The background for the use of hartmetals and MMCs based on Niobium Carbide (NbC) as cutting tools and for wear resistant tribosystems

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ABSTRACT

In this present study, the mechanical properties (strength, hardness, moduli) and the dry sliding properties of stoichiometric and sub-stoichiometric NbC were compared. Micro-hardness and elastic properties of NbC depend from the C/Nb ratio, because the binary phase diagram Nb-C shows a region of homogeneity of NbC_x of $0{,}72 \leq x \leq 1.0$. At RT, hard metals of stoichiometric NbC have an elastic modulus E of ~440 GPa, those of sub-stochiometric $NbC_{0.88}$ an E of 405 GPa. The hot hardness of sub-stoichiometric NbC is above 600°C higher than of WC. The dry sliding wear resistance (0,1-7/10 m/s) of the present Fe_3Al-$NbC_{0,94}$ with ~61 vol.-% NbC as hard phase was close to those known of NbC-based hard metals. No grain pull-outs or fragmentations of the NbC grains were seen in the wear tracks of the Fe_3Al-NbC composite (MMC), as a metallurgical interphase was formed between matrix and NbC grains. Stoichiometric and sub-stoichiometric niobium carbides have at RT and 400°C under dry sliding a prone intrinsic wear resistance more or less independent from sliding speed, either as hardmetal or as hard phase in metal matrix composite, associated with an exceptional high load carrying capacity.

Keywords: NbC, niobium carbide, cobalt, Fe_3Al, hardmetal, metal matric composite, wear resistance, cutting, milling

INTRODUCTION

Historically, “wear protection” is dominated by tungsten carbide (WC), either under abrasive conditions or especially for tool materials. Due to the high solubility of WC in alloys and in their melts as well as due to the mismatch in density between melts and WC, hardmetals are mainly produced by sintering or powder metallurgy. Niobium carbide, a refractory metal, like tungsten, has been well known for decades. The tribological properties of niobium carbide are, thus far, unexplored. The supply of niobium is today assured and the reserves of the actual operating niobium mines, including the known deposit and secondary resources, largely exceed those of Tungsten. Niobium carbide offers several benefits:

a. the density of NbC is with 7,71-7,81 gr./cm³ close to Fe, Ni, Co-alloys favorable for casting and dynamic, mechanical applications,
b. the solubility of NbC_x at high temperatures in alloys are few percents (reduced tribo-chemical wear at cutting edges) and enables casting of MMCs,
c. NbC has a thermo-mechanical fit (linear expansion coefficient times elastic modulus) to alloys in comparison to WC.

The recently established tribological profile of NbC bearing materials revealed a strong position under tribological considerations and for closed tribosystems against established ceramics and hard metals [1].

EXPERIMENTAL

-Material

The procedures for plasma-spark sintering (SPS) of the different NbC grades bonded with cobalt or Fe_3Al shown in Table 1 are described elsewhere [1,2]. The cobalt and Fe_3Al bonded NbC hard-metals were SPS sintered using a stoichiometric and commercially available $NbC_{1.0}$ (Treibacher 100, Austria; d_{90}= 3.66 µm, measured powder raw density= 7.60 gr./cm³) denoted in the diagrams by “T. The sub-stoichiometric powder $NbC_{0,87}$ had a granulometry of d_{90}= 7.42 µm) with a measured powder raw density of 7.37 gr./cm³ and is denoted in the diagrams as “H1. Its primary grain size was ~100 nm.

The MMC was directly produced by alumino-carbothermic reduction of powder mixtures of Nb_2O_5, Fe_2O_3, Fe_3O_4, Fluoride, Lime, aluminium and excess of carbon (as coke). This Fe_3Al-NbC MMC had ~61 % of $NbC_{0.94}$ as hard phase. The carbon content was determined by combustion analysis (LEUCO test) NbC grains leached out of the MC. Figure 1 displays the microstructure of the MMC with coarse NbC grains metallurgically bonded in the metallic matrix, where the colours ”light-brown” (Fe_3AlC) and “light-blue” (Fe_3Al) distinct the two metallic phases [3]. The hardness of the metallic matrix can be tailored from ~480 HV0,05 by Fe_3Al to ~670 HV0.05 with Fe_3AlC.

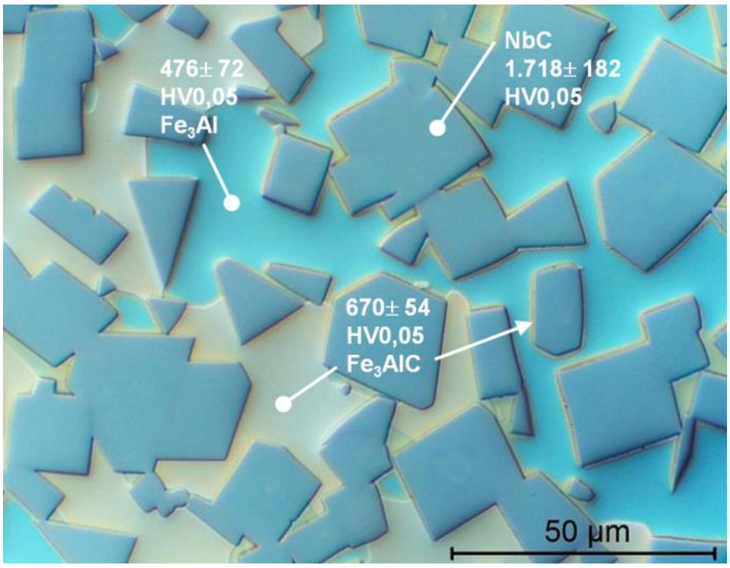

Figure 1: Microstructure of NbC-based MMC (light optical microscope, polished with SiO_2-based suspension “OP-U”)

Table 1 Properties of Niobium Carbides (development grades)

Property	T	Method	HP-NbC	NbC-8Co	NbC-12Co	NbC-12Fe_3Al	$NbC_{0,88}$-12Co
Powder	—	—	NbC (AO7132)	NbC100	NbC100	NbC100	$NbC_{0,88}$ (H1)
Densification	—	—	HP	SPS	SPS	SPS	SPS
Densification temperature [°C]	—	—	2.150 (4 h; 50 MPa)	1.280 (4 min; 30 MPa)	1.280 (4 min; 30 MPa)	1.300 (4 min; 30 MPa)	1.285 (6 min; 30 MPa)
Binder [vol.-%]		—	0	8	12	12	12
Density [gr./cm³]	RT		7,67	7,78	7,76	7,50	7,62
Elastic modulus [GPa]	RT	ASTM E1875	477	443	437	447	406
	1000°C		—	382	368	379	341
Bulk modulus [GPa]	RT		—	181	177,5	183,5	164
Poisson ratio	RT		—	0,22	0,225	0,22	0,235
4-point bending strength [MPa]	RT	DIN EN 843-1	353 ±42	742 ±180	1.215 ±197	822 ±117	1.005 ±158
Microhardness HV0.2	RT		1.681± 92	1.451±54	1.453±41	1.632±50	1.765±130
HV0.5	700°C		539±20	—	734±60	553±30	—

HP= hot pressing; SPS= Spark Plasma sintering

Figure 1 illuminates a rim of Fe_3AlC around the NbC grains. In consequence, an interphase is present, because carbon from the NbC dissolved into the Fe_3Al matrix. This clearly indicates a metallurgical bonding of NbC in the Fe_3Al matrix, which is beneficial in order to transduce tribological shear stresses. The present study compares the effect of increasing the binder (or matrix) content to ~40% on wear resistance in comparison to hard metals of NbC densified by spark plasma sintering (SPS) as well as the effect of stoichiometry on friction and wear.

-Properties of niobium carbides

The mechanical properties (strength, hardness, moduli) of different niobium carbide hardmetals are displayed in Table 1.

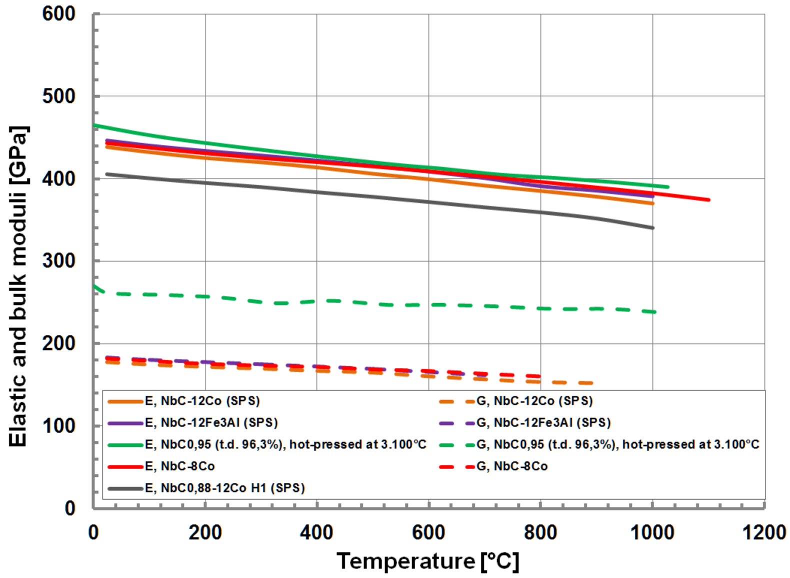

Figure 2 Evolution of moduli with temperature of stoichiometric NbC grades versus WC

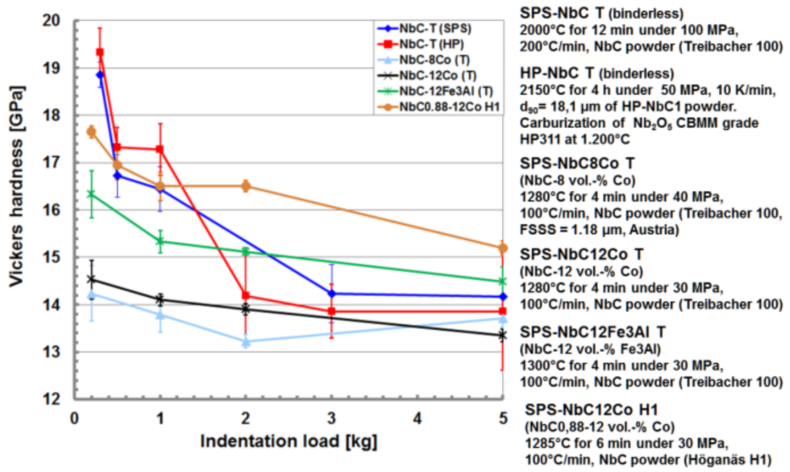

Figure 3 Micro-hardness as function of indentation load for binderless and metal bonded NbC hard metal grades

RESULTS AND DISCUSSIONS

-Properties

The evolution of moduli in Figure 2 is for NbCs less dependent from temperature and can be tailored through stoichiometry. The sub-stoichiometry reduced the elastic modulus of $NbC_{0.88}$-12Co H1 by ~7%.The micro-hardness can be tailored by the stoichiometry and the type on binder. Overall, the NbC bonded by the intermetallic phase Fe_3Al had a significantly higher hardness at any indentation load than the cobalt-bonded homologues (see Figure **3**). The use of sub-stoichiometric NbC_x and Fe_3Al increased the micro-hardness of the NbC based hardmetal. The hot hardness is also of great importance for cutting. The drop in hot hardness is less pronounced for NbC grades than for WC grades. At 700°C, the NbC-12Co T presented the same hardness as the WC grades. The evolution of micro-hardness (See Figure **4**) of the sub-stoichiometric $NbC_{0.88}$-12Co H1 was parallel to the WC grades, whereas above 700°C, $NbC_{0.88}$-12Co H1 had a higher hardness.

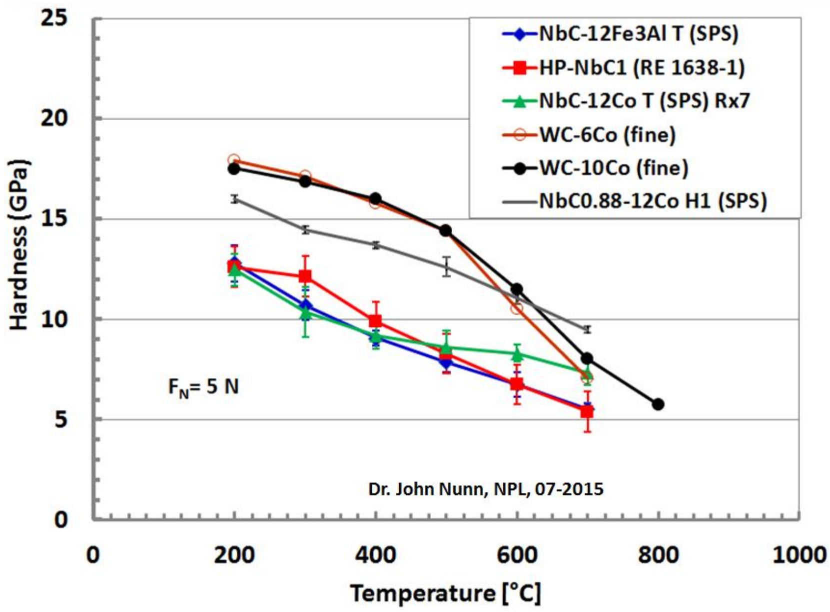

Figure 4 Micro-hardness as function of temperature for metal bonded NbC hard metal grades

-Wear resistance in closed tribosystems

The tribometers for unidirectional sliding are proprietary developments of BAM and the details are disclosed elsewhere [4]. Total wear rate is the sum of both specimen. As shown in Figure 5, the RT wear rates of the MMC Fe_3Al-$NbC_{0,94}$ are slightly higher than those of the NbC-bearing hardmetals and for all NbC grades the wear rates decreased with increasing sliding speed, what is beneficial for cutting applications. It is also apparent, that metallurgically synthesized or sintered NbC bearing materials tribologically compete with WC and Cr_3C_2 bearing hardmetals or cermets. The wear resistance of Co- and Fe_3Al-bonded NbC hard metals is highest at RT and high sliding velocities. The low solubility of NbC in alloys in association with the wear resistance enables casted MMCs with a high hard phase content. These casted MMCs give a high freedom in design (size, geometry) of wear resistant components, in comparison to sintered hard metals or ceramics.

At 400°C, the cobalt bonded NbCs presented lower wear rates than the NbCs bonded with Fe_3Al or having such a matrix, because of the well-known effect of Co_3O_4 formed by tribo-oxidation lowering the wear rate [5]. Basically, the wear particles from the wear tracks displayed in Figure 6 were wiped away. The microstructure of the matrix and NbC is still clearly visible and nor grain pull-out or fragmentation of NbC grains became predominant. The metallurgical interphase NbC-matrix withstands shear and NbC didn´t fragment (See Figure **6**).

The wear resistance of niobium carbide is determined by different material properties:

a. First, NbC has a very high melting point of 3,522°C, whereas WC melts at ~2.870°C

b. Tribo-oxidatively formed Nb_2O_5 melts at 1,512°C, whereas WO_3 tends to sublimate above 750-800°C and WC looses its tribo-oxidative wear protection. Nb_2O_5 is with 500-650 HV0.2 not so soft.

c. The elastic moduli and hardnesses of NbC are quite stable with increasing temperature as well as can be tailored through stoichiometry. The micro-hardness and hot hardness can tailored exceed those from WC.

d. It was recently shown, that reduced $Nb_{12}O_{29}$ contributes to the wear resistance of NbC [6], especially at high sliding speeds at RT, where the wear rate of $Nb_{12}O_{29}$ at 7 m/s of k_v= 4.9 10^{-6}

mm³/N·m is close to that of NbC-based cermets in Figure 5.

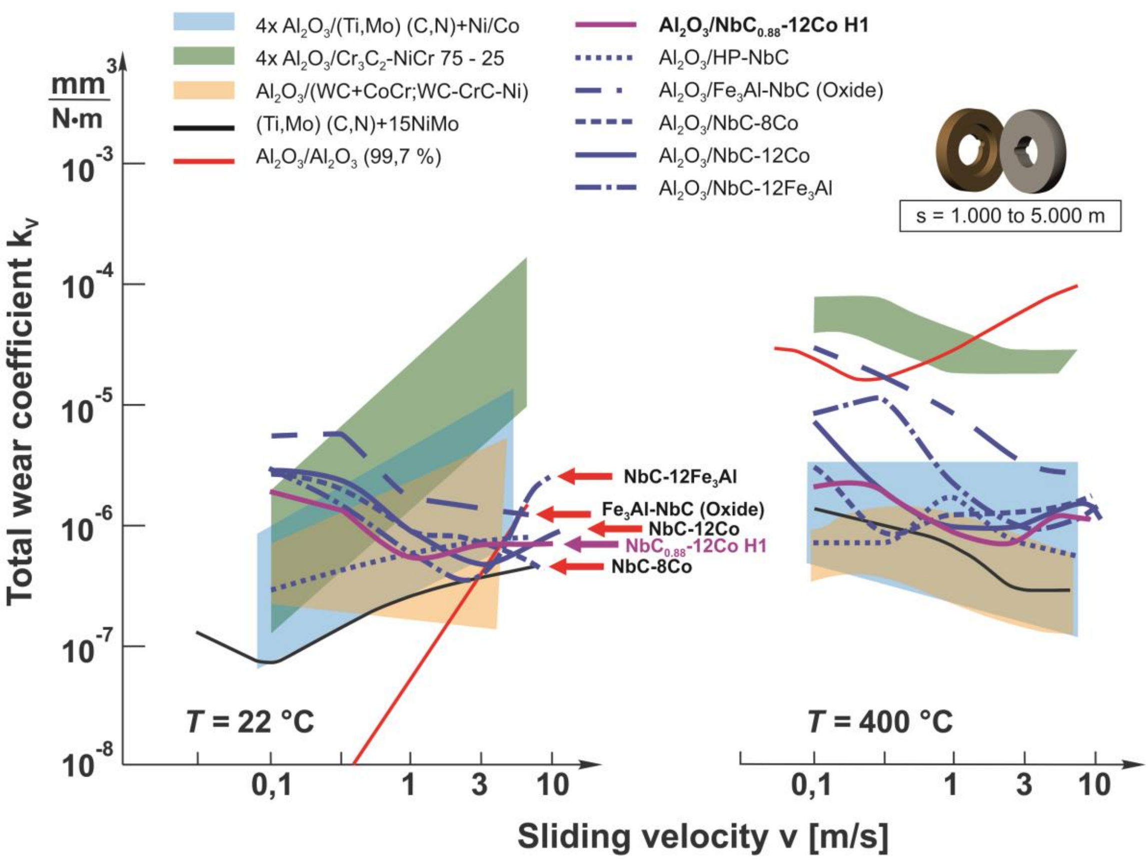

Figure 5 Total wear coefficients of cobalt or Fe_3Al bonded NbCs and Fe_3Al-NbC (MMC) compared to different ceramics and hard metals under dry friction

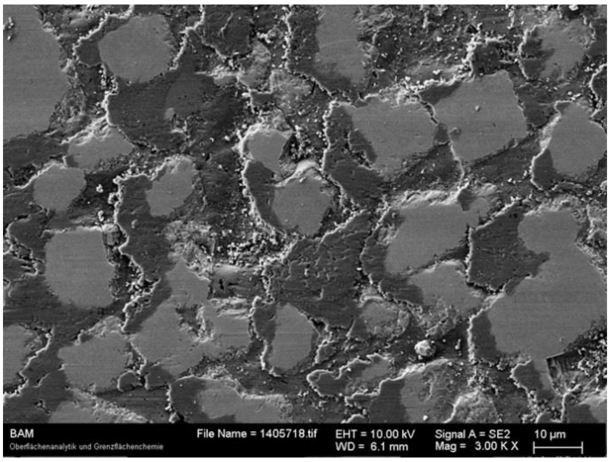

Figure 6 Morphology of wear tracks at 22°C (Fe_3Al-NbC, AD5258, (counter body: 99,7% alumina; v= 1 m/s, s= 5.000 m (or 50.000 cycles), P_{0max}= ~1020 MPa)

Figure **7** displays the load carrying capacity expressed as P·V values (contact pressure times sliding velocity). For all NbC grades P·V increased at room temperature from 1-2 MPa·m/s at 0,1 m/s up to 100 MPa·m/s at 8,0 m/s, because tribo-oxidation of NbC to different polytypes of Nb_2O_5 was enhanced with increasing sliding speed (or generated frictional heat) and a stable, non-volatile Nb_2O_5 was formed. In contrast at 400°C, the P·V values ranged more or less on the same level as at RT. The NbC grades illuminated a high wear resistance under dry sliding associated with exceptional load carrying capacity. Normally, P·V values of dry sliding tribo-couples decrease with increasing sliding speed [7]. The triboactive materials [8,9] like $Ti_{n-2}Cr_2O_{2n-1}$-phases, (Ti,Mo)(C,N) are coming close to NbC-based materials having slightly lower P·V values or maximum frictional heat flows.

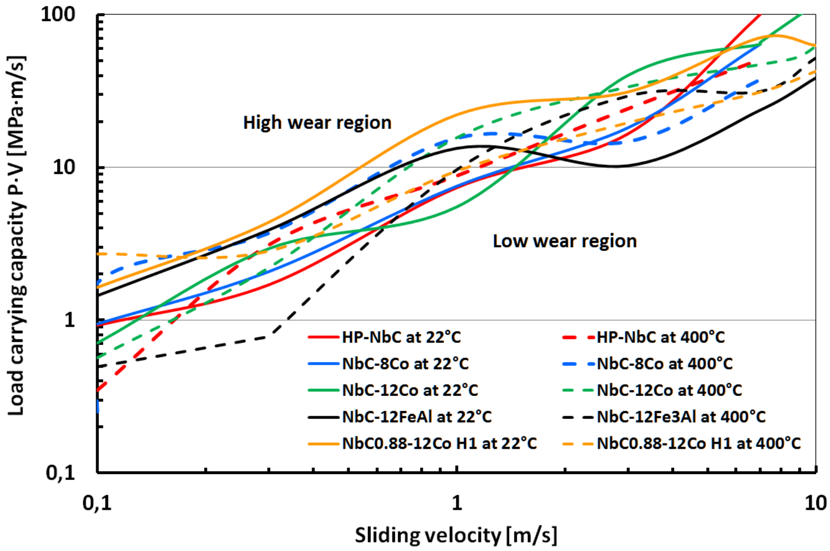

Figure 7 Load carrying capacity (maximum frictional power loss) of NbC-based materials as function of sliding speed under dry sliding conditions at room temperature and 400°C

-Cutting

Cutting tests of inserts in SNMA geometry are presented in Figure 8 and Figure 9 [10]. In semi-finishing with an emulsion under 10 bar, the NbC inserts have a very good strength. The NbC-12Fe_3Al (SPS) insert is less sensitive to sticking of machined material [10]. The comparison of the flank wear and the crater wear is shown in Figure 8 for WC-6%Co and NbC-12%Fe_3Al. The flank wear is until 50% of the turning distance parallel between both. The advantages in flank wear of the WC-6%Co insert can be explained by its (Ti,Al)N coating applied on the WC-6%Co insert. The crater wear was even 3 times greater for the WC-6%Co than for the NbC-12%Fe_3Al after only 1 minute of machining. These results show that uncoated NbC inserts exhibit a higher resistance to abrasive wear than coated WC inserts. The low solubility of NbC in alloys and its stable hot hardness determines the high wear resistance of NbC inserts.

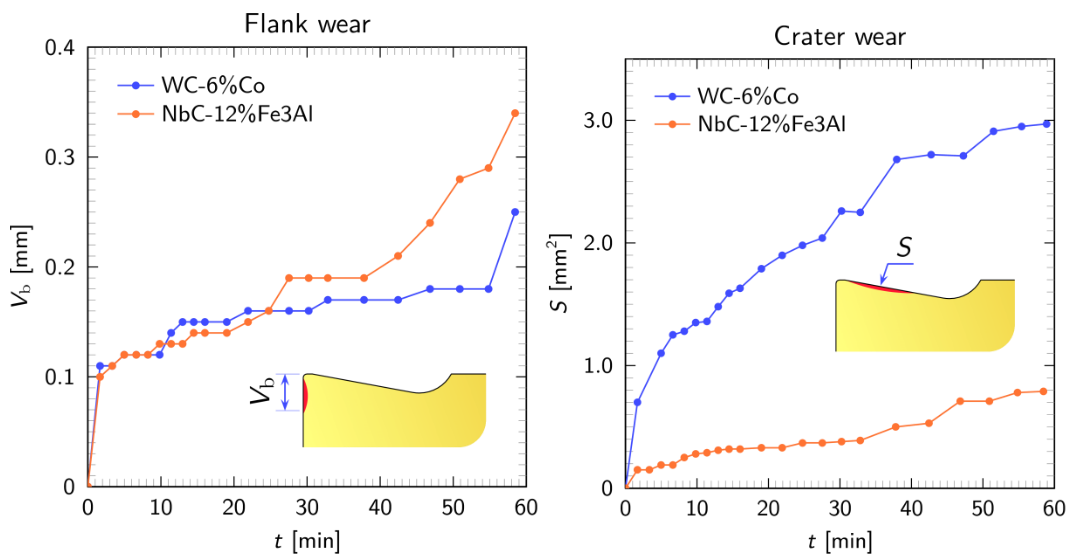

Figure 8 Comparison of the flank wear (left) and the crater wear (right) between the WC-6%Co insert and the NbC-12%Fe_3Al insert for the semi-finishing tests (100Cr6 205 HB, Vc =100 m/min, hex.= 0,2 mm, DoC = 1,5 mm, 10 bars emulsion, lead angle at 75°, nose radius 0,8 mm) [10]

In hard turning with an emulsion under 10 bar, the cratering for the WC insert is substantial, while the flank wear remains acceptable as shown in Figure 9. In contrast, for the uncoated NbC insert, the wear on flank wear and cratering (See Figure **9**) remained acceptable. The initial machining striae from the edge preparation are still visible indicating a very low crater wear. On the other hand, after about five minutes of hard turning, a crack appeared from released residual stresses generated during SPS sintering.

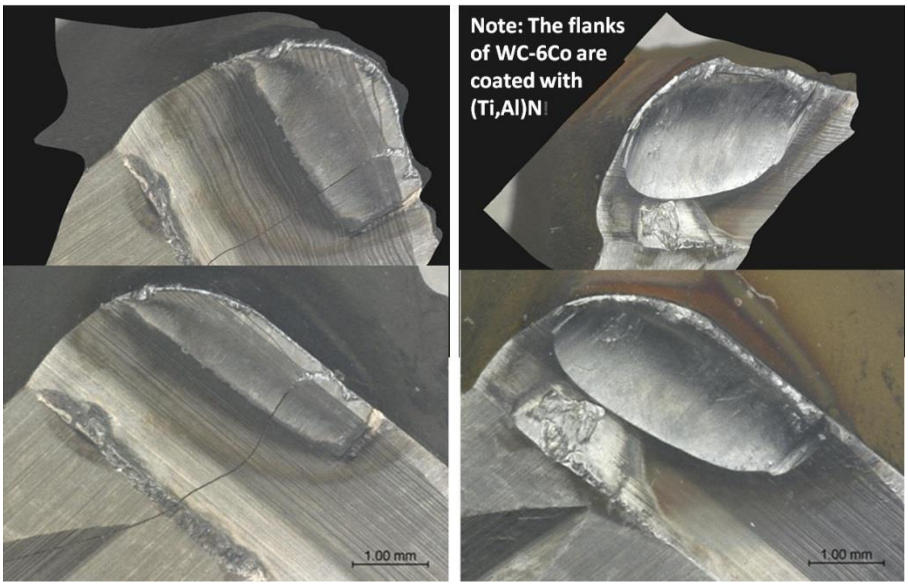

Figure 9 Comparison of crater wear in hard turning of NbC-8Co SPS (left) and WC-6Co (right) (100Cr6 (205 HB), machining time= 5 min. 33 s., Vc= 100 m/min, f = 0,415 mm/rev, hex= 0,4, DoC = 3 mm, Kr (lead angle) = 75°, nose radius= 1,5 mm, emulsion 10 bars) [10]

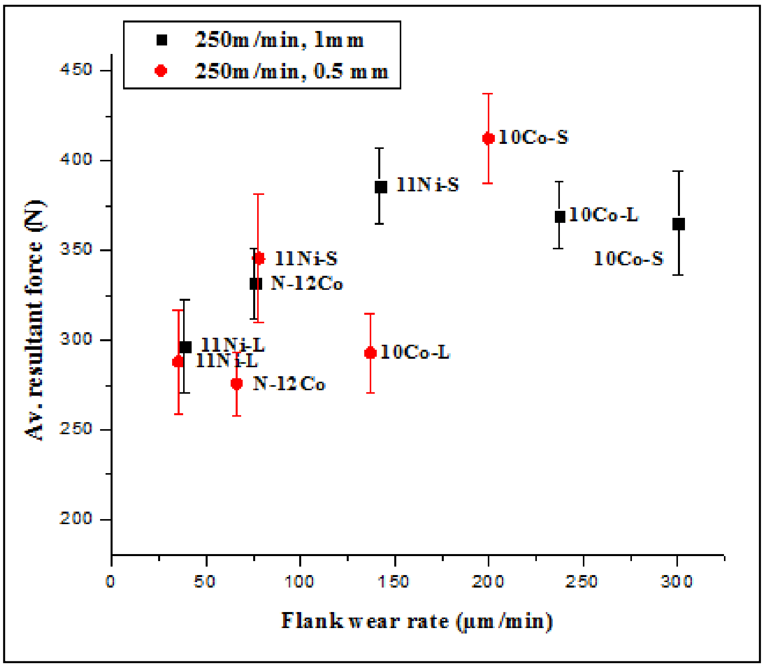

Figure 10 Comparison of insert behaviour during coolant-free interrupted milling of SABS 1431:300WA-SS (98,2 ± 0,66 HRC) at v_c = 250 m/min (a_p = 0,5/1 mm) [11]

Effect of reduction of axial depth of cut a_p from 1 mm to 0.5 mm at a v_c of 250 m/min in coolant-free interrupted milling of uncoated SNMA inserts is shown in Figure 10. During coolant-free milling at 250 m/min, the NbC-12Co SPS insert performed better than both the SPS and LPS WC-10Co (wt%) [11]. It has to be noted, that the N-12Co (NbC-12Co) presented an attractive profile with low friction and flank wear rates, which compete with nickel bonded WC. The nickel bonded WC grades (7Ni and 11Ni) contained secondary carbides, like TiC and Mo_2C, which improved the resistance to chemical wear, whereas the NbC-12Co were straight grades without secondary carbides.

CONCLUSIONS

Stoichiometric or sub-stoichiometric niobium carbides have under dry sliding at RT and 400°C a pronounced intrinsic wear resistance associated with an exceptional high load carrying capacity, either as hard metal or as metal matrix composite. The wear rates decreased with increasing sliding speed and were associated with high load carrying capacities (P·V-values), in excess of 100 MPa·m/s. Tribological properties, micro-hardness and elastic modulus can be tailored through stoichiometry and/or binder type. The dry sliding wear resistance of the sub-stoichiometric $NbC_{0.88}$-12Co H1 were at the lower end of the stochiometric NbC grades. From the tribological point of view, the cobalt binder in the NbC hardmetals can be substituted by Fe_3Al. At RT, the wear rates of the MMC Fe_3Al-$NbC_{0,94}$ are very close to those of the NbC-bearing hard metals.Cobalt-free niobium carbide inserts have been shown to be very efficient for semi-finishing operations and are very promising under hard turning. Properties, like micro-hardness, hot hardness, sliding wear resistance, elastic modulus and toughness can be tailored by the C/Nb ratio, the addition of secondary carbides and the type of binder.

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