



Niobium carbide for machining and wear protection – Evolution of properties

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Basics about physical, mechanical and tribological properties of straight NbCs, including paths to tailor these properties, were laid down in Metal Powder Report, Vol. 71(4), 2016 and Vol. 71(5), 2016. The object is now to give an up-date on the progress in the key properties, like HV30, K_{IC} and strength, followed by machining and tribological results of the respective NbC grades.

The sales of niobium carbide (NbC) have grown in the last years from ~350 tons p.a. to 500 tons p.a. recently, but NbC is still a hidden carbide and mainly used as grain growth inhibitor in hard metals. Another driver is the intention of hardmetal producers and downstream manufacturers to substitute tantalum carbide (TaC) by NbC in order to compensate the increased cobalt prices, which likely will persist on midterm.

1. Niobium carbide grades and cermets

Niobium carbide is used as grain growth inhibitor. In terms of action as grain growth inhibitor, Huang et al. [1] and Genga et al. [2] studied mixed WC-NbC-xxCo systems and found, that up to 10 wt.-% of NbC in WC had no adverse effects in WC-xxCo for SPS sintered and up 3 wt.-% of NbC in WC for conventionally sintered compositions. The aim remains still to use NbC as main hard phase.

2. Materials preparation

Straight NbC and NbC cermets can be processed by the same routes and in the same equipment as well known for hardmetals. NbC (CBMM, FSSS = 1.75 μm , Brazil), Mo_2C (Langfeng, FSSS = 3.50 μm , China), VC (Langfeng, FSSS = 3.38 μm , China), WC (H.C. Starck, DS250, 2.5 μm , Germany), $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ (H.C. Starck, Standard 120, d_{50} = 1–3 μm , Germany) and Ni (T123TM, VALE, FSSS = 3–7 μm , UK) powders were used to prepare the NbC based cermets. The NbC powder has a total carbon content of 11.2 wt.-% C and oxygen content of 0.17 wt.-% O. respectively Table 1 summarizes the chemical composition of the investigated NbC based cermets with different combinations of carbide/ $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ additions, prepared by spark plasma sintering and

conventional sintering. The NbC-12Co grades, using a carbon deficient and right balance carbon NbC starting powders were initially investigated and were prepared by SPS. With the replacement of Co by Ni, more complicated cermet systems, containing various amounts of $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ and WC, VC, Mo or Mo_2C were also prepared. All the powder mixtures were mixed on a multi-directional mixer (Turbula, WAB, Switzerland) in ethanol for 24 h using WC-6 wt% Co milling balls (Cerazit grade H20C, $\text{\O}10$ mm). The suspension was dried in a rotating evaporator at 65 °C. Cold isostatically pressed (200 MPa, EPSI) powder compacts were pressureless sintered for 1 h at different temperatures in a dynamic vacuum (~20 Pa) with a heating rate of 5 °C/min in a resistively heated furnace with a graphite heating element.

3. Evolution in mechanical properties

Initially, the development started with binderless NbC densified by hot-pressing in order to determine basic functional properties. Table 1 summarizes the properties of selected NbC grades, of which data on machining tool life was established and published. The first spark plasma sintered (SPS) NbC-8Co had a four point bending strength (σ_{4pb}) of 810 MPa, which was improved to σ_{4pb} ~ 1300 MPa for NbC-12Co T SPS. Subsequently, the micro-hardness was improved by using sub-stoichiometric and submicron $\text{NbC}_{0.88}$ -12Co SPS, but the strength dropped down to 1000 MPa. The following changes were multiple:

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TABLE 1
Mechanical properties of NbC grades (all processed by ball milling).

Grade	Sintering	HV2 [GPa]	HV30 [GPa]	K _{IC} Palmqvist method [MPa√m]	4-point bending strength [MPa] (m)
Method	—	ISO 6507-1		ISO 28079	DIN EN 843-1
NbC _{0,88} -12Co H1 SPS	SPS, 1.285 °C, 30 min, 30 MPa	16,50 ± 0,07	14,99 ± 0,16	5,78 ± 0,17 (5,5 ± 0,13)*	1.005 (7,3)
NbC _{1,0} -12Co T SPS	SPS, 1.280 °C, 4 min, 30 MPa	13,90 ± 0,12	12,77 ± 0,07	7,87 (./.)*	1.297 (6,8)
NbC _{1,0} -10Ni4Mo4VC	CS, 1.420 °C, 1 h, vacuum	14,58 ± 0,23	14,02 ± 0,06	9,02 ± 0,25 (7,5 ± 0)*	738 (12,7)
NbC _{1,0} -12Ni4Mo4VC	CS, 1.420 °C, 1 h, vacuum	13,93 ± 0,18	12,80 ± 0,10	10,03 ± 0,10 (8,8 ± 0,04)*	1.001 (4,3)
NbC _{1,0} -12Ni4Mo ₂ C4VC	CS, 1.480 °C, 1 h, vacuum	13,99 ± 0,20	12,76 ± 0,09	10,3 ± 0,3 (./.)*	1.198 (4,7)
NbC _{1,0} -12Ni5VC	CS, 1.350 °C, 1 h, vacuum	12,96 ± 0,02	11,97 ± 0,17	11,7 ± 0,5 (10,6 ± 0,47)*	1.222 (12,5)
(NbC _{1,0} -10TiC)-6Ni7,5VC	CS, 1.420 °C, 1 h, vacuum	15,50 ± 0,15	13,60 ± 0,3	7,99 ± 0,05 (6,5 ± 0,1)*	626 (6,6)
42NbC-14Ni20TiC ₇ N ₃ -20WC4Mo ₂ C	CS, 1.450 °C, 90 min, vacuum	14,70 ± 0,21	13,42 ± 0,1	9,3 ± 0,1 (9,2 ± 0,2)*	1.599 (12,5)
70NbC-15TiC ₇ N ₃ -5Ni-7,5WC 2,5Mo ₂ C	CS, 1.450 °C, 90 min, vacuum	17,60 ± 0,28	14,67 ± 0,1	6,1 ± 0,1 (6,6 ± 0,4)*	1.222 (7,6)

* By notch acc. to DIN EN ISO 23146:2016; (m) = Weibull's parameter.

- a. SPS was substituted by conventional, liquid phase sintering (CS)
- b. nickel substituted cobalt binder and
- c. sub-stoichiometric NbC_{0,88} by stoichiometric NbC and the use of secondary carbides.

These changes improved significantly the toughness to >11 MPa√m and the strength recovered to σ_{4pb} ~ 12,22 MPa with an associated loss in hardness (NbC-12Ni5VC CS) as shown by Figure 1. Depending from Weibull's parameter, the 3-point bending strength data calculated from 4-point bending strength in Figure 1 would be 20–30% higher.

In the following NiMo and NiMo₂C grades reached 1400 HV30 while keeping toughnesses between 9 to 11 MPa√m and 4-point bending strengths ranged between 1.000 and 1.200 MPa.

The application of Ti(C₇N₃) and higher contents of WC resulted in an attractive functional set of properties with fracture toughnesses K_{IC} > 9 MPa√m, associated micro-hardnesses of >1450 HV30 and more or less σ_{4pb} ~ 1600 MPa for

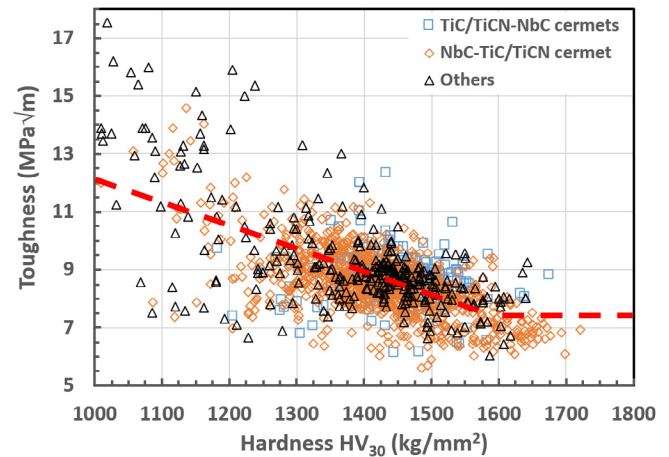


FIGURE 2
Plot of toughness versus micro-hardness of NbC-TiC/Ti(C_xN_y) and TiC/Ti(C_xN_y)-NbC cermets.

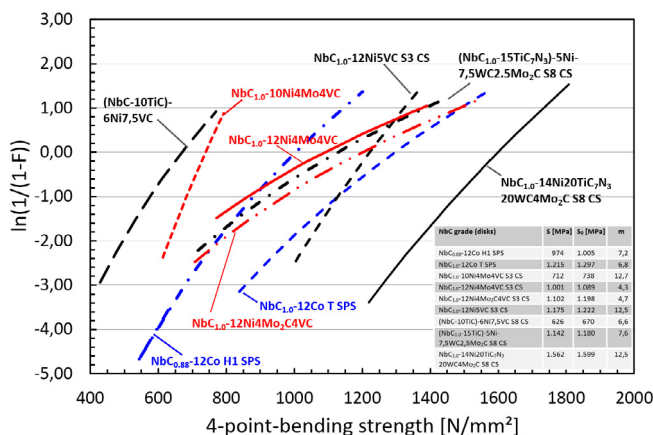


FIGURE 1
Weibull-plots of 4-point bending strength according to EN 843-1 of straight NbC grades.

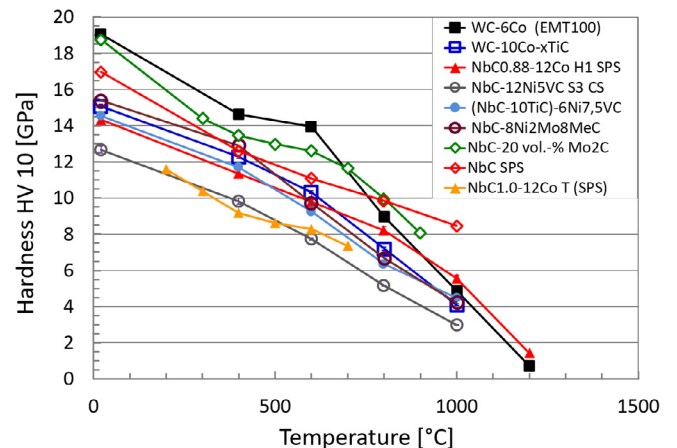


FIGURE 3
Comparison of hot hardness of NbC development grades with commercial WC grades [3].

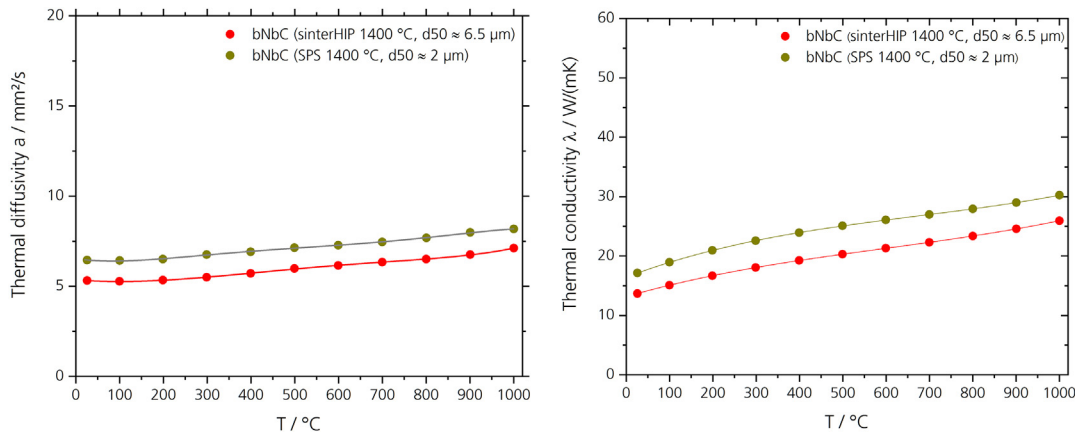


FIGURE 4

Thermal properties of binderless tungsten carbide and niobium carbides [11].

$\text{NbC}_{1.0}\text{-14Ni20TiC}_7\text{N}_3\text{ 20WC4Mo}_2\text{C CS}$. The associated Weibull parameter of 12.5 indicates a quite homogenous distribution of properties.

By varying the sintering conditions for the composition “70NbC-15TiC₇N₃-5Ni-7,5WC 2,5Mo₂C”, its micro-hardness was increased from 1467 HV30 to 1616 HV30 for endmill appli-

cations, like carbon fiber reinforced plastics. As stated in Table 1, the progress with NbC-Ti(C₇N₃) over straight NbC-NiMo lies in the significant higher strength.

The NbC grades shown in Table 1 displayed lower microhardnesses than typically for WC-Co grades (1.500-1800 HV30) with similar binder contents. It is well known, that when

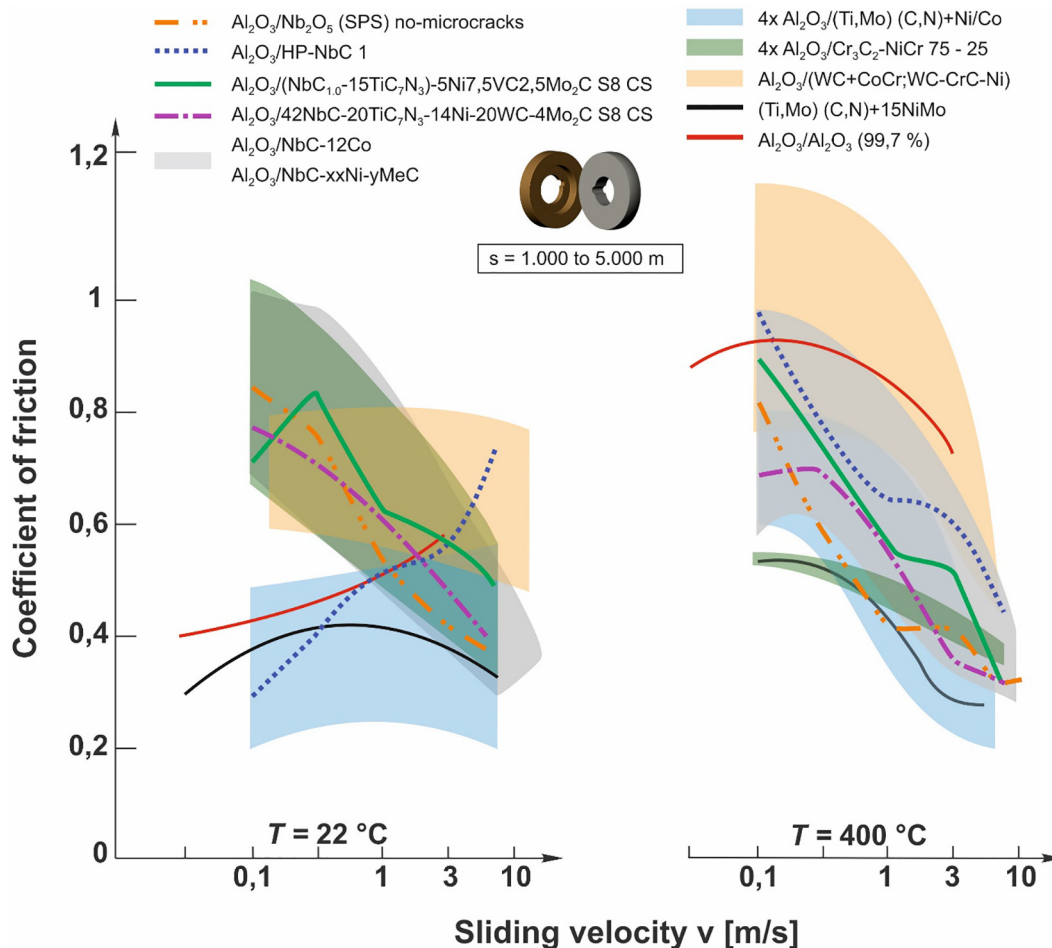


FIGURE 5

Evolutions of coefficients of friction under dry sliding of NbC grades and NbC-TiC₇N₃ grades in comparison to carbidic hardmetals and cermets.

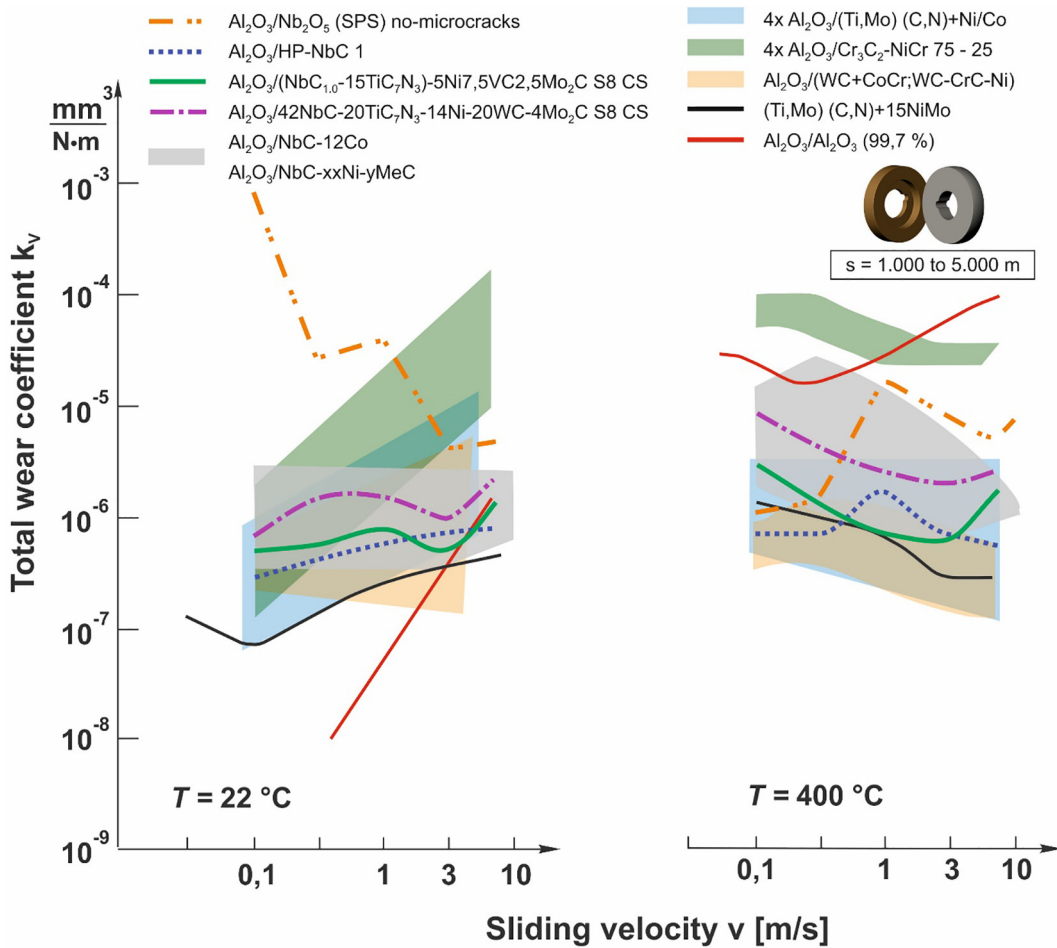


FIGURE 6 Evolutions of wear coefficients under dry sliding of NbC grades and NbC-TiC₇N₃ grades in comparison to carbidic hardmetals and cermets.

Evolutions of wear coefficients under dry sliding of NbC grades and NbC-TiC₇N₃ grades in comparison to carbidic hardmetals and cermets.

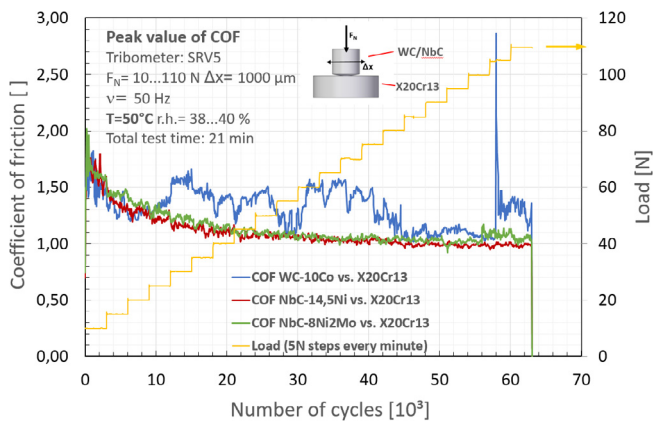


FIGURE 7 Dry galling SRV Tests under high contact pressures.

Dry galling SRV Tests under high contact pressures.

substituting cobalt in WC with nickel reduces hardness by about 100–150 HV30.

Figure 2 plots the fracture toughness K_{IC} versus micro-hardness HV30 of ~2000 development cermet grades in NbC-TiC/Ti(C_xN_y) and TiC/Ti(C_xN_y)-NbC, which are distinct themselves by compositions and/or processing/sintering cycles. It is visual from Figure 2, that the properties depend from process,

sintering cycle and composition. A multitude of these grades passes the borderline of the minimum property requirements of hardmetals for applications (red line). Grades with functional properties of 1500–1600 HV30 with associated fractures toughnesses of $K_{IC} \sim 9.0 \text{ MPa}\sqrt{\text{m}}$ were realized.

The hot hardness of hard materials is of importance, as cutting edges reach during machining easily 1000 °C and up. Several parameters, like applied indentation load, composition and stoichiometry [4–6] influences the exact hardness values of NbC grades. As reported from literature, sub-stoichiometric NbC_{0.88}-12Co not only gave at RT 150–200 HV30 extra hardness [7] over NbC_{1.0}-12Co, but also a very good stability of hardness with increasing temperature (see Figure 3). The binderless NbC-20 vol.-% Mo₂C represents another option to increase hardness by strain hardening with an associated good retention of hot hardness.

In general, NbC is at room temperature (RT) softer than WC, whereas the stability of hot hardness for binderless NbC is remarkable. Figure 3 illuminates, that the micro-hardness of WC drops at around 500–700 °C (932–1292°F). Niobium carbide exhibited this transition at a higher temperature interval around 900–1000 °C (1652–1832°F) [8,9], likely due to its higher melting point of 3522 °C (6372°F) versus WC with ~2870 °C (5198°F). This resulted either in a higher hot-hardness of NbC

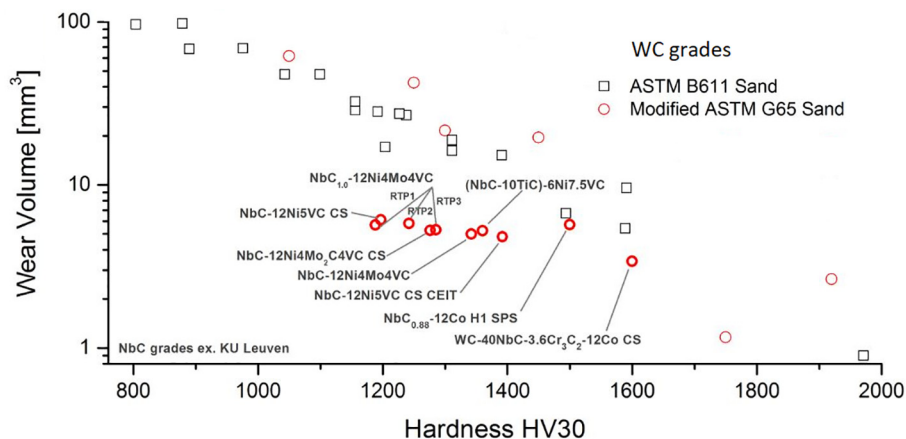


FIGURE 8

Abrasive wear of NbC grades versus WC grades (opened tribosystems, with data for WC taken from ISO 28080).

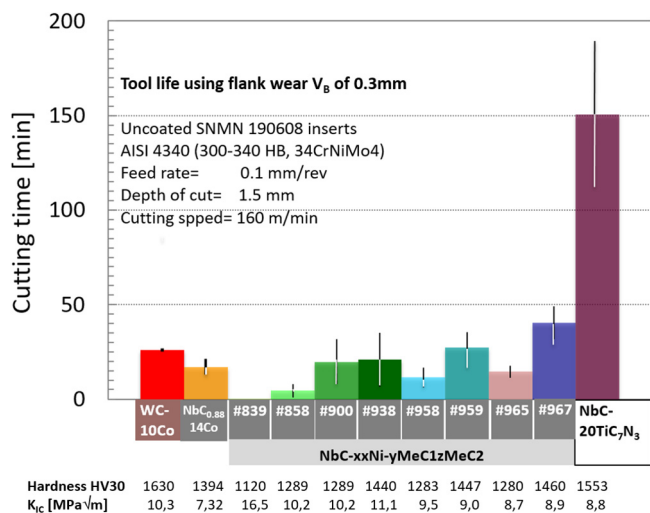


FIGURE 9

Hard cylindrical turning under flood cooling of gear steel with different NbC grades [12].

(NbC_{0.88}-12Co, NbC-20Mo₂C) as compared to WC (WC-6Co), or the hardness gap is reduced with increasing temperature, e.g. at 1000 °C. The grades NbC_{0.88}-12Co, NbC_{1.0}-8Ni₂Mo₈MeC, (NbC_{1.0}-10TiC)-6Ni_{7.5}VC illuminate in Figure 3 this trend. The stable and high hot hardness of NbC assures at high sliding velocities the load carrying capacity in combination with the tribo-oxidatively formed Nb₂O₅. It has to be reminded, that NbC is insoluble in alloys.

4. Thermophysical properties

The thermal conductivity of WC at RT is significantly higher as for NbC. Emelyanov et al. [10] found, that the thermal conductivity of NbC increases and the one of WC decreases with increasing temperature. Thus, the gap in heat conduction between WC and NbC is reduced with increasing ambient temperature, especially when using the thermal diffusivity, which takes into account density and heat capacity.

The evolutions in thermal properties with temperature of Emelyanov et al. were recently confirmed by Pötschke et al. [11] on binderless WC and NbC (see Figure 4).

5. Tribological behavior of NbC-based hard materials

Figure 5 displays a simultaneous decline in coefficients of friction with increasing sliding velocity at 22 °C and 400 °C in air for niobium oxides (Nb₁₂O₂₉) and several NbC-based cermets as well as Cr₃C₂-based systems. This leads to the conclusion, that the frictional behavior of NbC in air is rather dominated by tribo-oxidation than by the carbide itself. NbC-based cermets offer at higher sliding speed frictional benefits against titanium-based cermets ((Ti,Mo)(C,N)) and WC-based hardmetals. At 400 °C, the coefficients of friction dropped for all with increasing sliding speed due to the formation of sub-oxides with planar defects (Ti_nO_{2n-1}, Ti_{n-2}Cr₂O_{2n-1}, W_nO_{3n-2}) or with block-structures (Nb_{3n+1}O_{8n-2}). The NbC-based cermets are at 400 °C within those offering the lowest friction.

The wear rates at 22 °C of niobium oxide (here: Nb₁₂O₂₉) (See Figure 6) plunged downward under dry sliding by two orders of magnitude (200×) when increasing sliding velocity from 0.1 m/s to 7 m/s. At 7 m/s, the wear rate of 4.9 · 10⁻⁶ mm³/N·m for Nb₂O₅ is close to those of the NbC-based cermets, which compete at RT and higher sliding velocities with WC-based hardmetals. The wear rates at 400 °C of Nb₁₂O₂₉ (See Figure 6) were low until 0.3 m/s and superior to those of NbC cermets. When compared to Nb₂O₅, the much higher strength and hardness of NbC cermets determined the wear resistances, even a contribution of Nb₂O₅ (Nb₁₂O₂₉) is seen depending from the operating conditions.

In comparison to NbC, the tribo-oxidative reaction rates for Ti&W-based substrates are at RT much lower limiting the tribo-oxidative formation of oxide films. It is visual from Figure x, that tribo-oxidation is not beneficial for Cr₃C₂ at high sliding velocities and 400 °C.

Dry SRV galling tests at RT (modified from ISO 19291, ASTM D7421, SAC NB/SH/T 0882) were run against X20Cr13 (1.4006; AISI 410, UNS S41000, 12X13-III). The dry coefficients of friction are represented in Figure 7 over test time under the associated

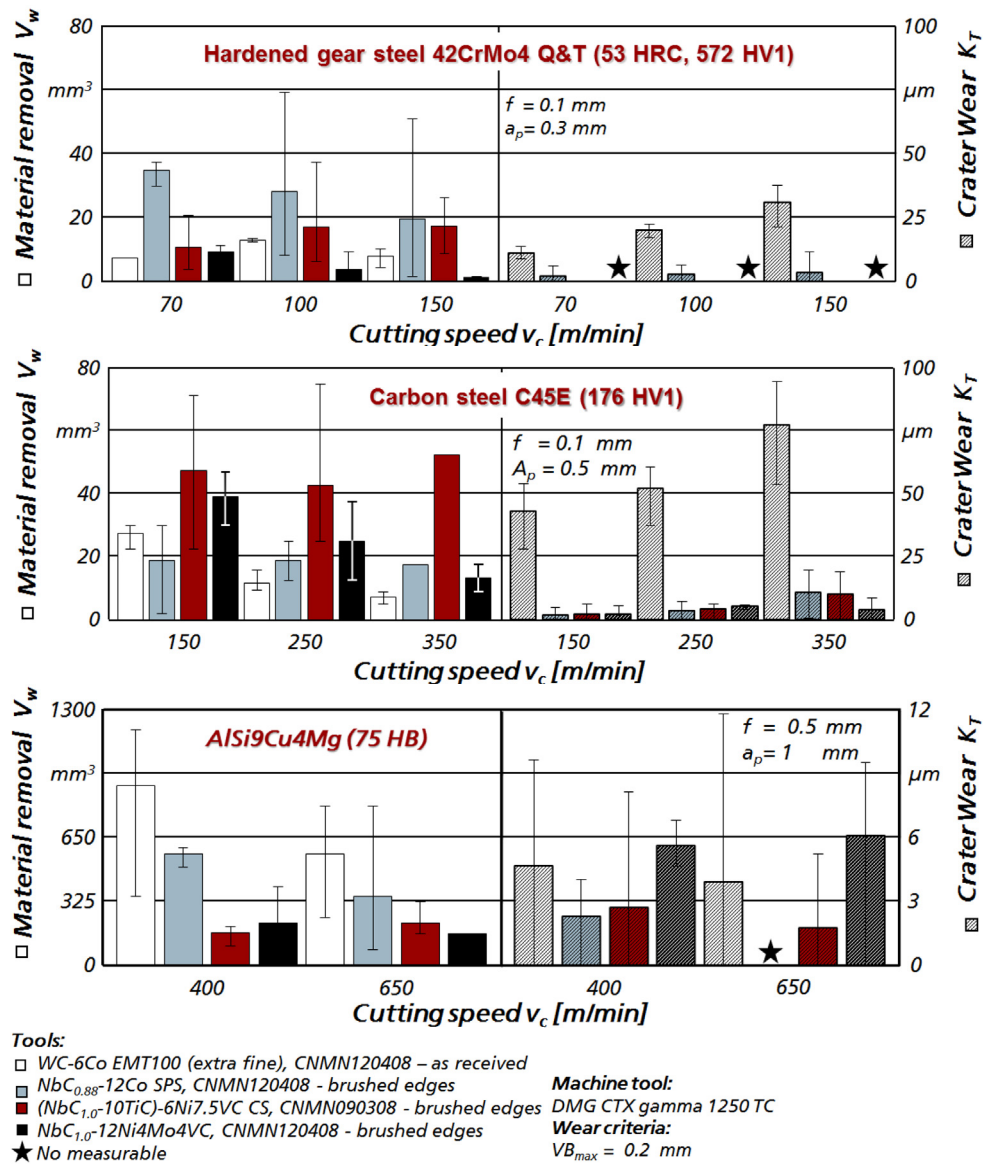


FIGURE 10

Dry cylindrical external turning under semi-finishing conditions [13].

load, which was increased every minute by 5 N. WC&NbC displayed quite high unlubricated coefficients of friction, but both NbC grades had lower friction with smooth and stable evolutions in the friction signal compared to WC-10Co (grade H10F).

The wear volumes under dry abrasion according to ASTM G65 are shown in Figure 8. Dry abrasive wear decreases for WC grades with increasing micro-hardness. This trend isn't seen for NbC. Dry abrasive wear seems to be independent from micro-hardness and most NbC grades offered under the test conditions of G65 an improved wear resistance.

6. Machining

Figure 9 displays hard turning tests under flood cooling of SNMA 190608 (square-shaped) inserts machining gear steel (AISI 4340, 34CrNiMo4, 42 ± 3 HRC). NbC-10Ni12WC14TiC (ex. BRATS, Brazil, code #967) presented superior performances than commercially available hardmetal WC-10Co11TiC2NbC (class P10).

The cermet NbC₂₀Ti(C₇N₃)-7Co7Ni20WC4Mo₂C (ex. K.U. Leuven) presented in Figure 9 had three times longer tool lives than the best NbC development grade. The process and sintering conditions impact hard turning performances of NbC grades. It is also apparent from Figure 9, that hardness and toughness for the softer NbC, when compared to WC-Co grades, do not determine the tool life. This is understood through the very low solubility of NbC in metal alloys and NBC's good retention of hardness over temperature. The experience illuminated, that NbC grades should exceed 1.400 HV30 for machining.

NbC cermets are also suitable for machining very hard gear steel materials and aluminum alloys as well, which are represented the Figure 10, under semi-finishing dry turning conditions, especially in high cutting speeds. In consequence, NbC enhances at higher cutting speeds the productivity of end-users.

The performance of NbC-10Ni4Mo4VC, as shown in Figure 11, can sustain in flood cooled continuous hard turning

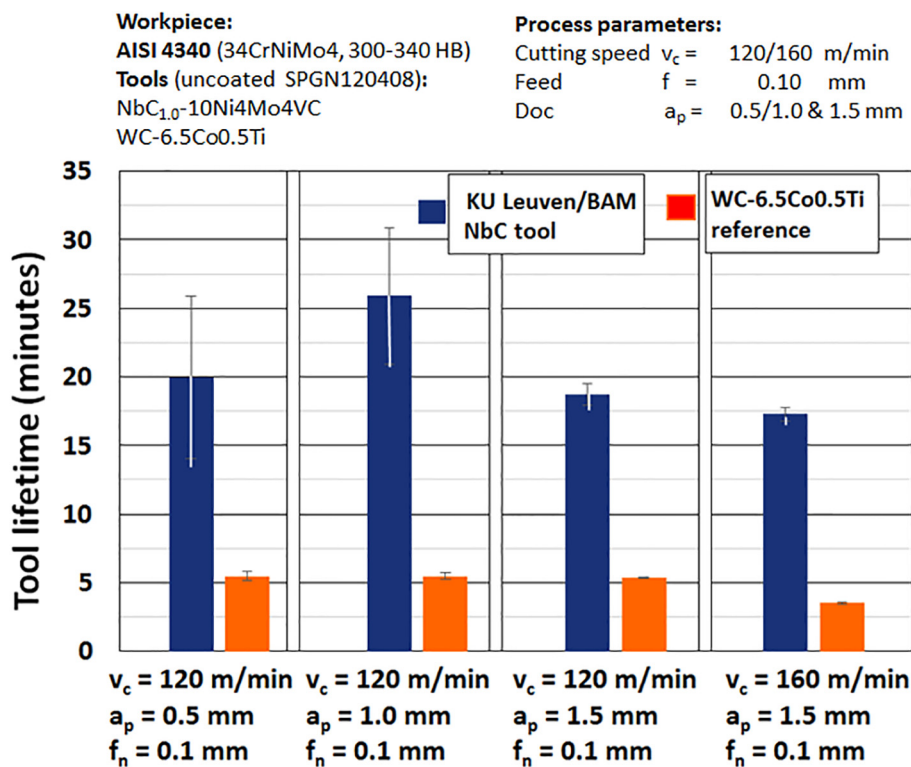


FIGURE 11

Hard turning under flood cooling of a gear steel AISI 4340 (34CrNiMo4, 300-340 HB) [12].

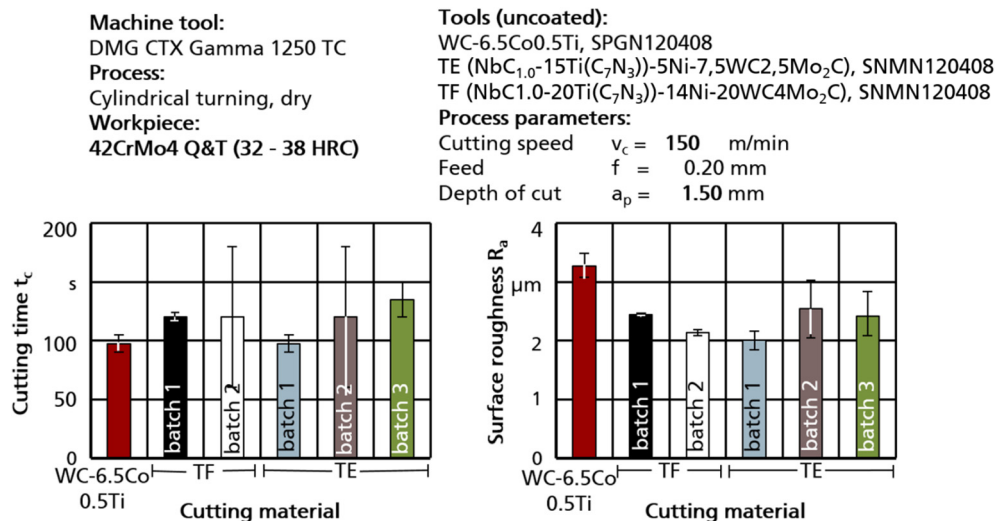


FIGURE 12

Dry hard turning of gear steel 42CrMo4 (32-38 HRC, AISI 4140) [14].

of gear steel (AISI 4340, 34CrNiMo4) over commercially available WC-Co Class H10, proving the higher wear resistance of the NbC in comparison with WC. The test was made in two different cutting speeds at variables cutting depth.

Figure 12 compares the toolslives and resulting finishing quality of experimental NbC-TiC₇N₃ cermets with a commercially available WC-6.5Co0.5Ti reference tool under dry hard turning. In average, the NbC-TiC₇N₃ grades competed or showed longer tool lives when compared to WC-6.5Co0.5Ti. Interestingly, the

NbC-TiC₇N₃ cermets achieved a superior surface quality (e.g. lower surface roughness) on the work piece materials despite longer cutting times.

7. Conclusions

Cermets in NbC have now achieved mature and competitive level of properties with $HV_{30} > 1.450$, $K_{IC} > 8$ MPa \sqrt{m} and $TRS > 2.000$ MPa near to hardmetals. Further improvements by process and compositions are awaited as well as up-scaling in

industry and its use in complex tool geometries. The experiences with a variety of NbC compositions illuminated for turning, that NbC grades should exceed 1,400 HV30 and possess a high bending strength. The large availability and stability in price makes nickel bonded NbC an attractive substitute for cobalt bonded WC and also for TaC in hardmetal compositions. The machining results indicate that a lower level in micro-hardness of NbC-TiC₇N₃ is sufficient to compete with WC-xxCo grades.

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