive ion images of representative oxide-scale cross-sections are demonstrated in Figure 4.53. All micrographs were taken prior to SIMS analysis. After a total duration of 24 h exposure in 200 mbar pure oxygen, the oxide scales are highly comparable to the one observed on the same alloys after 24 h thermogravimetry. Due to the changed contrast conditions in SI images, the internal precipitation region ($d_3$) appears less clear in the displayed cross-sections. However, closer examination reveals a particularly pronounced zone of Al$_2$O$_3$ precipitates for the sample that contains 10 at.% W. Similar dimensions of $d_3$ were obtained for 9Wsx and 10Wsx after 24 h tracer experiments at 900 °C.

The results of SIMS investigations after two-stage tracer oxidation experiments in oxide scales on 7Wsx are displayed in Figure 4.54. The oxide scale grown at 900 °C on 7Wsx during 24 h exposure is
substantially thicker than the one observed on 9Wsx. Newly formed oxide is evident at the outer scale interface as well as in the region directly above the IOF. Computed depth profiles of isotopic enrichment in the marked section exhibit a significant enrichment of $^{18}\text{O}^-$ at the transition from $d_2$ to $d_3$. No apparent diffusion paths can be seen in the outer oxide layer, even though the total secondary ion image indicates the presence of several grain boundaries in the displayed part of the scale. Due to the substantial amount of newly formed oxide phases in the internal oxidation zone, sole transport of oxygen by diffusion along grain boundaries seems improbable. Formation of microcracks and subsequent transport of molecular oxygen through the outer oxide layer can be one explanation for the absence of visible indications for oxygen transport. The extent of outer oxide layer growth during the second stage, indicated by $^{18}\text{O}^-$ enrichment, exhibits variation over the width of the investigated oxide scale section. These variations might be caused by altered diffusion velocities of Co cations through the oxide lattice, depending on the grain orientation.

Distribution of oxygen isotopes along with a map of relative tracer enrichment after 24 h of two-stage exposure of 10Wsx at 900 °C are displayed in Figure 4.55. Due to the higher W content, the oxide scales exhibited overall lower thickness. Enrichment of $^{18}\text{O}^-$ in the 5 μm below the oxide surface indicates the transport of metal cations through the outer layer. A clear demarcation between the inner oxide layer ($d_2$) and the internal precipitation region is evident in the $^{18}\text{O}^-$ map and
in the relative tracer enrichment across the investigated section of the scale. Minor traces of newly formed oxide along grain boundaries of the outer layer can be seen at the right-hand side of the displayed scale. Once again, $^{18}\text{O}^{-}$ is evidently enriched around pores inside the outer oxide layer.

The results gained after two-stage oxidation experiments revealed similar transport mechanisms for all considered ternary Co-base model alloys at 900 °C. Counter current transport of reactants through the growing scale is evident. The amount of oxide phases formed during the second stage of the experiment is determined by the prevailing oxidation kinetics and therefore dependent on the W content. Expansion of the outer oxide layers can only be sustained by continuous outward diffusion of metal cations. Transport mechanisms for the penetration of oxygen to form new oxide at the scale/ alloy interface are less clear. Evidence of new-formed oxide phases were apparent at only a few localized spots of the outer oxide layers on 9Wsx and 10Wsx. However, the migration of molecular oxygen through microcracks formed during oxidation seems highly probable. For intermediate W contents of 9 at.%, further two-stage tracer experiments with altered duration were conducted. The ratio between the length of the first and second stage remained constant.

Furthermore, oxygen tracer distribution after two-stage oxidation experiments was analyzed to elucidate whether paths for material transport change with longer exposure times. In order to minimize
sputter damage during SIMS analysis, primary ion beam currents require careful selection. For relatively thin oxide scales, lower currents are mandatory, which consequently leads to less secondary ion yield, particularly reflected in low $^{18}$O$^-$ signal. Due to these limitations, the calculation of relative tracer enrichment for two-stage experiments conducted for shorter times and lower temperatures cannot reach the significance of the previously presented results. Therefore, in the following, secondary ion images are displayed along with maps of $^{16}$O$^-$ and $^{18}$O$^-$ signal across the scale. Figure 4.56 displays a total positive secondary ion image with corresponding FIB-SIMS mappings ($^{16}$O$^-$ and $^{18}$O$^-$) of a representative section of the oxide scale after 5 h two-stage oxidation of 9Wsx at 900 °C.

![Figure 4.56](image-url)

**Figure 4.56:** (a) Total positive secondary ion image with corresponding negative FIB-SIMS elemental mapping ((b) $^{16}$O$^-$ and (c) $^{18}$O$^-$) after 5 h two-stage exposure of 9Wsx at 900 °C.

Due to the shorter duration of exposure, an overall thinner oxide scale with particularly less-pronounced internal precipitation region ($d_3$) developed. As described above, lower overall $^{18}$O$^-$ levels were measured. Newly formed, $^{18}$O-containing oxide is evident at the external scale interface as well as in the region above the IOF. In contrast to oxides scales after 24 h experiments, the $^{18}$O$^-$ intensity is almost completely spread over $d_3$. Intermediate $^{18}$O$^-$ signal are also detected in the inner oxide layer. Minor enrichment of $^{18}$O$^-$ is apparent around small pores in the outer oxide layer. As expected, the intensity of $^{16}$O$^-$ exhibits higher values in the internal oxidation zone. Altered secondary ion yields cause the differences in $^{16}$O$^-$ intensities between outer oxide layer and the internal oxidation zone. The isotopic tracer distribution in scales developed during 48 h two-stage oxidation experiments are demonstrated in Figure 4.57.
4.2 Oxidation in $^{16/18}$O atmospheres

![Figure 4.57:](image)

*Figure 4.57:* (a) Total positive secondary ion image with corresponding negative FIB-SIMS elemental mapping ((b) $^{16}$O$^-$ and (c) $^{18}$O$^-$) after 48 h two-stage exposure of 9Wsx at 900 °C.

Longer total duration of exposure in $^{16/18}$O-containing environments does not affect the position of newly grown oxide phases. Countercurrent diffusion is indicated by clear $^{18}$O$^-$ isotopic enrichment at the inner and outer interface of the oxide scale. Since a relatively wide internal precipitation region already developed during 32 h in natural oxygen, only a comparably small section of $d_3$ (10 $\mu$m) exhibited considerable $^{18}$O$^-$ signal. The porosity in the outer oxide layer is more pronounced after 48 h exposure. In all cases, observed porosity is accompanied by significant $^{18}$O isotopic enrichment in the regions surrounding these pores. In contrast to the sample oxidized for 24 h, no apparent oxygen diffusion paths were observed in the outer oxide layer.

Thermogravimetry indicated considerably slower oxygen penetration through scales grown on ternary Co-base model alloys at 850 and 800 °C. To verify whether the slower transport of oxygen can be also explained by alteration in the predominating transport paths, additional two-stage oxidation experiments were conducted with 9Wsx samples at lower temperatures. For comparison with the results presented so far, a total duration of 24 h exposure at 800 and 850 °C was selected. Distribution of $^{16}$O$^-$ and $^{18}$O$^-$ in the displayed section of the scale developed at 850 °C are summarized in Figure 4.58.

After exposure at 850 °C, enrichment of the marked oxygen isotope is evident on the interface between alloy and oxide scale as well as in the upper region of the outer oxide layer. The porosity in $d_1$ is accompanied by increased $^{18}$O$^-$ signal. The pure Co-containing oxide that is formed during the second stage of the experiment at 850 °C is not limited to a narrow region at the topmost microns of this layer. Instead, the oxide containing $^{18}$O appears broadly distributed over $d_1$. 


Figure 4.58: (a) Total positive secondary ion image with corresponding negative FIB-SIMS elemental mapping ((b) $^{16}O^-$ and (c) $^{18}O^-$) after 24 h two-stage exposure of 9Wsx at 850 °C.

The uneven distribution of $^{18}O^-$ over the entire outer oxide layer is even more pronounced after two-stage oxidation experiments at 800 °C, as demonstrated in Figure 4.59. Furthermore, enrichment of labeled oxide phases at the interface between oxide and alloy is less pronounced. A section of transverse $Al_2O_3$ is included in the investigated region of the scale and marked in the mapping of oxygen isotopic distribution (compare Fig. 4.59). For the lowest considered oxidation temperature, the appearance of significant $^{18}O^-$ signal once again accounts for simultaneous transport of Co cations to the outer interface and oxygen to the IOF. The distribution of newly formed oxide in the outer layer at 900 °C is highly localized for all investigated ternary Co-base alloys. Consequently, the majority of transport processes in opposite directions occur via different paths at higher temperatures. The clear demarcation between scale sections formed during the first and the second stage diminishes at lower exposure temperatures. Outward expansion of pure CoO is known to be sustained by cation diffusion over the entire considered temperature regime [54]. Therefore, alteration of oxygen transport processes resulting from lower oxidation temperatures is

Figure 4.59: (a) Total positive secondary ion image with corresponding negative FIB-SIMS elemental mapping ((b) $^{16}O^-$ and (c) $^{18}O^-$) after 24 h two-stage exposure of 9Wsx at 800 °C.
more plausible. A comprehensive summary on the role of material transport for the development of morphological features within the multilayered oxide scales will be provided in the discussion.

### 4.2.3 Material transport in scales on Cr-containing model alloys at 900 °C

Fundamental differences in prevailing reaction kinetics during scale formation on Co/Ni-base model alloys were demonstrated in the previous sections. The altered oxidation rates, depending on the ratio of Co and Ni in the alloy, can be partly explained by the formation of protective layers. However, rapid reaction rates evident during the early stages of oxidation, cannot solely originate from the blocking effect of the Cr-containing scale section in the internal oxidation zone. For a more detailed understanding, the transport of reactants through growing oxide scales on Co/Ni-base model alloys at 900 °C is elucidated in the following. For the same reasons provided during the investigation of reaction kinetics (compare Sec. 4.1.3.1), two-stage oxidation experiments were conducted for the pure Co- and Ni-base alloy as well as for the intermediate composition with equal Co and Ni contents. The data presented in the following were acquired in cooperation with Richard Chater from the Department of Materials at the Imperial College in London. Some of the results were published in a study demonstrating the applicability of the employed approach to visualize oxygen transport in growing oxide scales [132].

![Figure 4.60: Total positive secondary ion images of (a) NC0osx, (b) NC5osx and (c) NC100osx after 24 h two-stage oxidation experiments at 900 °C. All images were taken prior to the acquisition of SIMS maps.](image)

After 24 h oxidation in pure oxygen, the investigated cross-sections exhibit three layers. Total positive secondary ion images of scales grown
during exposure for 24 h in $^{16/18}$O-containing oxygen atmospheres are displayed in Figure 4.60. The dimension of each layer corresponds to the extent of scale formation, as anticipated from previous results at this exposure temperature. Higher Co/Ni ratios lead to thicker oxide scales. For the Ni-containing alloys, the mechanically polished sample was subject to considerable delamination and material dropouts. FIB-milling of a trench was used to improve the quality of the considered regions prior to the acquisition of SIMS data. No detrimental effect of the milling marks in ion beam direction, which are particularly apparent for NC50sx (compare Fig. 4.60b), could be seen. Due to projection of the displayed cross-sections, the dimensions of typical feature in Y-direction may therefore appear slightly altered. The displayed section of the outer oxide layers on NC50sx and NC100sx includes few grains with a size of several microns. The outer scale interface exhibits the curved nature reflecting the dimensions of these grains. Outer oxide layers on pure Ni-base model alloys demonstrated much smaller grain size. The distribution of considerably smaller grains in NiO developed in the course of 24 h oxidation at 900 °C on NCOosx are clearly visible in Figure 4.60a). The highest degree of porosity was obtained for the outer oxide layers on pure Co-base model alloys. Since the cross-section of NC100sx was mechanically polished, porosity might have further increased during sample preparation. However, the two samples prepared by FIB-milling also exhibited a different degree of porosity. This finding clearly confirms the assumption that oxide layers developed on Co-containing alloys generally contain higher porosity, especially in the outer layer. For better comparability, SIMS data from 24 h two-stage oxidation experiments for Cr-containing model alloys are presented similar to the data obtained for ternary Co-base alloys under the same experimental conditions. Mappings of $^{16}$O$^-$ and $^{18}$O$^-$ along with calculated distribution of relative tracer enrichment of the pure Co-base alloy NC100sx at 900 °C are summarized in Figure 4.61. The distribution of oxygen isotopes in scales grown on NC100sx during two-stage tracer exchange experiments at 900 °C is comparable to the distribution determined for ternary Co-base model alloys.

Considerable portions of new oxide are found in the lower region of $d_3$ IOF and on the outer oxide scale interface. The high porosity in the outer oxide layer is accompanied by substantial enrichment of $^{18}$O in the surrounding regions. Narrow transport paths along grain boundaries in the outer oxide layer are evident in the tracer
4.2 Oxidation in $^{16/18}O$ atmospheres

Figure 4.61: SIMS data including $^{16}O^-$ and $^{18}O^-$ intensity mappings along with calculated distribution of relative tracer enrichment after 24 two-stage oxidation of NC100sx at 900 °C. Displayed average tracer enrichment profiles were calculated from the marked region of the oxide scale.

enrichment map. In all cases, these paths are connected to comparably large pores, which also causes a remarkable increase in the computed tracer enrichment depth profile. Minor amounts of labeled oxide can also be found in the inner oxide layer. Partial substitution of Co by Ni was demonstrated to significantly decrease oxidation kinetics (compare Sec. 4.1.3.1) while the oxide scale remains similar in appearance. Figure 4.62 depicts oxygen isotope distribution as well as calculated data for relative tracer enrichment in the oxide scale on NC50sx after two-stage oxidation experiments at 900 °C.

Figure 4.62: SIMS data including $^{16}O^-$ and $^{18}O^-$ intensity mappings along with calculated distribution of relative tracer enrichment after 24 two-stage oxidation of NC50sx at 900 °C. Displayed average tracer enrichment profiles were calculated from the marked region of the oxide scale.
4 Results

As expected all layers exhibit smaller thickness. However, the location of labeled oxide observed during SIMS analysis is similar to that described for NC100sx. The majority of oxide that formed during the second stage is located on the oxide/air and the oxide/ alloy interface, indicating counter-current transport of reactants. Further $^{18}\text{O}$ enrichment is apparent around small pores in the lower part of $d_1$. For the intermediate Co/Ni-base alloy, only slight traces (marked by a white arrow) of oxygen diffusion along grain boundaries are recognizable. A closer look at the $^{18}\text{O}^-$ distribution map reveals also considerable amounts of new oxide phases at the $d_2/d_3$ interface. Furthermore, comparison of both tracer distribution maps confirms that only the lower part of the internal precipitation region consists of $^{18}\text{O}$-containing $\text{Al}_2\text{O}_3$. SIMS data after a total 24 h exposure in $^{16}/^{18}\text{O}_2$-containing environments are provided in Figure 4.63. Material transport in opposite directions is also confirmed for the pure Ni-base alloy by the presented SIMS data. New oxide is found on the interface between $d_2$ and $d_3$. The increased $^{18}\text{O}^-$ signal might be due to slower expansion of the Cr-containing barrier layer which is assumed to proceed during the second stage on basis of previous kinetic investigations (compare Sec. 4.1.3.1).

![Figure 4.63: SIMS data including $^{16}\text{O}^-$ and $^{18}\text{O}^-$ intensity mappings along with calculated distribution of relative tracer enrichment after 24 two-stage oxidation of NC00sx at 900 °C. Displayed average tracer enrichment profiles were calculated from the marked region of the oxide scale.](image)

Paths for the penetration of oxygen through the outer oxide layer via diffusion were not detected. The absence of any traces of oxygen diffusion in the externally grown NiO layer once more supports the assumption, that part of the oxygen transport occurs via microcracks.
Several studies correlated the extent of crack formation in outward growing oxides on Co- and Ni-alloys to the overall growth kinetics of the respective alloy [59, 120, 133]. Following this line of argumentation, relatively wide cracks should form during scale growth on pure Co-base alloys. These models provide a consistent explanation for the evident increase of porosity in the outer layers with higher Co/Ni ratios during isothermal exposure.
5 Discussion

In the following chapter, the presented results are reviewed and classified. All experiments contributed to a deeper understanding of the elementary mechanisms during oxide scale growth on two-phase Co/Ni-base model alloys. A comparably broad set of data, that uses several surface analytical techniques was presented in the preceding chapter. Therefore, the discussion of these results is provided in two parts. In the first part, relevant findings are reviewed according to available literature and ultimately combined into model predictions explaining the onset and progress of scale formation from early stages to quasi-steady state conditions (Sec. 5.1). In the second part, the reliability of acquired data and utilized techniques will be assessed (Sec. 5.2 - 5.3). Whenever possible, suggestions are provided in how to overcome constraining experimental factors that may lead to reduced reproducibility of data.

5.1 Model predictions

5.1.1 Role of two-phase microstructure during individual oxidation stages

In the present study, the transient oxidation behavior of ternary Co-base model alloy was investigated in high detail. In addition to the chemical composition of the inner oxide layer, another focus was set on the early stages observed during the first 12 h of oxidation. With the insights obtained by high-resolution STEM and various other results, it is possible to discuss the mechanisms which lead to the disadvantageous oxidation properties of ternary Co-base Superalloys at temperatures above 800 °C. The existence of two oxidation fronts moving towards the alloy was confirmed by two-stage tracer experiments (compare Sec. 4.2.2).
The IOF classically describes the region of the deepest penetration of oxide. The IOF is followed by a second oxidation front, the interface between inner oxide layer ($d_2$) and internal precipitation region ($d_3$). It can be concluded from the growth rates of $d_2$ and $d_3$ (compare Sec. 4.1.1 and Sec. 4.1.2.2) that these oxidation fronts generally advance at different rates, irrespective of exposure temperature. Particularly at the early stages of scale growth on ternary Co-base alloys, the rapid penetration of oxygen towards the interface between the alloy and scale leads to the formation of various phases in regions surrounding the IOF. More detailed insight on the role of the matrix and hardening phase in the expansion of $d_3$ was obtained with the help of STEM-EDX mappings for 9Wsx exposed at 900 °C for up to 5 h (compare Sec. 4.1.2.4). The observations regarding phase stability and appearance of the IOF (Sec. 4.1.2.5) from all considered ternary alloy compositions suggest that these findings can be applied for the entire range of elucidated exposure temperature. A series of schematic drawings that illustrate the development of the IOF in ternary Co-base alloys during scale growth is demonstrated in Figure 5.1. The focus is on the impact of the (intact) $\gamma/\gamma'$ microstructure on the appearance of the advancing IOF during the first stages (e.g. $t < 12$ h at 900 °C) of scale growth.

![Figure 5.1](image.png)

**Figure 5.1**: Schematic diagram, highlighting the structural changes on the IOF. Shown are four different durations of exposure ($t_1 < t_2 < t_3 < t_4$). For simplicity, besides the diffusion of oxygen only the diffusion and depletion (gradient in $\gamma$ channel) of Al is taken into account [116].

In addition to the formation of new phases, fluxes of reactants are considered in the schematic as well. For reasons of simplicity, only Al depletion is indicated as a gradient (from dark (greater Al content) to bright (lower Al content)) in the gray value of the $\gamma$ phase. The thermodynamically most stable phase present in the scale is unequivocally $Al_2O_3$. Following a short duration of exposure, precipitation of $Al_2O_3$ occurs solely in the $\gamma$ phase. Due to the high thermodynamic stability
5.1 Model predictions

of Al$_2$O$_3$, the least amount of oxygen is sufficient to form this phase compared to all other possible oxide phases. Therefore, this phase can be expected to grow, as long as sufficient amounts of Al from adjacent regions are available. The order of favorable oxide species identified different oxygen potentials in quaternary Co-base Superalloys, was recently assessed with a first principle approach [75]. In the investigated system, Al$_2$O$_3$ was identified to be the most stable species, followed by CoAl$_2$O$_4$ and then CoWO$_4$. The least stable oxide, CoO is characterized by low thermodynamic stability but exhibits the most rapid rates for layer expansion. Consequently, the Co oxide is primarily observed in the outer oxide layer. The investigated composition of phases found in d$_2$ (Fig. 4.23 and Tab. 4.5) demonstrated the presence of CoO in the inner oxide layer as well. The STEM-EDX mappings after 5 and 30 min (Fig. 4.25a and b) document the localized precipitation of Al$_2$O$_3$ in a γ channel. At this early stage of oxidation (t < t$_3$), after all the Al from a certain volume increment is consumed, enough oxygen remains to form less stable oxides. These oxides are CoWO$_4$ and later CoO, which can be found in close proximity to Al$_2$O$_3$ in the former γ channels. Due to the increase in scale thickness with longer duration of oxidation, the flux of oxygen at the IOF continuously decreases. In contrast, prior to the establishment of an extensive Al-depleted zone, the Al flux from the alloy can be assumed to remain nearly constant. During scale formation, the balance between the described fluxes changes.

As described by several authors, the appearance of alumina precipitates is mainly determined by the progress of oxidation as well as the nucleation and growth rate of Al$_2$O$_3$ in the alloy. That internal precipitates that form on the IOF grow larger for decreasing O fluxes during early stages of scale formation. Referring to the study of Zhao et al. [28], a high number of discrete precipitates indicates a high nucleation rate of Al$_2$O$_3$ in the matrix, e.g. as observed in the STEM-EDX mappings of the region enclosing the IOF (Fig. 4.23). The morphology of Al$_2$O$_3$ precipitates observed at the IOF after 5 h still speaks for a state of relatively rapid internal oxidation. This finding is also confirmed by characteristics of the instantaneous time exponent (n$^{inst}$) that was demonstrated as an example for scale growth on 9Wsx at 900 °C (Fig. 4.1b). For 9Wsx, dissolution of the γ’ phase was demonstrated following the depletion of Al (compare Fig. 4.25c) after 5 h exposure at 900 °C. Consequently, the two-phase structure starts to lose its importance beyond this stage.
No formation of Co₃W phases was apparent in STEM-EDX mappings of the IOF after 5 h exposure.

Figure 5.1 provides a schematic summary of the formation of phases in a constant volume increment surrounding the IOF. The sequence of processes was determined for all elucidated ternary Co-base alloys between 800 and 900 °C. Individual occurrence is determined by the combination of W content and exposure temperature. The first two images were chosen to describe the conditions during the rapid internal progress between the initiation stage and 30 min oxidation. At this stage, the supply of Al proceeds solely from the γ phase. The gradient of Al concentration along the channels (compare Fig. 4.25a and b) offers the striking proof for this hypothesis. Since no Al partitioning preference could be determined in ternary Co-base Superalloys [108], the observation of evident Al depletion that only expands along the γ channel is even more outstanding. Stronger binding of Al in the intermetallic γ′ phase might further hinder the diffusion of Al from the precipitate into the channel. For longer durations of exposure, the gradient that indicates Al depletion spreads further into the alloy.

The initiation of γ′ depletion is schematically demonstrated in t₃ (Fig. 5.1). At this stage, the flux of Al arises from both phases, accompanied by the onset of γ′ dissolution. At t₄, which represents a stage before quasi-steady-state conditions are reached, stronger depletion of Al leads to the formation of unfavorable needle-like Co₃W structures in the internal precipitation region. At a given temperature, the oxidation time t₄ before growth of Co₃W is evident and was demonstrated to shorten with increasing W content (compare Fig. 4.27 and 4.26).

Transition to steady-state growth was classically correlated with the formation of a continuous protective oxide layer on the IOF [45]. After the development of this barrier layer, the overall growth rate is expected to be mainly governed by the expansion of the protective film. In this study, a closed Al₂O₃ layer was only found for samples with low and intermediate W content after 100 h oxidation at 800 °C. This finding corresponds to the result from Klein et al., where continuous alumina layers were observed for polycrystalline Co-base alloys that also contain considerable levels of B at 800 °C [69, 70]. The most intensely investigated model system that demonstrates a clear transition from internal oxidation to the formation and expansion of an alumina layer between 800 and 900 °C is binary NiAl (compare Sec. 2.1.3.3). In Hindam model
predictions, the alumina layer growth originates from random impingement sites that are expanded by neighboring precipitates to larger, more protective scale sections [27]. Ultimately, all transverse Al$_2$O$_3$ segments are combined to one continuous layer. For ternary Co-base alloys, nucleation of Al$_2$O$_3$ was demonstrated to occur exclusively in the matrix phase during early stages of scale growth (compare Sec. 4.1.2.4). At a presumably constant nucleation rate, narrow channels caused by higher W contents in the alloy can be assumed to increase the probability for two precipitates to join and form an impingement site. On the other hand, especially at lower temperatures, high W levels appeared to be detrimental to the development of an alumina-rich layer (compare Fig. 4.17). In order to explain these contradictory results, nucleation and expansion of alumina parallel to the original alloy surface has to be considered separately. No clear dependency of nucleation rate on the W content could be determined in this study. Due to slower O transport towards the IOF, Al$_2$O$_3$ precipitates grew larger in alloys with higher W contents after the same duration of exposure. For isothermal oxidation of 7Wsx, an advancing Al$_2$O$_3$ front could be observed next to isolated precipitates within the matrix of an intact $\gamma/\gamma'$ microstructure (compare Fig. 4.17). Figure 5.2 exhibits a representative section of the scale with the relevant region in high magnification after 72h of exposure at 800 °C.

![Figure 5.2](image)

**Figure 5.2:** (a) BSE micrographs of multilayered scale on 7Wsx after 72 h exposure at 800 °C. (b) Magnified section of the IOF containing a high number of Al$_2$O$_3$ precipitates near an advancing alumina layer.

As previously stated, for most conditions, the two-phase microstructure dissolves before significant spreading of protective scale sections is initiated. However, the micrographs obtained from 7Wsx (Fig. 5.2), capture the stage of scale growth shortly before individually developed Al$_2$O$_3$ sections are combined to form a continuous layer. The magnified IOF contains an unaltered high number of precipitates without
apparent impingement events in the $\gamma$ phase. It can therefore be concluded that reduced oxygen fluxes during expansion of oxide scales are a key factor for the formation of protective oxide layers in ternary Co-base alloys. Higher W levels might reduce the diffusion rate of Al in the $\gamma$ phase and facilitate an earlier formation of W-rich intermetallic phases at the IOF. The Co$_3$W needles constitute an obstacle for the transverse spreading of alumina on the IOF.

The addition of 8 at.% Cr to the ternary alloy 9Wsx, improves the overall oxidation resistance, but leads to the severe formation of nitrides over the entire range of considered temperatures. For the pure quaternary Co-base model alloys, no distinct impact of the two-phase microstructure on the oxidation behavior was evident during the conducted experiments. Moreover, dissolution of $\gamma'$ and simultaneous formation of Co$_3$W was already apparent after 5 h of exposure (compare Fig. 4.33 and 4.41) during the transient stage of scale growth within the complete range of elucidated temperatures. The increase of Ni levels in Cr-containing model alloys significantly reduces the susceptibility to third phase formation. However, the development of $\gamma'$-depleted zones further limits the noticeable impact of original alloy microstructure on the very early stages of scale formation, a topic that is beyond the scope of this study. Instead, this alloy system of intermediate Co/Ni-base model alloys was used to investigate the alteration of transport processes caused by the fraction of alloying elements. Associated mechanisms are discussed in the following section.

5.1.2 Sub-scale morphology and transport of alloying elements

The preferential diffusion of Al along $\gamma$ channels of 9Wsx alloys at 900 °C was demonstrated in Section 4.1.2.4. Only a few studies addressed the impact of two-phase microstructure on the advancing of internal oxidation. Edmonds et al. demonstrated the preferential oxidation of $\gamma'$ particles in a Ru-bearing fourth-generation Ni-base Superalloy during long-term exposure at 750 °C in air [134, 135]. Comparable results were presented in an *in situ* TEM study on the progress of internal oxidation that was observed in a second-generation Ni-base Superalloy at 850 °C [136]. In this study, diffusion of oxygen was postulated to referentially occur along the coherent interfaces between $\gamma$- and $\gamma'$ phase. Despite the high resolution of the explored technique,
differences between the $\gamma/\gamma'$-interface and the mid-channel region could not be recognized in the investigated ternary Co-base model alloys after short-term exposure at 900 °C. For the highest considered exposure temperature, the unveiled depletion of the lightest alloying element is restricted to the matrix phase of the ternary alloy only for the first 5 h. Lower W content and reduced oxidation temperature, were demonstrated to expand the initiation stage during which the two-phase microstructure remains stable close to the IOF (compare Sec. 4.1.2.5).

Figure 5.3: Internal oxidation zone of Co-base alloys above 800 °C [116].

A schematic cross-section of the internal oxidation zone ($d_2+d_3$) in ternary Co-base alloys during quasi-steady state oxidation is demonstrated in Figure 5.3. In addition to the obvious and sufficiently discussed Al depletion, another region that is also depleted in W was measured by STEM-EDX. In the foregoing, the diffusion behavior of W was only briefly discussed. Apparent depletion of W within the internal precipitation region could be demonstrated to start during the initial period of rapid oxidation kinetics. The reason for the considerable decrease of W in this zone can be attributed to the formation of CoWO$_4$. The high availability of oxygen in the transient stage leads to extensive growth of the W-containing oxide phase after the available Al is consumed. Referring to XRD measurements, Klein et al. assumed a considerable amount of CoWO$_4$ to be present in the inner oxide layers of polycrystalline ternary and quaternary Co-base Superalloys [69, 70, 115, 137].
5 Discussion

The dark appearing W-depleted zone directly below the \(d_2/d_3\) interface is observed in BSE micrographs of oxide scales from all ternary model alloys after exposure at 850 and 900 °C (compare Fig. 4.13 and Fig. 4.9). To date, considerable depletion of the heaviest alloying element in the internal precipitation zone was not reported in literature.

Directly below the \(d_1/d_2\) interface, a narrow oxidized region that displays a morphology comparable to the original two-phase microstructure can still be recognized. Due to the location, it is reasonable to assume that these structures were formed during the early stages of scale formation. As demonstrated by the elemental distribution maps of samples that were oxidized for up to 30 min (compare Fig. 4.25a and b), large quantities of Al from the \(\gamma\) phase are instantly consumed by the formation of \(\text{Al}_2\text{O}_3\) on the IOF. After short exposure times, \(\text{CoWO}_4\) was observed in close proximity to \(\text{Al}_2\text{O}_3\) in the \(\gamma\) channels at the IOF. During the ongoing oxidation process, a second oxidation front advances into the alloy. Right below the original alloy surface, only the \(\gamma\) channels were oxidized due to rapid internal oxidation during the first minutes of exposure. Since Al is still present in regions that were formerly covered by \(\gamma'\) cubes, additional Al-containing oxides form there. One deliberately chosen part of the aforementioned area is magnified in Figure 4.24 and clearly exhibits lamellar \(\text{CoAl}_2\text{O}_4\) spinels embedded in \(\text{CoWO}_4\). Yan et al. used convergent beam TEM-EDX to determine the average composition from individual inner scale sections of Cr-containing quaternary Co-base Superalloys [71]. The development of the spinel phase could be demonstrated in the upper region of the inner oxide layer. Due to the previously unattained high level of detail in terms of partial resolution, the present study was not only able to confirm theoretical predictions found in the literature [75, 137], but also to provide mechanistic insights into the very early stages of scale formation on ternary Co-base alloys. The distinctive structure in this narrow region was observed in all investigated scales on ternary Co-base model alloys. Due to the retarded decay of the former \(\gamma/\gamma'\) structure, this region of \(d_2\) is most pronounced for \(\gamma\text{W}_{0.85}\) oxidized at 800 °C.

From recent studies on diffusion of alloying elements in binary Co-X alloys, it can be concluded that W diffusion is orders of magnitude slower than Al diffusion in ternary Co-base Superalloys [38–40]. Nevertheless, after Al is completely consumed, the next stable oxide phases observed is \(\text{CoWO}_4\). With steadily decreasing propagation rate of the identified second oxidation front, the content of the more slowly
diffusing W also visibly declines. As soon as the oxide formation in an intact two-phase Co- or Ni-base Superalloy is discussed, segregation behavior of alloying elements should be considered as well. In ternary Co-base model alloys, almost equal distribution of Al in $\gamma$- and $\gamma'$ phase were reported [108, 110]. Despite the similar trend in the partitioning of alloying elements, the overall compositions of $\gamma$ and $\gamma'$ alter with increasing W content. Although, no information on diffusion rates of Al dependent on the overall W levels in the alloy were elucidated, it is reasonable to assume that increasing concentration of the heavier element W has a retarding effect on the diffusion of Al at a given temperature.

In Section 4.1.3.1, the scale growth of Co/Ni-base model alloys was investigated in detail. The PhD project of Christopher Zenk elucidated elemental segregation by means of atom probe tomography in this alloy series [141]. Distribution of the elements Al and Cr, which are of pivotal importance for the barrier properties of high-temperature alloys, were demonstrated to be strongly dependent on the ratio of base elements. Generally, partitioning of Cr in the matrix and Al in the precipitation phase was determined. The extent of segregation is higher for decreasing Co/Ni ratios. Almost equal partitioning coefficients $k_{\gamma}^{\gamma'/\gamma}$ were determined for Al and Cr in the Ni-rich model alloys NC00sx and NC25sx. The value $k_{\gamma}^{\gamma'/\gamma}$ gradually decreases from NC25sx to NC100sx for the two alloying elements. For pure Co-base model alloys, considerable Cr enrichment in the matrix phase was measured, whereas the increase of Al in $\gamma'$ was not significantly higher. At 900 °C, the pure Ni-base alloy exhibited extensive $\gamma'$-depletion after already 5 h (compare Fig. 4.33). Although, the development of a depleted zone was less pronounced for the intermediate Co/Ni-base model alloy, no precipitation of Al$_2$O$_3$ was found in the entire considered temperature window. Since extensive formation of Co$_3$W below the advancing IOF in NC100sx was observed between 800 and 900 °C, any influence on the individual two-phase microstructure for the onset of protective scale formation can also be excluded for this alloy series.

Figure 5.4 provides a schematic comparison of the appearance and the specific morphological features of the internal precipitation region, which are dependent on the Co/Ni ratio. Apparent differences in phase stability as well as transport properties of Al and Cr in the oxidation-affected sub-scale region were observed in the course of this study and are therefore included in the figure. During (quasi-)steady-state
Discussion

conditions, the interface between inner oxide layer and the internal precipitation layer of all Co/Ni-base model alloys is covered by fractions of a Cr-containing barrier layer at 900 °C. As pointed out in Section 4.1.4, sustainability of protective Cr-containing scale sections decreases with increasing Co content of the alloy for the entire range of elucidated exposure temperatures.

Figure 5.4: Schematic representation of $d_3$ and adjacent alloy region in Co/Ni-base model alloys after considerable exposure at 900 °C.

Long-term stability and oxidation resistance of Co-Cr alloy were already subject to several studies in the literature. Stott et al. compared the oxidation behavior of M-Cr-Al (M = Ni, Fe, Co) model alloys between 1000 and 1200 °C. In this early study, Ni-base alloys containing intermediate Cr and Al contents already exhibited superior adherence and therefore less susceptibility to cracking of the initially formed protective layers [68]. The results obtained from the thermogravimetry (compare Sec. 4.1.3.1) confirm this trend. No striking impact of the W content could be observed throughout this study. For this relatively complex model system, the identification of all developed oxide phases during the isothermal exposure in the inner oxide layer is beyond the scope of this study. After carefully reviewing the available literature, formation of (Co/Ni)Cr$_2$O$_4$ spinel layers at the $d_2/d_3$ interface seems highly probable in (model) alloys that contain intermediate Cr and Al (<10 at.%) contents [59, 125, 142–145]. The products of high-temperature oxidation of alloys in the Co-Cr-Al and Ni-Cr-Al system were subject to several studies (e.g. [126, 146]). Significant discrepancies were observed between the calculated and experimentally determined values for the minimum Cr concentration that is required to form a protective Cr$_3$O$_3$ layer in binary Ni-Cr alloys [146]. In order to explain these differences, transport of alloying elements to the advancing reaction front have to be considered. The initially formed, thermodynamically most stable phases in the investigated model alloys are Al$_2$O$_3$ and Cr$_2$O$_3$. Following
the depletion of for example Cr in the sub-surface zone, the activity of Cr on the IOF can fall below the required value to sustain a protective Cr$_2$O$_3$. Consequently, the initially developed chromia reacts to the NiCr$_2$O$_4$ spinel phase. Furthermore, the relatively rapid transport of O to the d$_2$/d$_3$ interface leads to a relatively high O activity, that is detrimental for the long-term stability of Cr$_2$O$_3$ layers in Co/Ni-base model alloys. Due to the described kinetic considerations, the formation of Cr-containing spinels can be expected to occur regardless of the base element. To suppress the development of spinel phases and guaranty higher oxidation resistance, a sufficiently high concentration of Al/Cr in the alloy is needed to sustain the required activity at the d$_2$/d$_3$ interface. Furthermore, high diffusion rates are beneficial to ensure the minimum Al/Cr activity below the expanding protective layer. However, rapid diffusion leads to considerable depletion of alloying elements, which will certainly affect other essential properties such as mechanical stability.

Higher phase stability below the IOF with increasing Ni content was apparent throughout the present study. This result could already be predicted from the recently published literature on novel $\gamma'$-strengthened Co-base Superalloys [9, 73, 74]. Despite the broadening of the two-phase field due to the addition of 19.8 at.% Ni in NC75sx, unwanted formation of thin Co$_3$W needles (compare Fig. 4.30) adjacent to Al$_2$O$_3$ or AlN precipitates was observed after 100 h exposure. In the other alloys with higher Ni levels, Co$_3$W needles formed over the entire duration of exposure. The occurrence of nitrides in d$_3$ during oxidation of untreated Co/Ni-base alloys in air is dependent on the Ni content. It should be noted, that Al$_2$O$_3$ and AlN precipitates are not distinguished in the above presented schematic drawing provided in Figure 5.4. Nevertheless, a huge amount of long needle-like AlN precipitates were apparent in NC100sx, regardless of whether a continuous Cr-containing barrier layer had established at the d$_2$/d$_3$ interface or not (compare Fig. 4.31a-b). Over the last decades, several studies pointed out the insufficient performances of Co- or Ni-base alloys that were solely protected by Cr$_2$O$_3$ barrier layers. Penetration of N could be demonstrated to be a core issue, especially for environments with low oxygen contents [147–149]. Nevertheless, Han et al. observed considerable formation of AlN and Cr$_2$N below a continuous Cr$_2$O$_3$-Al$_2$O$_3$-scale during cyclic oxidation in lab air [150]. In their study, the authors associated the severe nitridation with repeated cracking of the initially protective oxide scale during the thermal cycling. The growth of AlN precipitates during the
oxidation of Co/Ni-base alloys is explainable by its higher free energy of formation compared to Cr$_2$N [150]. In the investigated Co/Ni-base alloy system, cracking could be demonstrated to be a core problem for Co-containing samples. The N permeability of Cr-containing barrier layer is evidently dependent on the Co/Ni ratio in the alloy and decreases with increasing Ni content. As stated above, chromia forming Co-Cr alloys are also known to be subject to severe cracking even under isothermal conditions for a long time [151].

Among all conceivable oxide phases in Co/Ni-base model alloys, Al$_2$O$_3$ exhibits the highest free energy of formation. Therefore, alumina remains the first oxide that forms at the IOF. Growth of mostly discrete precipitates instead of transverse layer sections once again accounts for the high availability of O corresponding to a simultaneously insufficient flux of Al. Details of these morphological particularities are well-known and were mostly reviewed for internal oxidation of binary Ni-Al alloys in the transient stage of scale growth [152, 153]. In the elucidated model systems, the majority of Al and part of O is already consumed by the formation of Al$_2$O$_3$ precipitates at the advancing IOF. Therefore, Cr diffuses to the d$_2$/d$_3$ interface to ultimately form a continuous spinel layer. The width of the developed Cr-depleted zone is dependent on the diffusivity of Cr in the alloy. Figure 4.44 depicts the longest expanded depletion of Cr for the intermediate Ni/Co-base alloy NC50sx. Davin determined the diffusion coefficients for Cr and W in pure binary Co and Ni alloys [154]. From this study, Cr diffusion in the pure Ni-base alloy can be estimated to be higher than in the pure Co-base alloy at 900 °C. This trend can also be observed in the EPMA line scans across the Cr-depleted region (compare Fig. 4.44). The considerably expanded depletion of Cr in the intermediated Co/Ni-base alloy suggests a higher diffusion coefficient, which in addition to sufficiently high Cr content, entails a property needed to further improve the oxidation resistance by alloying. The overall higher Cr content in the affected sub-scale zone of NC00sx might be an indication of more effective barrier properties of the grown Cr-containing scale section. The repeated cracking and immediate healing lead to overall higher consumption of Cr during the oxidation of NC50sx.

Sub-scale regions that are depleted in γ’ were observed for NC50sx and NC00sx below the IOF. The BSE micrographs after various exposures at 900 °C, depicted in Section 4.1.3.1 and 4.1.3.2 demonstrate that the γ’ phase in the intermediate Co/Ni-base model alloys is less
susceptible to dissolution. However, it is noteworthy, that the formation of AlN in NC50sx makes it difficult to quantify and compare the expansion of the $\gamma'$-depleted zones between the two alloys. For exposure of NC50sx at lower temperatures, no growth of nitride was apparent in $d_3$. At 800 °C, Cr depletion for NCo0sx and NC50sx spread over similar distances. The observed change of Al2O3 precipitates towards a needle-like morphology documents an insufficient Al flux toward the IOF at this temperature. The diffusion of Cr also decrease at lower temperatures and consequently, no barrier layer evolves in the pure Ni-base alloys. The addition of W to Co- or Ni-base alloys appears to decrease the diffusion of Al and Cr in the alloy. The impact of exposure temperature on the probability to develop a continuous barrier layer in pure Co/Ni-base model alloys is significantly enhanced by the relatively high W levels in all alloys.

5.1.3 Expansion of the outer oxide layers on investigated model alloys

The outward expansion of oxide scales on ternary Co-base model alloys generally followed the growth characteristic of pure Co and binary Co-X (X = Al, Cr) alloys already introduced in Section 2.1.4. As was seen in the two-stage tracer diffusion experiments that were presented in Section 4.2.3, the expansion of $d_1$ via outward diffusion of cations could be confirmed on all investigated alloys. For ternary Co-base model alloys, $d_1$ is assumed to be almost exclusively composed of CoO at 850 and 900 °C. In recent studies on the oxidation behavior of polycrystalline Co-base Superalloys, considerable quantities of Co3O4 were found in the outer oxide layers after exposure at 800 °C [69, 71]. These findings are in reasonable accordance with literature on the oxidation mechanisms of pure cobalt and its alloys.

Systematic studies on the specific impact of W on the oxidation behavior of high-temperature alloys are rarely conducted. The addition of 1.3 and 2.6 at.% W to Co-Cr alloys was reported to successively decrease the overall growth rates of oxide scales on the investigated alloys at 1050 °C during the early stages of scale formation [155]. In the present study, the growth kinetics of $d_1$ exhibits a similar dependency on increasing W contents between 800 and 900 °C. Since no W was observed in the outer oxide layer, the transport properties of Co to the $d_1/d_2$ interface is lowered by the increasing W content in the
alloy. Altered defect properties in outer oxide layers on ternary Co-base alloys that are dependent on the W levels of the alloy are conceivable. However, the formation of defects in externally grown oxide layers on Co is generally attributed to significantly increased temperature and/or oxygen partial pressures [156].

The observed coarsening of grains in the CoO layer on 9Wsx during oxidation at 900 °C, is an indication for relatively rapid transport processes. Several experimental and theoretical studies considered the formation of duplex oxide films on metals and binary alloys [58, 59, 121, 122, 157]. Such oxide layers are composed of fine epitaxial grains, which are overgrown by large columnar grains without preferential orientation. Following Atkinsons model predictions, rapid outward expansion and high exposure temperatures generally favor the formation of duplex structure in external oxide layers [121]. The dependency of grain size on oxidation temperature was clearly demonstrated by the investigation of grain structures on ternary Co-base model alloys in Section 4.1.2.3. Duplex oxide films that expand by rapid diffusion of cations are generally characterized by high porosity [120, 122]. Even though porosity was not systematically elucidated in this study, a significant role of the observed pore structure in d1 with regards to the insufficient resistance to internal oxidation can be assumed. Considerable development of pores was particularly obvious for oxidation of Co-base model alloys without Ni additions at 900 °C. Kofstad et al. reported high porosity in CoO layers grown on binary Co-Cr alloys during exposure between 800 and 1300 °C [59, 61]. In these early studies, rapid penetration of molecular oxygen was already postulated to proceed along pore networks.

Cation transport was determined to proceed significantly slower in NiO compared to CoO, even though similar activation energies could be measured [158]. For the investigated Co/Ni-base model alloys, the substitution of Co by Ni leads to slower expansion of the outer oxide layer in the considered temperature range 4.1.3.1. These findings are in good agreement with studies on the oxidation behavior of Co-Ni binary alloys [120, 130]. Wood et al. observed successively lower oxidation rates following the increase of the Ni content in the elucidated alloys. The alteration of oxidation rates was explained by an increase of vacancy density due to higher Co levels [129].
5.1.4  Oxygen transport through growing oxide scales

In the present study, the penetration of oxygen through growing oxide scales was repeatedly demonstrated to be of crucial importance to the observed mechanistic changes of oxidation behavior. The applied techniques provided detailed insight during transient and quasi-steady-state scale growth. Despite intriguing findings, the evident complexity of the inner oxide layer renders sound statements regarding the exact mechanisms difficult to make. To avoid excessively speculative interpretation of results, discussion in the following is limited to unambiguous processes in the outer oxide layer, as well as the internal precipitation region.

5.1.4.1  Porosity and formation of microcracks

At a given temperature, diffusion of Co is generally reported to be several orders of magnitude faster than diffusion of O through CoO \[57\]. Still, only slightly smaller rate constants for the expansion of the internal oxidation zones \((d_2 + d_3)\) compared to the growth rate of \(d_1\) during exposure of ternary Co-base model alloys were calculated in Sections \[4.1.2.2\]. These findings go along with significant amount of new oxides found on the oxide/alloy interface after two-stage oxidation experiments of all considered alloys at 900 °C (compare Sec. \[4.2\]). As briefly mentioned during the presentation of results, the only valid explanation for the massive internal oxidation observed for all model alloys is the transport of oxygen through microcracks in the outer oxide layers. The first experimental evidences of the transport of oxygen through microchannels was determined for the oxidation of Fe-Cr alloys at 1000 °C \[159\]. The underlying theory corresponding to the highly-acclaimed model of crack formation in externally grown oxide layers was introduced by Mrowec and expanded by Gibbs et al. \[120, 122, 160\]. In both studies, the formation of microchannels is concluded to start with extensive consumption of metal, which causes the accumulation of vacancies. After condensation of metal vacancies below the considered interface, development of an inner porous layer initiates. During continuous outward diffusion of cations, the pores expand and ultimately form microchannels. In the case of model alloys, which were investigated in the present study, the relevant interface evolves directly above the former sample surface. In the course of microchannel development at elevated temperatures, repeated scale
detachment was postulated. This assumption is in good agreement with occasionally observed spallation of outer oxide layers during cooling after isothermal exposure. Sheasby and Gleeson confirmed the validity of the aforementioned model prediction for the oxidation of Co between 1000 and 1300 °C [161].

After considering all presented results and carefully reviewing model predictions from the literature, the access of O$_2$ and N$_2$ to the d$_1$/d$_2$-interface is unequivocally proven for all investigated oxide scales after considerable duration of exposure. Since high growth rates were described to favor the formation of pores and microcracks in the relevant oxide layers, the development of relatively wide microchannels between columnar grains can be assumed during scale growth at 900 °C for ternary Co-base model alloys. However, traces of new oxide were observed around grain boundaries in the columnar outer layer of d$_1$ for 9Wsx after 24 h two-stage oxidation experiments at this temperature (compare Fig. 4.50). The outer oxide layers of 10Ws and NC100sx exhibited less pronounced enrichment of $^{18}$O along grain boundaries. In all cases, the evident formation of new oxides in the described regions can be interpreted as lattice expansion instead of an indication for preferential ionic diffusion of oxygen anions and metal cations along grain boundaries. This is in good agreement with the early studies of Sheasby et al. on the high-temperature oxidation of Co. In their mechanistic tracer study, the authors concluded that the formation of new oxide on pore surfaces can be attributed to outward diffusion of cations [97].

The internal precipitation region after tracer studies could be clearly divided into two parts. Directly below the d$_2$/d$_3$ interface, the internal alumina precipitates exhibited only considerable $^{16}$O$^-$ intensities, whereas new oxide phases were found in the region above the IOF. No apparent porosity was observed in d$_3$. Furthermore, EPMA measurement indicated Co/Ni depletion only in d$_2$. Therefore, transport of gaseous reactants through the internal precipitation region can definitely be ruled out. Since only alumina precipitates grow in this region of the oxide scale, opportunities for possible diffusion paths are limited. Previous investigations of oxygen transport during internal oxidation in Ni-Al alloys, postulated enhanced diffusion of O along incoherent interfaces between precipitates and surrounding matrix [162–164].
5.1.4.2 Influence of base material and temperature on oxygen transport

In the course of the present study, only a minor impact of the base element on the preferred oxygen transport path could be observed. The significantly lower oxidation rates of Ni-containing model alloys originate from generally slower diffusion of metal cations through the outer scale. Due to reduced kinetics of material transport, less metal vacancies on the original alloys surface form. Therefore, a minor tendency for the detachment of outer oxide layers as well as reduced accumulation of growth stress in $d_1$ can be expected with increasing Ni content. For NiO, duplex structures are reported to occur during exposure at 1000 °C and above [178]. This is in good agreement with the comparable small grain sizes that were observed during SIMS analysis of NCoosx after two-stage tracer experiments (Fig. 4.60a).

Basically, the same considerations apply for lower oxidation temperatures. It was demonstrated that the outer oxide layers on 9Wsx after 100 h exposure at 800 and 850 °C exhibit a significantly finer grain structure (compare Fig. 4.21). Furthermore, considerably more $^{18}$O was detected in the interior of $d_1$ after two-stage oxidation experiments at lower temperatures (compare Fig. 4.59 and 4.58). Due to evident porosity in the outer layers of oxide scales that developed at 800 and 850 °C, the transport of oxygen via cracks is still highly probable. With finer grain structures, the ratio of inner-pore surface to outer-oxide interface increases. Furthermore, slower cation diffusion at lower temperature enhances the duration of metal-oxygen interaction on pore surfaces. These considerations are a possible explanation for significant growth of new oxides in the outer layers of scales at 800 and 850 °C.

5.2 Kinetic analysis using thermogravimetric data

During an extensive part of chapter 4, the alteration of reaction kinetics during the development of multilayered oxide scales were in the center of attraction. Due to the high complexity, isothermal thermogravimetry for 100 h was supplemented by detailed information on the morphology and composition of individual regions within the oxide scales. The usage of several approaches to characterize instantaneous kinetics during the growth of protective scale sections can be found in literature.
In the following, the applicability of such treatments that derive from kinetic considerations is tested for part of the acquired weight gain data.

5.2.1 Steady-state scale growth of 7Wsx at 800 °C

In the classical descriptions of characteristic stages during the high-temperature oxidation of superalloys, steady-state kinetics are unambiguously associated with the development of continuous, protective oxide layers within the scale [152]. Using this classification for the oxidation behavior of ternary Co-base model alloys, transitions to steady-state scale growth was only observed for 7Wsx and 9Wsx at 800 °C during 100 h exposure. To confirm, whether the protective properties of the Al$_2$O$_3$ layer sustain over longer duration of isothermal exposure, 7Wsx was oxidized for 250 h. A sequence of cross-sections after different length of exposure is demonstrated in Figure 5.5.

![SEM sequence of 7Wsx at 800 °C in synthetic air.](image)

**Figure 5.5:** SEM sequence of 7Wsx at 800 °C in synthetic air.

As already stated in Section 4.1.1.2.2, considerable but not yet continuous growth of Al$_2$O$_3$ was observed after 72 h oxidation. Following 12 h longer exposure, no more discontinuities were evident. However, the calculated mean values of $d_2$ still increase between 84 and 100 h (compare Fig. 4.18). After 100 h, no considerable layer expansion was measured. As demonstrated in Section 4.1.1, a transition from initially fast reaction kinetics to a stage of relatively constant oxide growth rates between 24 and 100 h were observed for 9Wsx at 900 °C. This state was referred to as quasi-steady-state, since overall reaction kinetics were not governed by slow diffusion through a barrier layer. Fitting of measured
individual oxide layer thicknesses by a parabolic law achieved reasonably high accuracy over the whole range of considered exposure conditions.

To determine the instantaneous oxidation kinetics from thermodynamic data, two main approaches can be found in literature. Details concerning the calculation of instantaneous rate constant $k_{w}^{\text{inst}}$ and time exponent $n_{w}^{\text{inst}}$ were given in Section 2.1.2. Using Equation 2.11 and 2.12, $n_{w}^{\text{inst}}$ and $k_{w}^{\text{inst}}$ values for 250 h exposure of 7Wsx were directly calculated from the measured weight gain data at 800 °C. The computed results are plotted over oxidation time in Figure 5.6.

![Figure 5.6: Kinetic data of 7Wsx at 800 °C in synthetic air.](image)

For better orientation, the intermediate durations after which the morphology of the evolved oxide scale was reviewed are marked in the plot. The calculated $n_{w}^{\text{inst}}$ value decreases significantly during the first 2 hours of exposure. After this initial period of scale growth, the $n_{w}^{\text{inst}}$ curve increases towards a maximum after approximately 22 h of oxidation. Following this maximum, the curve decreases steadily until a local maximum between 80 and 100 h exposure is reached. The instantaneous rate constant for this reaction approaches a maximum at the exact same position. Naumenko et al. investigated instantaneous oxidation kinetics of alumina-forming Fe-Cr-Al alloys. The authors assigned a local maximum in $k_{w}^{\text{inst}}$ value curves to cracking in alumina scale due to the transition from $\theta$ to $\alpha$ alumina [93]. In the present study, no apparent indications for cracking within the alumina layer could be found. Nevertheless, comparison with available BSE micrographs after shorter exposure times (Fig. 5.3) confirm that the maximum is associated with the formation of a continuous alumina layer at the IOF. After the $\text{Al}_2\text{O}_3$ layer is continuously spread over the entire sample
surface, both $n_{\text{inst}}$ and $k_{w_{\text{inst}}}$ decrease to significantly lower values. For Fe-Cr-Al alloys, the duration till instantaneous growth rates decrease to considerably lower values were demonstrated to significantly depend on exposure temperature [92, 93]. Similar kinetic analysis were used to confirm the impact of grain coarsening on the decrease of oxidation rates during the exposure of pure Ni above 700 °C [86, 87].

5.2.2 Instantaneous kinetic data of scale growth on model alloys

In the present study, different intriguing processes especially during the extraordinary long transient oxidation stages of ternary Co-base model alloys were investigated. The instantaneous values for the time exponent $n$ and the growth rate $k_w$ are used to verify the assumption of quasi-steady-state scale growth beyond 12 h exposure (compare Sec. 4.1.2.2 and 4.1.3.1).

![Figure 5.7: Instantaneous kinetic data of ternary Co-base model alloys at 900 °C in synthetic air:](image)

(a, c, e) $n_{\text{inst}}$ depending on the W content in the alloy;
(b, d, f) $k_{w_{\text{inst}}}$ $10^{-3} / \text{mg}^2 \text{cm}^{-2} \text{s}$ depending on the W content in the alloy;
5.2 Kinetic analysis using thermogravimetric data

Figure 5.7 summarizes the instantaneous values of $n_{\text{inst}}$ and $k_{w}^{\text{inst}}$, that were calculated from thermogravimetric data of ternary Co-base model alloys at 900 °C. No continuous alumina layer was observed during analysis of multilayered cross-sections. The $n_{\text{inst}}$ value curve is particularly sensitive to changes within the prevailing oxidation kinetics. At the highest oxidation temperature, all curves exhibit a (local) maximum during the early stages of scale growth. The grain size of the outer oxide layer was demonstrated to significantly coarsen within the first 5 h of exposure (compare Fig. 4.19). Models for the evolution of duplex layers were briefly introduced in the previous section. Following the formation of microchannels, the access of molecular oxygen directly to the internal oxidation zone is highly probable. It is reasonable to assume, that such events are assigned to a temporary acceleration of oxidation kinetics. The evolution of pore structure in oxide scales was not subject to detailed investigations in this study. Nevertheless, slower growth kinetics of the outer oxide layer should definitely result in lower porosity and therefore cause less pronounced changes in the $n_{\text{inst}}$ value curve of 10Wsx. Evident formation of considerable transverse alumina sections was observed in cross-sections of 10Wsx for 72 and 100 h exposure at 900 °C (compare Fig. 4.9). This maximum may be assigned to considerable formation of alumina segments, that spread parallel to the original sample surface during the early stages of exposure. The latter conclusion is based on the above presented analysis of instantaneous kinetics during the transition from internal oxidation to the expansion of a continuous alumina layer in ternary Co-base alloys. Interestingly, instantaneous growth rates after 100 h do not exhibit the characteristic steep decrease, that would be expected for the development of a continuous alumina layer. The presented curves of instantaneous rate constants are characterized by a significantly less sensitivity to small changes in reaction kinetics, especially during early stages of scale growth. However, they still reveal relatively constants values, when steady-state growth can be expected. The reason for the evident broad maximum in the $k_{w}^{\text{inst}}$ value curve during scale growth on 10Wsx at 900 °C might lay in the observed lower accuracy during fitting of layer thicknesses (compare Fig. 4.10).

The extent of transversely spread alumina sections in oxide scales on ternary Co-base alloy with intermediate W content of 9 at.% could be demonstrated to depend on the exposure temperature. The instantaneous kinetic values were calculated from thermogravimetric data
of 9Wsx at 800 and 850 °C to verify, whether the proposed processing of weight gain measurements is able to indicate this dependency. Figure 5.8 summarizes the computed instantaneous values over oxidation time. During the exposure of 9Wsx at 850 °C, instantaneous kinetics undergo a steady decrease over the entire duration of experiment. The transition from initially rapid oxidation rates to overall slower growth kinetics is not indicated by a maximum in any of the two curves. A hardly visible inflection of the \( n_{\text{inst}} \) value curve between 65 and 70 h can most probably be attributed to the onset of considerable formation of alumina at the IOF. Nevertheless, expansion of alumina perpendicular to the advancing reaction front might be too slow to make a significant impact on the computed instantaneous values.

![Figure 5.8: Instantaneous kinetic data during isothermal exposure of 9Wsx in synthetic air:](image)

(a) \( n_{\text{inst}} \) at 850 °C; (b) \( k_{w}\cdot10^{-5}/\text{mg}^2\text{cm}^{-4}\text{s} \) at 850 °C;
(c) \( n_{\text{inst}} \) at 800 °C; (d) \( k_{w}\cdot10^{-5}/\text{mg}^2\text{cm}^{-4}\text{s} \) at 800 °C;

The evolution of the multilayered oxide scale on 9Wsx during exposure at 800 °C indicates that the transition from transient to quasi-steady-state oxidation occur between 24 and 72 h of exposure (compare Fig. 4.17). Furthermore, the \( n_{\text{inst}} \) value curve confirms this assumption. The characteristic decrease of \( n_{\text{inst}} \) values starts after 52 h of oxidation. Similar to the instantaneous data presented for 7Wsx at 800 °C, the onset of considerable spreading of alumina parallel to the original alloy surface is accompanied by a maximum in the \( k_{\text{inst}} \) value curve. Both
5.2 Kinetic analysis using thermogravimetric data

curves indicate, that the evolution of a continuous Al$_2$O$_3$ layer is not completed after 100 h exposure at this temperature.

Growth kinetics of NC50sx and NCo00sx were controlled by material transport through a Cr-containing barrier layer at the interface between d$_2$ and d$_3$ after a transient stage of initially rapid oxidation at 900 °C. For the kinetic analysis of individual layer expansion, steady-state growth was assumed after 12 h exposure. The instantaneous kinetic parameters, n$^{inst}$ and k$^{inst}$$_w$ were calculated for three Co/Ni-base model alloys. The results are plotted separately over oxidation time in Figure 5.9. A steep decrease of n$^{inst}$ during the first hours of exposure is observed for all three Cr-containing model alloys. Both, the n$^{inst}$ and the k$^{inst}$$_w$ values that were calculated for the pure Co-base alloy exhibit local maxima after approximately 12 and 54 h exposure. In Section 4.1.3.1, clear indications for the repeated failure and healing of the rate-controlling barrier layer in the internal oxidation region were demonstrated. These events restrict the usability of the applied kinetic analysis since even the presumably constant oxidation rate during the quasi-steady state undergoes severe changes. Despite the above described discrepancy from ideal parabolic growth, a nearly constant value is approached within the last 25 h of isothermal exposure. The n$^{inst}$ curve of the pure Ni-base alloy significantly decreases after 5 h and approaches another plateau for durations longer than 25 h. During ongoing oxidation, the overall growth rates are governed by the stable layer of Ni-Cr-spinels. Due to the overall lower mass gain values, the transition caused by the formation of a diffusion-limiting Cr-containing barrier layer is less pronounced in the k$^{inst}$$_w$ value curve. The intermediate Co/Ni-base alloy NC50sx exhibits rather rapid decrease of both kinetic parameters within the first 6 h of oxidation. The scattering in the calculated instantaneous time exponent considerably increases after 40 h exposure. The k$^{inst}$$_w$ exhibit no clear indication of local breakdown of the developed barrier layer.

After reviewing the analysis of instantaneous changes in the oxidation kinetics of Co/Ni-base model alloys, a reasonably defined steady-state can be assumed for NC50sx and NCo00sx. Following the establishment of steady state conditions due to the completion of a Cr-enriched barrier layer, the instantaneous kinetics for both samples exhibit moderate decrease. The evident decline might be attributed to the formation of additional Cr$_2$O$_3$ sections underneath the spinel layers. Even though, the development of transverse chromia sections
Discussion

Figure 5.9: Instantaneous kinetic data of Co/Ni-base model alloys during exposure at 900 °C in synthetic air:
(a, c, e) $n^{inst}$ depending on the W content in the alloy;
(b, d, f) $k^{inst}_w \cdot 10^{-5} \frac{mg^2}{cm^4 s}$ depending on the W content in the alloy;

would definitely increase the oxidation resistance, clear experimental proofs were not obtained in the course of this study. Despite the significant inhomogeneities that were found during the analysis of cross-sections following exposure at 900 °C (compare Sec. 4.1.3.1), a relatively stable description of kinetic parameters can be achieved for the pure Co-base alloy. The above conducted analysis of the instantaneous oxidation kinetics were directly derived from mass gain data. Generally, the majority of findings from classical elucidation of scale growth kinetics is also reflected in the change of instantaneous kinetic parameters. Since thermogravimetry provides a continuous set of mass gain data, the processing of these data generates no additional effort. The exact duration between the initiation of transverse spreading and the development of a continuous Al$_2$O$_3$ layer in ternary Co-base model alloys at 800 °C can be determined from both $n^{inst}$ and $k^{inst}_w$ data sets. Furthermore, this treatment facilitates the exact prediction of elementary changes in the oxidation mechanisms by only one thermogravimetric measurement. The applicability of the instantaneous analysis of kinetic data for alloys
that exhibit a certain degree of protective properties already after short-term exposure, was demonstrated to be more challenging. Since sound knowledge of dominant elementary processes are essential for correct interpretation, the instantaneous analysis appears particularly helpful for screening of the oxidation resistance dependent on variation of alloy compositions.

In general, most conclusions that were drawn during the elucidation of morphologies that were observed in cross-sections along with corresponding weight change data can be confirmed by the comparison of instantaneous kinetic values. Even though the correlation between the fast transition of reaction rates during short-term exposure of ternary Co-base model alloys at 900 °C and the formation of microchannels could not be proved with absolute certainty, further indications that support this conclusion were presented. Compared to the available data from the literature, formation of diffusion-limiting scale sections in the investigated ternary model alloys occurs over an exceptionally long period of exposure. This is due to the fact, that alumina formation in the investigated alloys with constant W levels occurs only at 800 °C. Furthermore, at the prevailing oxygen partial pressure, the available amount of Al and/or Cr on the IOF is not sufficient to sustain the development of a protective Cr$_2$O$_3$-Al$_2$O$_3$ layer. To overcome such limitations and to enable the usage of Co-base Superalloys for high-temperature applications, Klein et al. suggested a pre-oxidation step at low oxygen partial pressure and low temperature [137]. However, the slow growth kinetics of alumina layers that were observed in the relevant temperature regime (compare Sec. 5.1.1) would require an unacceptable long duration of the proposed pre-treatment. In addition to that, the beneficial effect of vacuum annealing on the oxidation resistance of binary Co alloys was already demonstrated for the Co-Cr system with intermediate Cr contents [63].

5.3 Reproducibility of collected data

The thermogravimetric experiments were conducted in a state-of-the-art analyzer that provided the required high mass resolution. Nevertheless, several experimental factors can reduce the reproducibility of acquired mass gain data. In the following, a criterion is suggested that can be applied to verify the accuracy of thermogravimetric data without
significantly increasing the number of conducted experiments. The last part of the section briefly considers undesired sample inhomogeneities and its impact on the significance of the conducted investigation.

## 5.3.1 Evaluation of reproducibility

Various factors can influence the accuracy of thermogravimetric data acquisition. In the selected configuration, the utilized thermogravimetric analyzer reaches a mass resolution between 5 to 20 \( \mu \text{g} \). For the assessment of data reproducibility, the most investigated model system provides a reasonable starting point. The elementary processes during scale growth of the ternary Co-base model alloy with intermediate W levels were extensively investigated in the present study. To document the evolution of a multilayered oxide scale on 9Ws at the highest considered exposure temperature, 8 experiments (compare Fig. 4.2) with increasing duration of exposure were conducted. A quasi-steady state oxidation was observed after 12 h of exposure. Consequently, weight gain data that was measured for 24 h and longer can be used to evaluate the validity of the above estimation. Figure 5.10 summarizes the weight gain measurements of 9Ws at 900 °C for 24, 72 and 100 h.

![Figure 5.10: Consecutive weight change measurements of 9Ws at 900 °C in synthetic air for different durations.](image)

The displayed data exhibit highly comparable values even during the transition from initially rapid to almost-steady scale growth kinetics. For the entire range of the conducted measurements, the general behavior of samples during this critical stage can be used to evaluate the significance of the acquired data. To do so, the mean value of mass gain
per sample area \((\Delta m/A)\) and the corresponding standard deviation at 24 h were determined from the conducted experiments. The results of all investigated ternary Co-base alloys at 900 °C are summarized in Table 5.1. The actual number \(N\) of available data sets that were used to determine the displayed values varied and is therefore included in the table. For comparison of the significance of each experimental series at a given temperature, the relative standard deviation (rel. \(sd\)) is used.

### Table 5.1: Mean value of mass gain per sample area \((\Delta m/A)\) and corresponding standard deviation \((sd)\) at 24 h for sufficiently long thermogravimetric exposures of ternary Co-base model alloys at 900 °C.

<table>
<thead>
<tr>
<th>sample</th>
<th>(N)</th>
<th>((\Delta m/A))/ mg cm(^{-2})</th>
<th>(sd)/ mg cm(^{-2})</th>
<th>rel. (sd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7Wsx</td>
<td>4</td>
<td>9.45</td>
<td>0.49</td>
<td>0.05</td>
</tr>
<tr>
<td>9Wsx</td>
<td>3</td>
<td>4.23</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>10Wsx</td>
<td>5</td>
<td>2.43</td>
<td>0.23</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Mass change data of samples that contained lower W levels exhibit a particularly low standard deviation at 24 h exposure. Overall low protective properties of the ternary model systems at the highest investigated temperature, have a beneficial effect of the achieved significance. Considerable amount of discontinuous Al\(_2\)O\(_3\) sections were demonstrated to cover the d\(_2\)/d\(_3\) interface of samples with 10 at.% W. The growth of alumina layers in Ni-Al was demonstrated to be strongly influenced by imperfections of the exposed sample surfaces [27]. Due to the generally low tendency of all investigated Co-base alloys to form transverse Al\(_2\)O\(_3\) sections, that start from impingement sites, small sample defects, can make a considerable impact on the weight gain of each specimen. The ternary model system exhibited overall high mass gain and fast kinetics within the first hours of scale growth at 900 °C. Therefore, detrimental influences on data reproducibility which are caused by sample chemistry are less pronounced. At lower exposure temperatures, more diffusion-limiting scale sections were found for pure Co-base model alloys. Consequently, data reproducibility decreases significantly in this temperature regime. The relative standard deviation of 4 weight gain measurements at 800 °C, calculated for 9Wsx, is 0.13. A particularly pronounced scattering in the acquired mass change was evident for 10Wsx at 800 and 850 °C (compare Fig. 4.11 and 4.15).
The accuracy of the used thermogravimetric analyzer is considered to be reasonably high for the detailed elucidation of oxidation mechanisms during exposure of high-temperature alloys. Nevertheless, statistical processes, such as the development of diffusion-limiting scale sections are evidently occurring over a large transient period. Consequently, this uncertainty leads to scattering in data that is more pronounced for lower exposure temperatures. Furthermore, growth stresses can lead to local breakdown of barrier layers are another detrimental influence which was observed for Co-Cr-Al alloys [68]. After consideration of all these points, the application of thermogravimetry for novel Co-base Superalloys is particular meaningful in combination with careful investigation of evolved cross-sections. Nevertheless, in recent years several computer-based approaches for alloy development were presented in the literature. For such projects, a less-detailed quantification of the oxidation resistance of promising alloy compositions might be sufficient. In these cases, setting a criterion to evaluate reproducibility of thermogravimetric data for each investigated alloy compositions at a given temperature is recommended. Such a criterion could for example be the relative standard deviation of three independently conducted thermogravimetric measurements after a sufficiently long duration of exposure. For ternary Co-base model alloys that were investigated at 900 °C, all elucidated compositions revealed relative standard deviation below 0.1 at $t = 24$ h, which can be seen as an appropriate criterion to confirm reproducibility of weight change measurements.

5.3.2 Influence of sample inhomogeneities

A defined sample state is mandatory for reproducible thermogravimetric measurements. In order to ensure unaltered surface condition prior to thermal exposure, both head sites were polished. Due to practical reasons, it is not possible to polish edges of the specimens. Therefore, the specimen height was kept in the range from 0.5 to 0.8 mm. The head areas of the samples are determined by the diameter of the shell molds that were used for single-crystalline casting. Despite the detrimental effect of the relatively rough and undefined sample edges on the overall oxidation behavior, casting defects and elemental segregation can also influence the scale growth. As demonstrated in Section 5.1, the microstructure of 10Wsx was disturbed by growth of unwanted W-rich phases. Significantly low relative standard deviations between the conducted thermogravimetric analysis of ternary Co-base model alloys

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at 900 °C (compare Tab. 5.1), confirms a neglectable impact of sample inhomogeneities at the highest investigated temperature. The lower reproducibility of weight gain curves that were observed for 10Wsx samples at 800 and 850 °C is primarily caused by variations of sample composition. Figure 5.11 summarizes the weight gain data and the corresponding cross-sections of scales after independently conducted 100 h experiments. The observed amount of transverse alumina sections in the investigated oxide scales differs considerably between the experiments. Overall, 6 measurements with a minimum duration of 24 h were conducted. The calculated value of the relative standard deviation at \( t = 24 \text{ h} \) approaches 0.8.

\[ \text{Figure 5.11: Representative cross-sections from oxide scales on 10Wsx after 100 h exposure at 850 °C. Cross-sections of samples that exhibited (b) intermediate mass gain and (c) particularly low mass gain.} \]

As discussed in Section 5.1.1, only a limited number of initiation sites for expansion of alumina parallel to the sample surface can be assumed. Therefore, small variation in the local composition may already influence the overall oxidation rate significantly enough to reduce the reproducibility of thermogravimetric analysis of the alloy. Several indications for the validity of these assumptions can be found in oxide scales after short-term exposure at 900 and 850 °C, that are demonstrated in Figure 5.12. In both displayed micrographs, onset of considerable \( \text{Al}_2\text{O}_3 \) growth is apparent. Due to the more rapid penetration of O through the growing scale at 900°C, the detrimental influence of the W-rich segregations is less pronounced (Fig. 5.12a). In the depicted region of the scale, the surrounding area is almost completely enclosed in the internal oxidation zone after 30 min exposure. Contrary to this, transverse alumina sections are observed to spread over several \( \mu m \) after 5 h of scale growth at 850°C in the same alloy. Consequently, the progress of the IOF is slowed-down for the region adjacent to the \( \mu \) phase. As already mentioned in Section 3.1,
the appearance of $\mu$ phases was obtained to be unpredictable, which explains the strong scattering of mass gain data of $10\text{Wsx}$ at 850 °C. It is evident that the severity of disadvantageous influences caused by sample inhomogeneities is strongly dependent on the complex interplay of the atmosphere, the exposure temperature and the general oxidation behavior of the intact microstructure.

**Figure 5.12:** BSE micrographs documenting $\text{Al}_2\text{O}_3$ growth around $\mu$ phase in $10\text{Wsx}$; (a) after $30$ min exposure at 900 °C and (b) $5$ min exposure at 850 °C.

### 5.3.3 Influence of the heating step on data reproducibility

The atmosphere in the closed device is constantly renewed by external supply of dry gases. The used gas mixtures revealed a maximum contamination of 5.0 ppm. The high purity of the gases nearly rules out detrimental influences caused by the atmosphere during the thermogravimetric analysis. Nevertheless, the onset of considerable alumina growth was demonstrated to be influenced by sample inhomogeneities such as elemental segregations during casting. The impact of compositional variations is additionally enhanced for stages of low oxygen availability. During the heating in Ar, residual traces of oxygen can not be avoided [11]. Consequently, the presence of W segregations in surface-near sample regions can act as initiation sites for the considerable spreading of alumina within the first hours of scale growth (compare Fig. 5.12a). If these considerations are true, the change of heating atmosphere to synthetic air should increase the reproducibility of collected weight gain data, especially for ternary Co-base model alloys with high W contents. To confirm this assumption, three additional thermogravimetric measurements were conducted. For this set of experiments, synthetic air was already present purged during the heating of the samples. The acquisition of weight gain data started after the target temperature was reached. Figure 5.13 demonstrates the obtained results. After
plotting the weight change over the respective sample area, only minor differences are evident between the individual curves. The obtained oxide scales after 100 h exposure in air exhibit comparable morphology as the one displayed in Figure 5.13c. Despite the rather small number of measurements with altered heating atmosphere, a definite impact of $\mu$ phase occurrence on the development of alumina layers could be demonstrated. During stages of limited oxygen access, the effect of W-rich precipitates in surface-near regions is additionally enhanced.

**Figure 5.13:** Mass gain of 10Wsx during exposure at 850 °C after heating in synthetic air.
6 Conclusion and future work

In the present study, elementary processes during oxide scale development at high temperatures have been investigated by means of two experimental approaches. The overall aim was to understand the low resistance of this new class of material above 800 °C.

Ternary Co-base model alloys characterized by an intermediate W level served as a model system to address the development of multilayered oxide scale at 900 °C, beginning from the early stages of oxidation. The scales obtained on Co-base model alloys after exposure between 800 and 900 °C were divided into three individual regions. The outer oxide layer grows on top of the former sample interface. Below this (d₁/d₂) interface, the internal oxidation zone is composed of a fully oxidized inner oxide layer and an internal precipitation region. EPMA confirmed that the outer oxide layer is exclusively composed of cobalt oxide, whereas the precipitates in d₃ were unambiguously identified as alumina. Complementary STEM-EDX analysis of samples that contained intermediate W levels exhibited the formation of primarily CoAl₂O₄, CoWO₄ and CoO in the inner oxide layer during exposure at 900 °C in synthetic air. Using 9Wsx as an example, overall parabolic growth kinetics for each of the three individual oxide layers could be confirmed. Parabolic rate constants strongly depend on the progress of scale formation and were approximated by a parabolic rate law. The presented results in combination with the investigation of instantaneous growth kinetics that were directly derived from thermogravimetric data indicated quasi-steady state growth kinetics beyond 12 h of exposure.

The oxidation behavior of ternary Co-base model alloys was investigated in detail with regards to the W content. The mass gain for three compositions was recorded during 100 h exposure at 800, 850 and 900 °C. Specific features in the oxide scale cross-sections could be
Conclusion and future work

directly attributed to the plotted weight gain data. The formation of protective $\text{Al}_2\text{O}_3$ scale sections caused a transition to slower reaction kinetics and were mostly obtained for lower exposure temperatures. Barely hindered progress of two internal oxidation fronts could be identified as a key issue preventing the growth of barrier layers on the IOF. An apparently high nucleation rate of $\text{Al}_2\text{O}_3$ furthermore consumes considerable amounts of Al before individual precipitates are able to spread parallel to the original sample surface. The principal mechanisms during scale growth on ternary Co-base alloys remained unaffected by the variation of W content, which is accompanied by changes in the individual microstructures of the investigated alloys. Higher W contents evidently slow down the transport kinetics of all reactants. The later finding was used to explain the obvious differences between the oxidation resistance of ternary Co-base model alloys during exposure in synthetic air.

For intermediate W levels, grain coarsening during the rapid expansion of the outer oxide layer was demonstrated. The specific role of two-phase microstructure during the early stages of scale formation was demonstrated for ternary Co-base model alloys in the considered temperature regime. $\text{Al}_2\text{O}_3$ starts to nucleate in the $\gamma$ channels. High-resolution STEM-EDX after short-term exposure of 9Wsx at 900 °C confirmed that only Al from the matrix phase is consumed in this stage. With ongoing oxidation time, the original microstructure lost its importance, since depletion of Al also affected the $\gamma'$ phase. Lower exposure temperatures lengthen the initial stage, in which the appearance of inner oxide layers can be attributed to the former $\gamma/\gamma'$ structure. Depletion of W was observed to a minor extent in ternary Co-base model alloys. Phase stability in regions adjacent to the IOF remained a key issue for all Co-containing model alloys with moderate Ni levels. The unwanted $\text{Co}_3\text{W}$ phases were demonstrated to nucleate as fine needles after comparably short exposure times in ternary Co-base model alloys. The onset and extent of this phase formation was demonstrated to strongly depend on temperature and alloy composition. High W contents and high temperatures could be associated with earlier and more extensive growth of these detrimental phases.

A second set of single-crystalline model alloys was included in the study to elucidate the specific influence of base element variation on the development of oxide scales. The oxidation behavior of Cr-containing Co/Ni-base model alloys was obtained to be a complex
interplay between exposure temperature and the ratio of considered base elements. At 900 °C, weight gain increases with higher Co contents in the investigated alloys. Generally, a certain degree of resistance was achieved by Cr-containing barrier layers that formed after a period of initially rapid reaction kinetics. The sustainability of these barrier layers was limited for alloys containing higher Co/Ni ratios. Extensive formation of nitrides occurred in the pure Co-base model alloy as well as in the sample with equal Co and Ni ratios. Penetration of the barrier layer was enabled by repeated cracking during isothermal exposure. At 800 °C, mass gain exhibited an exactly inverted dependency from the Co/Ni ratio.

The early formation of a diffusion-limiting spinel layer led to the lowest increase in sample weight for the pure Co-base model alloys. In contrary, no protective layer formed on the Ni-base counterpart at the lowest investigated temperature. Despite the apparently superior oxidation resistance of NC100sx indications of insufficient long-term stability were already evident during the first 100 h of exposure. The transport of alloying elements in sub-scale regions was reviewed at 900 °C. Only model alloys with equal or higher Ni contents, compared to Co, exhibited sufficient phase stability in the addressed temperature regime. Ultimately, it can be stated that alloy design of Co-base superalloys towards acceptable oxidation resistance seems nearly impossible without the addition of a minimum Ni content in the system.

The transport mechanisms of reactants were subject to closer elucidation by means of two-stage tracer exchange experiments. Counter-current transport of cations and oxygen was evident. Furthermore, usage of this highly-acclaimed method unambiguously confirmed the development of microchannels in the outer oxide layer of all investigated alloys during high-temperature exposure. The obtained results were used to validate the applicability of a classical theory describing the formation of duplex scales for oxide scale growth on Co-Al-W model systems at high temperatures. In contrary, the transport of cations occurs along the lattice of the outer oxide layer between 800 and 900 °C. For higher Co contents the development of porosity in the outward expanding layer is accompanied by considerable growth of new oxide phases on inner pore surfaces. In other words, the access of molecular oxygen to the internal oxidation zone could be concluded. Two-stage tracer experiments clearly visualize the existence of a second oxidation
front on the interface between d2 and d3. In the internal precipitate region, the incoherent interfaces between matrix and Al2O3 provide rapid transport paths for oxygen.

The elucidation of instantaneous growth kinetics that were directly derived from thermogravimetric data could confirm the initial assumption of quasi-steady state scale growth on the investigated model alloys. The applied treatment was used to reveal considerable changes in prevailing overall kinetics during the thickening of the multilayered oxide scales for selected experiments. Steady-state growth during which the transport through a continuous diffusion-limiting layer governs the expansion rates of the entire state could be confirmed for NC50sx and NCoosx at 900 °C. Considering the occurrence of various statistical processes in parallel, sufficient data reproducibility could be proved for the majority of the conducted experiments. The occurrence of unwanted μ phases in 10Wsx were demonstrated to be particularly detrimental during the heating step in Ar at 800 and 850 °C.

The present study is intended to enhance the understanding of elementary processes and their influence on the resistance to scale formation or more specifically degradation at high temperatures in air. Despite the deliberately limited complexity of the investigated alloy systems, the presented conclusions on crucial factors decisively affecting oxidation behavior of Co-base superalloys may be used as a starting point for the design of new, more-sustaining alloys. Selected intriguing aspects that were not specifically addressed but should be the basis for further research activities are listed below.

To date, only few studies have investigated the specific role of two-phase microstructures during the early stages of scale formation. The results of this thesis were exclusively obtained after exposure and required time-consuming metallographic sample preparation. In recent years, various in situ techniques indicated their potential to reach astonishing high-resolution. For example, the further exploration of heating experiments in the chamber of an SEM may provide unseen insight into the formation of oxide phases depending on the microstructure and orientation of the elucidated surface. Such studies could be conducted on the introduced series of Co/Ni-base model alloys to directly verify whether the choice of base element alters the individual behavior of the matrix and the hardening phase during the very early stages of oxide growth.
Conclusion and future work

Critical review of all results obtained through this study indicates that a key issue for the evident low tendency to form protective oxide layers is the constant, high level of W that was added to the alloys. After expanding the range of considered alloy elements, significantly lower W contents might be sufficient to obtain a stable two-phase microstructure. Ultimately, lower W levels should result in more rapid diffusion of all elements in the alloy. However, it could be observed that lower W contents increase the rate of outer oxide layer expansion of pure Co-base superalloys. To overcome these difficulties, the development of protective layers during the early stages directly after exposure is of uttermost importance. The outlined consequences that accompany the change of only one element illustrate the importance of integrated computational alloy design strategies.

In recent years, initial studies verifying the applicability of numerical multi-component approaches considering various property constraints were presented. To deliver an optimum alloy composition in terms of oxidation resistance as well, meaningful criteria and input parameters are needed. As previously indicated, the diffusivity D of elements crucial to the establishment of protective layers provides a key information for such numerical approaches. Diverse models can certainly be used to estimate the needed values. Nevertheless, experimental verification of predicted diffusivities is indispensable to ensure the quality of the conducted simulations. In multi-component alloys, the accurate determination of individual diffusivities appears challenging but not impossible. Advanced and innovative experimental techniques are available and might only require a little further developing effort.

Finally, after prediction of promising new alloy compositions, a reliable and fast evaluation of oxidation resistance is needed. The presented elucidation of continuous thermogravimetric data to extract detailed information on instantaneous growth kinetics might be a reasonable starting point for the development of such a standardized assessment. The significant advantage of this approach would be a variety of relevant results produced by a limited number of experiments. However, profound knowledge of the investigated base system and its oxidation behavior is of essential importance to the interpretation of data.
Appendix

A  EPMA line scans

In the following, supplementary EPMA line scans are provided. The intention of the measurements was to deliver additional information for the identification of specific oxide phases. All displayed line scans start from the outer scale interface (OSI). Due to the limited degree of complexity, compositions that are extracted from the outer oxide layer ($d_1$), the internal precipitation region ($d_3$) and the oxidation-affected alloy can be used to confirm assumptions that were made in Section 4.1.2.1 and 4.1.3.1.
Figure A.1: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of 7Wsx at 900 °C in artificial air (compare Fig. 4.5a).
Figure A.2: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of 9Wsx at 900 °C in artificial air (compare Fig. 4.5b).
Figure A.3: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of 10Wsx at 900 °C in artificial air (compare Fig. 4.5c).
Figure A.4: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of 9Wsx at 800 °C in artificial air (compare Fig. 4.6b).
Figure A.5: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of NC100sx at 900 °C in artificial air (compare Fig. 4.31a).
Figure A.6: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of NC100sx at 900 °C in artificial air (compare Fig. 4.31b).
Appendix

Figure A.7: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of NC50sx at 900 °C in artificial air (compare Fig. 4.3c).
Figure A.8: Quantitative line scans of the oxide scale and the adjacent substrate after 100 h exposure of NCoosx at 900 °C in artificial air (compare Fig. 4.31d).
Appendix

B  Parameters used for data handling of SIMS maps after two-stage tracer exposure

During the processing of SIMS data, measurement points that reveal low intensities for both $^{16}\text{O}^-$ and $^{18}\text{O}^-$ can still lead to unrepresentative high levels of isotopic enrichment. The selected threshold values for $^{16}\text{O}^-$ and $^{18}\text{O}^-$ maps along with maximum intensities are provided in Table B.1.

**Table B.1**: Parameters used for the calculation of relative isotopic enrichment from $^{16}/^{18}\text{O}$ intensity data. Considered Intensity Values (CIV) are given in counts prior to correction by the respective dwell time.

<table>
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<th>$^{18}\text{O}_2$ (in %)</th>
<th>Max $^{16}\text{O}^-$ Intensity</th>
<th>Max $^{18}\text{O}^-$ Intensity</th>
<th>CIV</th>
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<td>[6 3]</td>
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<td>49.9</td>
<td>102</td>
<td>146</td>
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Bibliography


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During operation at high temperatures, technical alloys inevitable react with the surrounding atmosphere. Therefore, the detailed understanding of oxidation processes is essential for the design of new materials. In the course of the present thesis, oxide scale formation on single-crystalline, γ′-strengthened Co- and Ni-base model alloys was investigated. Results derived by classical thermogravimetry and sequential exposure to $^{16/18}$O$_2$ were supplemented by various sophisticated, surface analytical techniques. The impact of the two-phase microstructure during the early stages of scale formation could be demonstrated by high-resolution transmission electron microscopy for the ternary Co-Al-W system. Kinetic processes during high-temperature oxidation of ternary model alloys were investigated depending on the W content between 800 and 900 °C. Furthermore, the role of base elements (Co or Ni) was elucidated with the help of another single-crystalline model alloy series. Using the obtained results, the development of diffusion-limiting barrier layers as well as the formation of unwanted phases could be directly correlated to the Co/Ni ratio in the alloy.

Two-stage tracer exchange experiments in $^{16/18}$O$_2$-containing atmospheres were conducted to investigate the transport of reactants through growing oxide scales. Besides counter-current transport of cations and anions along different paths also the development of pores and microchannels was confirmed by the selected experimental approach.

Martin Weiser

Elementary Mechanisms During the Early Stages of Scale Formation on Single Crystalline Co- and Ni-base Superalloys at High Temperatures

Martin Weiser