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To cite this article: N Kauss *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **373** 012020

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Age-hardening behaviour, microstructure and corrosion resistance of the copper alloyed stainless steel 1.4542

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Abstract. The copper alloyed stainless steel 1.4542 (X5CrNiCuNb16-4) is used in different areas due to its good mechanical properties and corrosion resistance. Strength and corrosion resistance can be adjusted by the heat treatment, which is of importance for the application of this alloy. The mechanical properties (strength and hardness) are attributed to the dispersive precipitation of the copper rich ϵ -Phase. The additional precipitation of chromium carbides can reduce the corrosion resistance. Different ageing states were produced to investigate the precipitation behaviour with various methods. Furthermore, the influence of cold-rolling on the precipitation behaviour was studied in comparison to a solution annealed state without deformation. The microstructure was studied by SEM and the variations of hardness and magnetic proportion were characterised. The electrochemical potentiodynamic reactivation (EPR) was used to determine the corrosion resistance and detect chromium depletion in all heat-treated states. The results show that a work hardening accelerates the precipitation rate, while ageing at 600 °C reduces the corrosion resistance due to chromium depletion.

1. Introduction

The X5CrNiCuNb16-4 (1.4542) is a nickel martensitic, age-hardening, stainless steel used in chemical plant construction, medical technology and aerospace. In these areas, there are high demands on mechanical properties (hardness, strength, ductility and toughness) and corrosion resistance at the same time. The stability of the passive layer is influenced by various factors. These include the distribution of the alloying elements in the microstructure, the surface roughness and the surface machining [1], as well as the passivation conditions [2]. To meet the requirements for mechanical properties and corrosion resistance, a heat treatment is necessary [4]. Chromium should be distributed homogeneous in the solid solution by solution-annealing for optimal passive layer stability [3, 4]. The age-hardening steel 1.4542 receives its hardness and strength not by the martensitic conversion but by subsequent ageing, whereby the copper-rich ϵ -phase is precipitated [5]. The maximum hardness is achieved at short ageing times, when the precipitates are still coherent and disperse in the steel matrix [5, 6]. Too high ageing periods result in coarsening of the ϵ -phase while stable austenite is formed, both effects reducing the hardness [6]. Carbon enables the undesired precipitation of chromium rich carbides at the grain boundaries. This leads to a local chromium-depletion at the interface of carbide and the surrounding steel matrix, which reduces the passive layer stability and corrosion resistance [4, 7, 8]. Niobium, alloyed in the 1.4542, binds carbon in niobium-carbides to counteract the sensitisation by chromium carbide precipitation. The formation of copper-rich precipitation and the distribution of copper in the microstructure also influence the corrosion resistance. Dissolved in the solid solution, copper lowers the hydrogen overvoltage and



thus facilitates passivation, which reduces the kinetic restraint of the cathodic reaction [9]. However, ϵ -precipitations, which contain up to 96 wt. % copper, do not form a passive layer. These spots act as initial defects susceptible to pitting corrosion and reduce the passive layer stability of stainless steels [10]. However, the age-hardening steel 1.4542 requires the ϵ -phase to achieve the required mechanical properties.

This work investigates how corrosion resistance and hardness are altered by the ageing process to give recommendations for appropriate heat treatment. To detect the sensitisation, the electrochemical potentiodynamic reactivation (EPR) is used. This method has already been standardised and used for austenitic and duplex stainless steels as well as, in modified form, on martensitic stainless steels [3, 4, 11-13]. The EPR method can detect local changes of the alloy content in the microstructure which result in a destabilised passive layer.

Additional cold rolling between solution annealing and age-hardening can be used to accelerate the precipitation of the ϵ -phase, which may shorten the ageing time. Dislocations, generated by cold rolling, can enhance the effect called "dislocation pipe diffusion" which reduces the activation energy for diffusion and thus increases the diffusion rate [14]. This effect was studied by comparing the ageing behaviour of a solution annealed state with and without further deformation. This paper characterises the influence of cold rolling and age-hardening on hardness and corrosion resistance.

2. Experimental

2.1. Material, heat treatment and cold forming

The material used was a 6 mm thick sheet metal of X5CrNiCuNb16-4 (1.4542), with the chemical composition shown in **table 1**. The plate was machined into samples with dimensions 9 mm x 9 mm x 6 mm on which a heat treatment, consisting of solution annealing (homogenisation) and ageing (to increase strength), was applied to achieve optimum hardness and strength.

Table 1: Chemical composition (wt. %) of the investigated steel X5CrNiCuNb16-4 (1.4542)

Alloy	C	Cr	Ni	Cu	Nb	Mn	P	S
1.4542 (X5CrNiCuNb16-4)	0.05	15.2	5.15	3.41	0.30	0.61	0.02	0.001

Thermodynamic calculations were made based on the chemical composition (**table 1**) with the software *ThermoCalc* to understand the microstructural evolution and the variation of the alloy's corrosion resistance and mechanical properties by the heat treatment. Figure 1 shows the fractions of the different phases occurring in the alloy 1.4542, depending on the temperature.

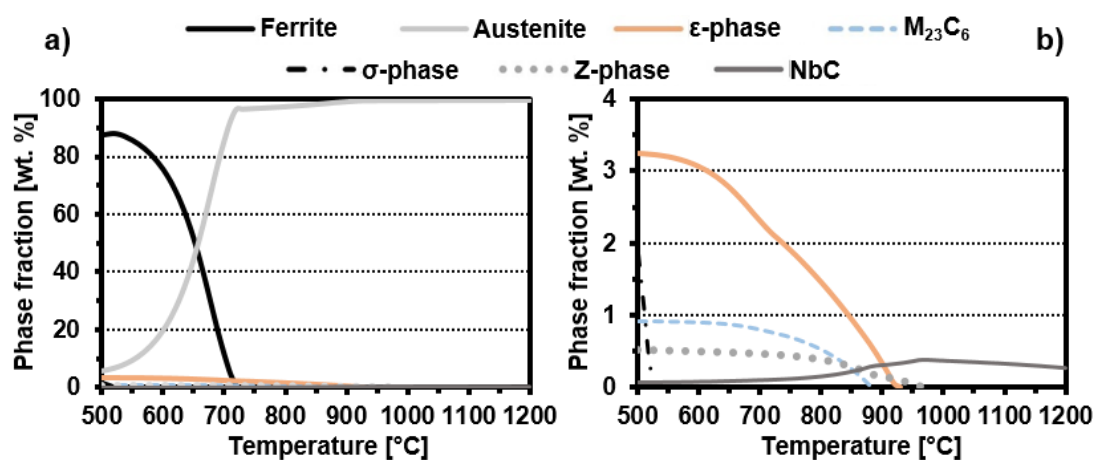


Figure 1: Phase fractions for the alloy 1.4542 a) 0 to 100 wt. % and b) detail from 0 to 4 wt. %

Starting from 920 °C, the copper-rich ϵ -phase is completely dissolved in the solid solution due to the increasing solubility for copper in the austenite. All chromium-rich phases (σ -phase, Z-phase and $M_{23}C_6$ -carbides) are dissolved at > 950 °C, while carbon is mostly bound in niobium-carbides of the MC type. These are uncritical for corrosion and postpone the formation of chromium carbides during ageing treatment to longer durations.

To study the effect of age-hardening on microstructure, corrosion resistance and hardness, a precipitation-free, homogeneous initial state is required. A martensitic matrix with some remaining niobium-carbides and retained austenite (shown in figure 3 ageing duration 0 h) was achieved by solution annealing at 1050 °C for 0.5 h, followed by water quenching to room temperature. To differentiate between the effect of "pipe diffusion" and the effect of pure cold forming, solution-annealed samples were cold rolled in several steps down to 20 % of their initial height and examined concerning hardness, magnetisable proportion and corrosion resistance without further ageing.

In the next step, the influence of ageing was studied on solution annealed samples with and without deformation to 50 % of their initial height by cold rolling. The ageing temperature of 600 °C was used, and the ageing time was increased up to 8 h to precipitate copper and carbon rich phases. **Table 2** shows the used ageing parameters.

Table 2: Ageing parameter after solution annealing at 1050 °C for 0.5 h with water quenching

	Temperature [°C]			Ageing time [h]				
Without deformation	600	0	0.25	0.5	1	2	4	8
With 50 % deformation	600	0	0.25	0.5	1	2	4	8

2.2. Microstructure, hardness and magnetic proportion

The microstructure was examined in a comparative way, depending on the performed heat treatment. The samples were wet ground with SiC abrasive paper until the oxidised and decarburised surface was removed (500 μm). This was followed by wet grinding with increasing grit size (80/180/360/600/1200/2400), polishing with 3 μm and 1 μm diamond suspension and etching in aged V2A stain (10 ml concentrated hydrochloric acid, 100 ml distilled water, 10 ml nitric acid) at 70 °C for 15 s. The microstructure was characterised in the scanning electron microscopy (SEM) DualBeam FEI Scios. The hardness was determined according to Vickers (HV10). In addition, the change in the magnetisable proportion was evaluated with a Feritscope, which was calibrated to 37 % and could not quantify higher levels. Therefore, the measured values show only the change of the magnetisable percentage and no absolute values.

2.3. Electrochemical testing

The DL-EPR method was used to detect the reduction of corrosion resistance by the formation of precipitations. For this purpose, the passivation current density ($i_{\text{passivation}}$) and the reactivation current density ($i_{\text{reactivation}}$) were determined depending on the sample condition. A classical three electrode arrangement consisting of Ag/AgCl reference electrode ($E_{\text{NHE}} = 197 \text{ mV}$), Platinum counter electrode and the sample as working electrode was used. The sample surface was wet-ground with grit 1000, cleaned with deionised water and alcohol and then dried in warm air. An area of 0,126 cm^2 was exposed to 0.1 mol/l H_2SO_4 solution with 0.001 mol/l KSCN, and polarised from -500 $\text{mV}_{\text{Ag/AgCl}}$ to +100 $\text{mV}_{\text{Ag/AgCl}}$ with 2 mV/s . In this anodic polarisation, the passive layer is formed and the necessary passivation current density ($i_{\text{passivation}}$) is determined. The maximum current density is indirect proportional to the alloying elements Cr and Mo dissolved in the solid solution [4]. The polarisation direction is reversed at +100 $\text{mV}_{\text{Ag/AgCl}}$. Weak points (chromium depletion) in the passive layer were reactivated during the cathodic polarisation from +100 $\text{mV}_{\text{Ag/AgCl}}$ back to -500 $\text{mV}_{\text{Ag/AgCl}}$. The measured reactivation current density ($i_{\text{reactivation}}$) is proportional to the dissolution of microstructural features with less corrosion resistance compared to the passive matrix. Increasing reactivation current densities show a destabilising effect of ageing treatments and microstructural alternations on the passive layer.

3. Results and discussion

3.1. Influence of cold rolling

Figure 2 shows the effect of cold rolling from 100 % to 20 % of the initial height on hardness, magnetisable proportion, passivation and reactivation current density.

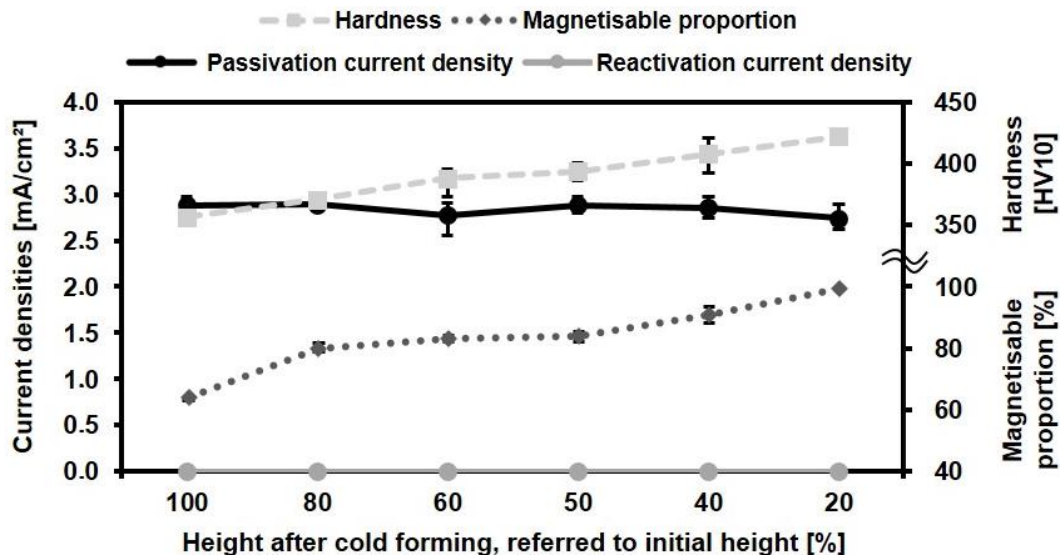


Figure 2: Hardness, magnetisable proportion, passivation and reactivation current density with increasing deformation due to cold forming

Hardness and the magnetisable proportion increase with the deformation. This is caused by the transformation of retained austenite into ferromagnetic deformation-martensite. At the same time, the deformation increases the dislocation density, which further increases the hardness. Furthermore, these dislocations reduce the electrical conductivity whereby the eddy current-based Feritscope does not determine a quantifiable value, but only indicates the change from the magnetisable percentage. The cold rolling has no influence on the passivation and reactivation current densities of the EPR method, and therefore it does not affect the corrosion resistance.

3.2. Influence of the ageing duration with and without deformation

Figure 3 and figure 4 show the influence of ageing time at 600 °C up to 8 h on the microstructure of the deformation-free and cold rolled states. All conditions show a nickel-martensitic matrix with finely distributed niobium-carbides. Precipitations were formed as a result of ageing, whose phase proportion increases with the ageing time.

The deformed samples, which were cold rolled to 50 % of their original height, show a significant higher proportion of precipitation in the microstructure at the same ageing time. This can be attributed to the increase in diffusion velocity due the effect of “dislocation pipe diffusion”. The microstructure of the rolled samples shows a dense allocation of precipitations at the grain boundaries, starting with an ageing duration of 1 h. A comparable precipitation state at the grain boundaries occurred in the samples without deformation after an ageing time of 2 h. Furthermore, the formation of precipitations (Cr_{23}C_6 -carbides, Z-phase and NbC-carbides) within the grains starts earlier with deformation (2 h), compared to the aging without deformation (4 h).

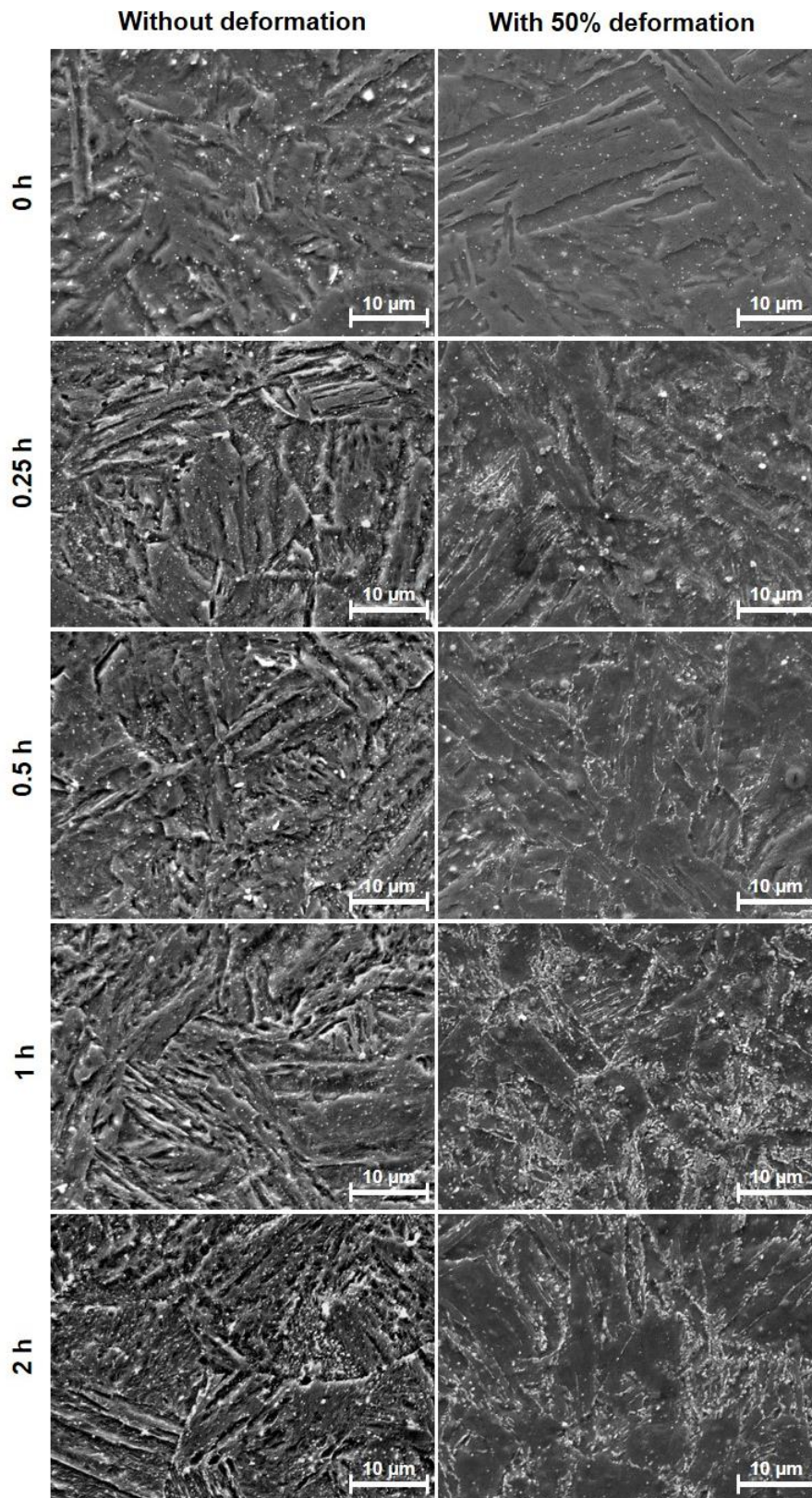


Figure 3: Microstructure of the steel 1.4542 after solution-annealing (1050 °C, 0.5 h, water quenched) and ageing at 600 °C for 0 h to 2 h for samples without and with 50 % deformation

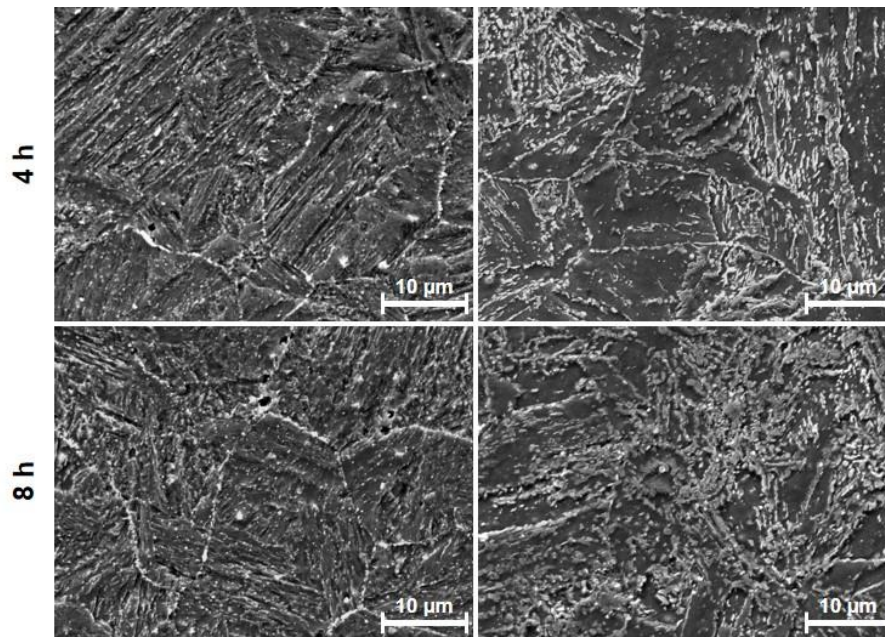


Figure 4: Microstructure of the steel 1.4542 after solution-annealing (1050 °C, 0.5 h, water quenched) and ageing at 600 °C for 4 h to 8 h for samples without and with 50 % deformation

Figure 5 shows the effect of ageing on hardness, magnetisable proportion, passivation and reactivation current density without deformation (figure 5 a) and with 50 % deformation (figure 5 b).

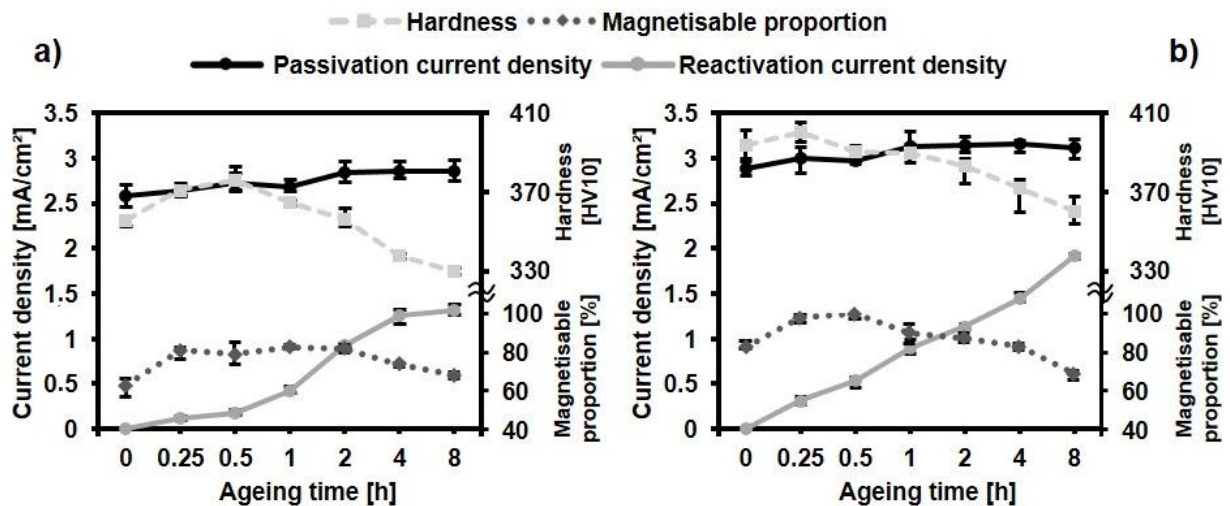


Figure 5: Effect of ageing duration at 600 °C on hardness, magnetisable proportion and passivation and reactivation current density, a) without deformation b) with 50 % deformation

The general magnetisable proportion is higher in the cold rolled samples than in the non-rolled samples, which is the result of the deformation induced conversion of residual austenite into martensite. The ageing increases the magnetisable proportion, and the maxima of magnetisable proportion were reached at ageing times of 1 h without deformation and 0.5 h with 50 % deformation.

Overall, the cold rolled samples showed a higher hardness as a result of the deformation induced work hardening and the transformation of retained austenite into deformation martensite. The heat

treatment related hardness maxima were achieved at an ageing time of 0.5 h without deformation (figure 5a) and an ageing time of 0.25 h with 50 % deformation (figure 5b).

The earlier maxima of hardness and magnetisable proportion in the deformed state can be explained by the increased precipitation rate of the hardness-enhancing ϵ -phase. After reaching the maxima, both values decrease with further ageing. The deformed samples showed a stronger drop in both values, which is a result of the reduction of the dislocation density. The decrease of hardness is also reinforced by the coarsening of the now incoherent ϵ -phase and the reconversion from martensite to austenite.

The passivation current density ($i_{\text{passivation}}$) is almost constant, which shows that no global reduction of the alloy content of the matrix occurs. The reactivation current density ($i_{\text{reactivation}}$) increases linearly with the ageing duration. This is the result of local sensitisation in the microstructure, which reduces the passive layer stability.

The deformation of the solution-annealed samples prior to the aging causes a faster increase of the reactivation current density ($i_{\text{reactivation}}$), which also can be explained by the effect of dislocation pipe diffusion. It could not be determined which precipitation (ϵ -phase, $M_{23}C_6$, Z-phase) causes the reactivation, since all three phases form during ageing at 600 °C. This could be clarified with further investigations concerning the localisation of the selective corrosion during the reactivation.

4. Conclusion

Deformation and ageing have a significant influence on the mechanical properties and corrosion resistance of the nickel martensitic, copper alloyed, age-hardening stainless steel 1.4542 (X5CrNiCuNb16-4). The maximum hardness was achieved when the copper-rich ϵ -precipitations were still coherent with the matrix. The optimum corrosion resistance, on the contrary, is achieved, when all precipitations ($M_{23}C_6$, ϵ -phase, and Z-phase) are dissolved by the solution annealing and the alloying elements are homogeneous distributed in the solid solution.

However, ageing at 600 °C causes the formation of sensitising precipitations, which was detected based on increasing reactivation current densities with the DL-EPR method. It has also been shown that a deformation before ageing leads to higher hardness values and to the earlier attainment of the hardness maximum, which is based on the effect of "dislocation pipe diffusion". The corrosion resistance of the solution-annealed condition was not affected by the sole cold forming. Only the hardness and the magnetisable proportion increase strongly with the degree of deformation, since residual austenite is transformed into martensite and the dislocation density is increased.

The sensitisation during ageing of the 1.4542 could be caused by $M_{23}C_6$ -carbides, the ϵ -phase or the Z-phase. Nevertheless, the sensitisation occurs even during very short ageing times (15 min for 600 °C). Carbon is tied by niobium in niobium-carbides and the formation of chromium-rich $M_{23}C_6$ -carbides, and the Z-phase may need a longer ageing duration. It seems likely that the precipitation of the ϵ -phase is responsible for the sensitisation.

5. References

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