THE TRIBOLOGICAL PROPERTY PROFILE OF HARD METALS AND METAL MATRIX COMPOSITES BASED ON NIOBIUM CARBIDE

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Abstract

The term “tribology” relates to the friction and wear behavior of materials, as well as their lubrication, and is essentially a system property involving the material itself, the counterbody material, operating condition stresses and also environmental conditions. Hard metals have been used extensively under typical tribological conditions encountered in the mining and processing industry with the intention of increasing lifetime and performance of components. The typical and well-established hard metal is WC-Co and its modifications, which have been developed over the last several decades and are used in a vast range of applications. In contrast surprisingly little work has been done on niobium carbide (NbC) based hard metal, despite repeated indications that this material should have very favorable tribological properties. Therefore, an extensive research program has been initiated firstly to identify the intrinsic properties of NbC and their influencing factors and secondly to develop hard metal, as well as metal matrix composite (MMC) materials, based on NbC. This work is focused on the tribological profile of NbC-based materials, as well as their potential applications and environmental implications.

Microhardness and elastic properties depend on the C/Nb ratio. At room temperature hard metals of stoichiometric niobium carbide ($NbC_{1.0}$) have an elastic modulus of around 440 GPa. Those of under-stoichiometric niobium carbide ($NbC_{0.88}$) have an elastic modulus of around 405 GPa while melt grown $NbC_{0.70}$ shows an elastic modulus of approximately 365 GPa. The microhardness, however, increases with decreasing C/Nb ratio. Stoichiometric and sub-stoichiometric NbC possess a pronounced intrinsic wear resistance, either as hard metal or as a hard phase in metal matrix composites.

Some of the recent activities have focused on the tribological behavior of Fe_3Al-NbC metal matrix composites prepared by pyro-metallurgical synthesis. It is compared to different Spark Plasma Sintered (SPS) NbC-based hard metals bonded by cobalt or Fe_3Al under dry sliding conditions. The wear resistance under dry sliding conditions of the present Fe_3Al-NbC, containing about 60 volume percent NbC, is shown to be close to that of NbC-based hard metals. No particle extraction or fragmentation of the NbC particles was seen in the wear tracks of the Fe_3Al-NbC composite, as a metallurgical interface was formed between the matrix and NbC grains. The physical properties of melt-grown NbC match those observed in sintered material originating from NbC powder converted from Nb_2O_5 by carbo-thermal reduction.

Introduction

Wear is defined as the irreversible, gradual and progressive loss of material due to the relative motion between the active body and a counterbody. Several basic principles can be involved in removing material from the surface: material can be disintegrated (fatigue) and detached mechanically (ploughing) or by tribo-chemical reactions occurring at the surface. Wear resistance of a material is a system property and not an inherent material property. It is controlled by a multitude of parameters consisting of material and counterbody properties, contact stresses and the environment.

The significant downtime and cost implications related to wear of components in earth moving and mining equipment, as well as in the materials processing industry, represents a continual challenge to material development. Components designed for sacrificial wear must possess, first of all, adequate abrasion resistance associated with impact loads and corrosive media. The requirement of good abrasion resistance, in combination with good toughness, is generally rather restrictive since, unfortunately, materials hard enough to resist wear are often found to be brittle. Therefore, a composite material, embedding the hard phase in a softer but ductile matrix, has the potential of offering a good property compromise. Such materials, depending on the combination of hard phase and matrix type, as well as their volume fractions, are known as hard metals, cermets or metal matrix composites (MMC).

Carbides of the transition metals, represented by groups IVB to VIB in the periodic table of elements, are typically used as hard phases in technical alloys. The hardness of these transition metal carbides is superior to that of most minerals, Figure 1. Metals with a high melting point, such as cobalt, nickel or molybdenum, can serve as ductile binders for hard metals and cermets. Casting alloys containing dispersed hard phase particles provide the platform for a wide variety of metal matrix composites.

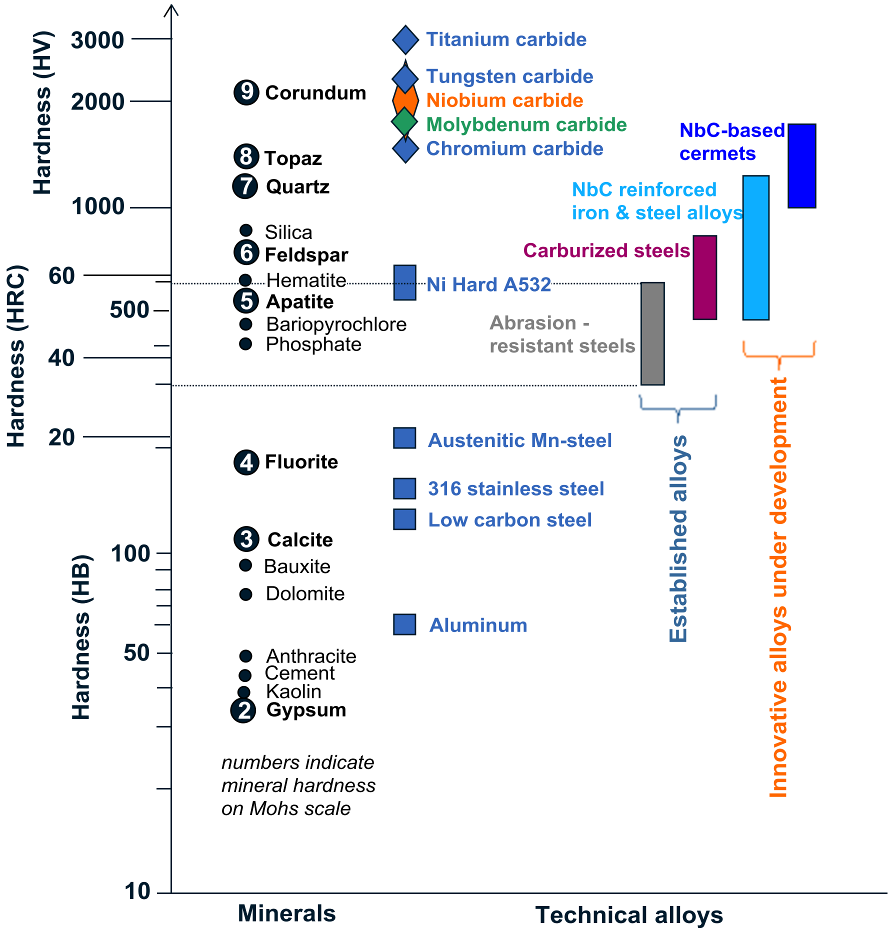


Figure 1. Hardness of mineral species compared to hardness of technical alloys.

In the arena of hard metals, tungsten carbide (WC) has been the dominating hard phase for decades. Other transition metal carbides, such as those of chromium, vanadium and titanium, are also well established. However, surprisingly, little attention has been paid to NbC. Nevertheless, NbC has been occasionally used as a minority phase in hard metals, castings and tool steels. In these applications it serves either as a grain refiner or as a hard phase helping to enhance wear resistance, limit grain growth and enhance hot hardness. While data on the fundamental properties of pure NbC have been reported [1], reliable information on its tribological performance was not readily available. Recently, it was shown however, that pure NbC and metal bonded NbC, have a pronounced wear resistance under dry sliding when compared to other monolithic ceramics and carbides [2].

Hard metals based on tungsten carbide are mainly produced by a powder metallurgy (PM) based sintering process due to the high solubility of the hard phase in alloys and in their melts, as well as the mismatch in density between the molten binder alloys and the hard phase. Cobalt and nickel primarily serve as the binder phase. The powder metallurgical route, however, limits the size of components, whereas a casting process would allow the fabrication of much bigger components. Alternatively, hard metals can be deposited as clad layers or thermally sprayed coatings onto a softer substrate material. Two well known properties of NbC are its similar density to and its low solubility in iron. The density of NbC is very close to that of iron so that the mismatch in densities, depending on the carbide stoichiometry and iron alloy composition, is less than 10 percent. Its solubility in iron-based alloys, as well as in nickel and cobalt, is particularly small. Utilizing these two properties makes alternative production routes feasible for producing components as compared to PM-based processing routes.

Material health and safety issues with established hard metals have recently caused significant concerns. The European "Registration, Evaluation, Authorisation and Restriction of Chemical substances programme", also known under the acronym REACH [3], currently classifies cobalt as very toxic for human health. Furthermore, the U.S. National Toxicology Program, (NTP) [4], states that tungsten carbide-cobalt hard metal dust was shown to be more toxic in combination than either pure cobalt or tungsten carbide alone. So far, nickel powders do not have the same hazardous classification as cobalt powders. Niobium, on the contrary, is known to be one of the most biocompatible metals. No particular hazards or critical notifications for its oxide (Nb_2O_5) and carbide (NbC) were filed in the framework of REACH.

Based on the considerations outlined above, CBMM initiated an extensive research and development program with the aim of exploring the potential of NbC-based hard metals and alloys. The following specific activities have been defined within the program:

- Production and property characterization of pure NbC and its sub-stoichiometric variants (NbC_{1-x}), including consideration of the effect of particle size;
- Analysis of various binder materials and processing routes for NbC-based hard metals and characterization of their microstructure, mechanical properties and performance;
- Exploration of processing routes for NbC-based MMC materials, as well as NbC particle reinforced castings and their performance;
- Characterization and benchmarking of the tribological property profile of such NbC-based materials;
- Field trials with components made from such NbC-based materials in various applications.

In the present paper several results emanating from this ongoing program are presented with particular attention to the tribological property profile of NbC and NbC-based materials.

Methods of NbC Synthesis

NbC can be synthesized by various practical methods, of which three are considered here. One method is the carbo-thermal reduction of pure niobium oxide (Nb_2O_5) at elevated temperature (>800 °C) by the solid-state reaction:

$$Nb_2O_5 + 7 \cdot C = 2 \cdot NbC + 5 \cdot CO(g) \tag{1}$$

Reaction (1) does not represent the actual steady state reaction, since the reduction process is controlled by a gas-solid phase reaction (2) involving the so-called Boudouard reaction (3) as an intermediate step:

$$Nb_2O_5 + 9 \cdot CO(g) = 2 \cdot NbC + 7 \cdot CO_2(g) \tag{2}$$

$$7 \cdot CO_2(g) + 7 \cdot C = 14 \cdot CO(g) \tag{3}$$

Thermodynamic data indicate that reaction (2) is feasible at temperatures higher than 1000 °C. However, experiments indicated that for a complete conversion of Nb_2O_5 to oxide-free NbC, reaction temperatures of at least 1200 °C must be applied. Since NbC oxidizes rapidly at temperatures above 480 °C the reaction atmosphere must be oxygen-free. An inert and reducing atmosphere of 95%N_2 + 5%H_2 was found to be practicable.

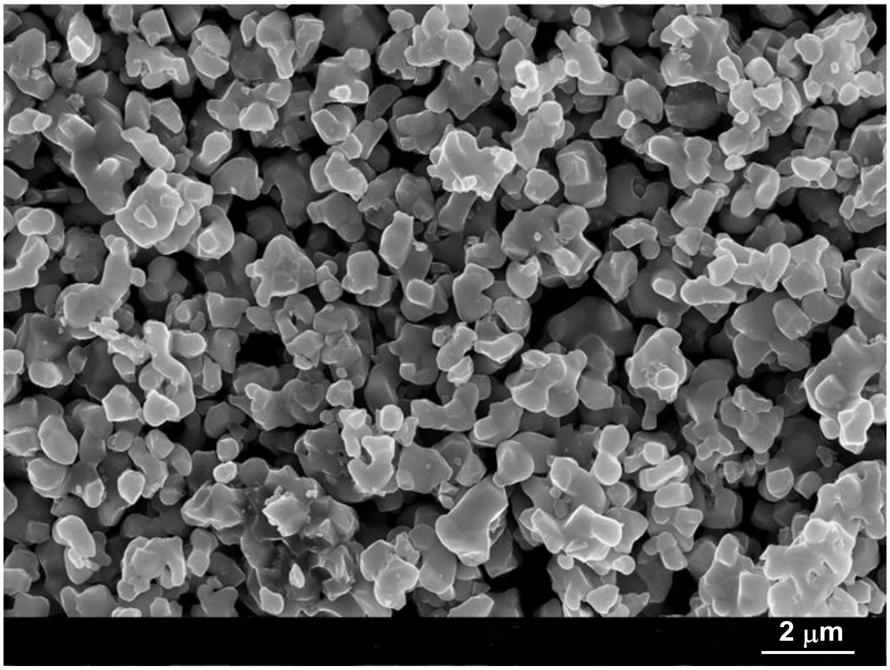


Figure 2. Morphology of NbC crystallites obtained by carbo-thermal reduction of CBMM's high purity Nb_2O_5 powder (de-agglomerated).

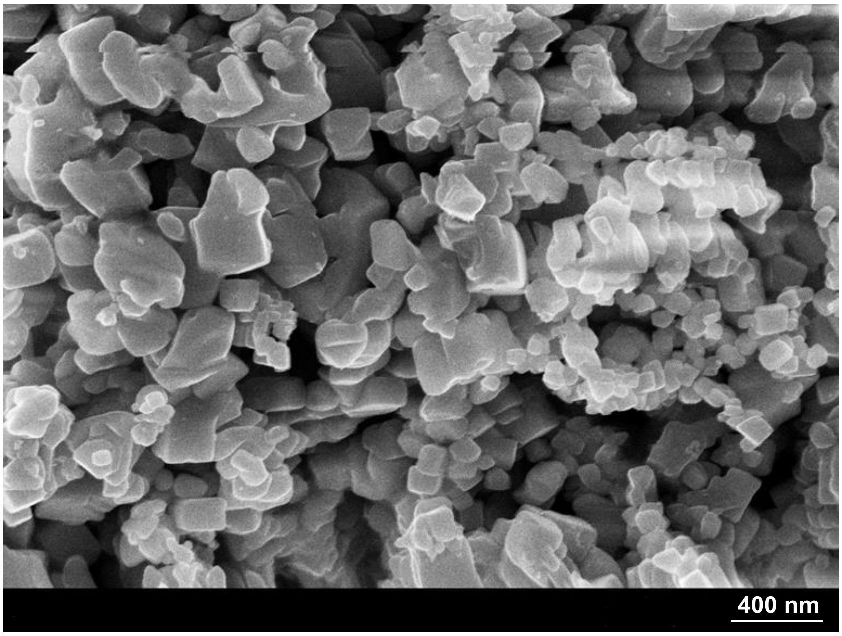


Figure 3. Agglomerated NbC crystallites after carbo-thermal reduction of CBMM's high purity Nb_2O_5 (used for $NbC_{0.88}$-12Co (H1)).

CBMM has a substantial production capacity for Nb_2O_5 powder that could be readily used in the above described process. Industrial trials utilizing converters that have been previously used for tungsten carbide synthesis demonstrated that stoichiometric NbC could be produced in a one-step carbo-thermal reduction, with high productivity. Thermal carbon black serves as the carbon supply in this process. Representative NbC powders have been synthesized from CBMM Nb_2O_5 powder, using the carbo-thermal reduction process described above, at two industrial powder manufacturers. The primary grain size of the NbC crystallites is in the sub-micron range (100 – 600 nm) reflecting the original oxide crystallite size, Figure 2. The NbC crystallites are agglomerated to larger particles, Figure 3, which can be broken down by an appropriate milling process after carbo-thermal reduction. XRD analysis indicated that these powders consisted of pure NbC, ie. without traces of residual oxides or free carbon.

A second method of producing NbC is by adding ferroniobium to an iron melt containing a substantial amount of carbon. Primary NbC is then precipitated as a solid phase in the liquid metal due to the very low solubility of NbC in iron. At the solidification temperature for eutectic iron (Fe-4.3%C), only around 0.1%Nb is soluble. At usual casting temperatures, the soluble amount of niobium increases to approximately 0.5%, suggesting that NbC particle reinforced iron alloys and MMCs can be produced directly by such in-situ carbide formation. A problem known to occur with this procedure is that in-situ formed carbide particles can grow to a large size with a branched morphology, thus having a detrimental effect on the toughness of the material [5]. On the other hand, large sized hard phases are beneficial in resisting severe abrasion.

As an alternative, CBMM developed an innovative ferroalloy containing a high amount of primary NbC, comprising a controlled size and compact morphology. The production route is based on the standard alumino-thermic reduction process utilized for ferroniobium production. Yet, by adding a carbon source directly to this process, primary precipitation of NbC occurs into an iron matrix instead of forming FeNb intermetallic phases, Figure 4. The carbide particles being formed in this process have sizes in the range of 10 to 50 µm and are of cubic morphology, Figure 5. At the current development stage, the volume fraction of NbC phase embedded in an iron matrix is around 60 percent. This ferroalloy can be directly added to an iron melt for producing iron-based alloys containing a lower volume fraction of dispersed carbide particles. On the other hand, the Fe-NbC ferroalloy, in particular after further increasing the carbide volume fraction, can serve as a source of pure carbide supply (melt grown NbC). In this process, the iron matrix is dissolved from the ferroalloy by a leaching process using either hydrochloric or sulfuric acid, Figure 5.

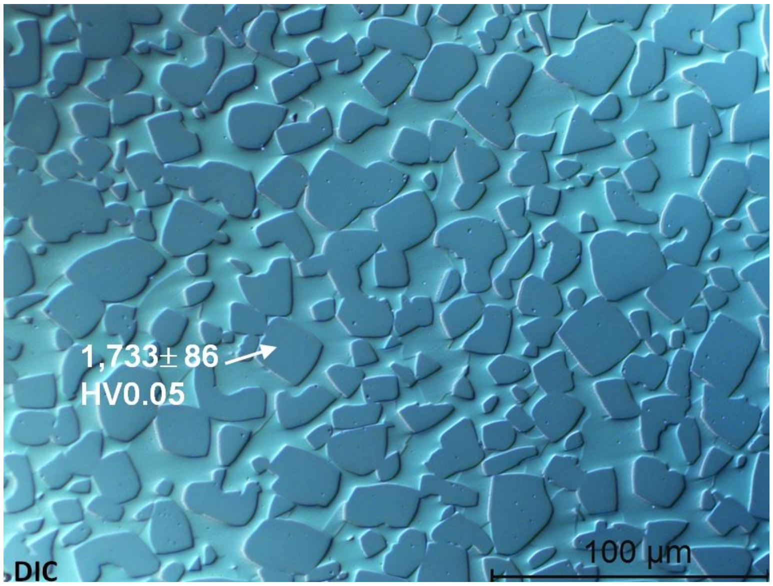


Figure 4. NbC particles formed by primary precipitation in a carbon-alloyed iron melt.

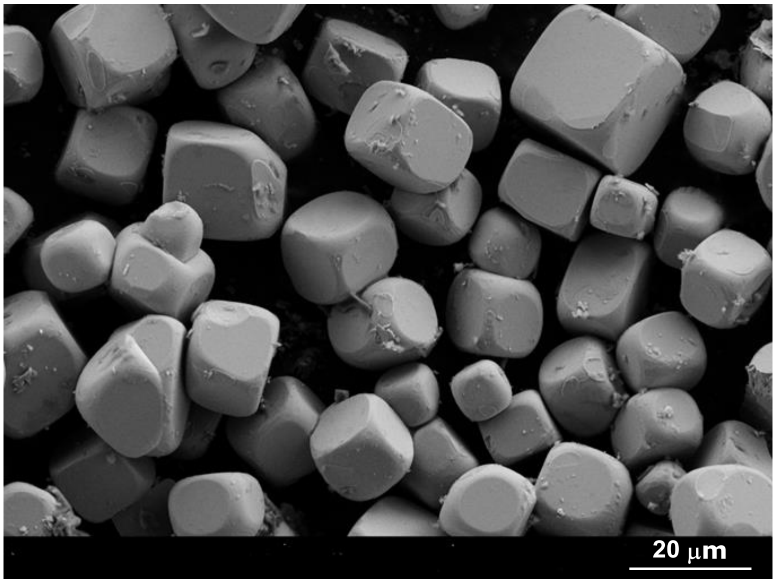


Figure 5. NbC particles precipitated in liquid iron after chemical leaching by sulfuric acid.

Basic Properties of NbC

The use of NbC as a hard material is much less established than that of tungsten carbide. Nevertheless, its physical and chemical properties indicate the outstanding potential of NbC for applications where currently tungsten carbide is being used as the standard material. Table I shows some of the key physical properties referring to room temperature measurements of stoichiometric NbC in comparison to those of tungsten carbide as published in the literature [1]. The melting temperature of NbC is particularly high, which is expected to limit thermal softening, as well as the tendency for adhesive wear. Data obtained by Kelly et al. [6] indicated that the yield strength of NbC at temperatures above 1000 °C is substantially higher than that of WC. The density of NbC is only about half that of WC. This means that for producing a given component only half the mass of carbide is needed, making the use of NbC potentially economically attractive. In dynamic applications where high accelerations and speeds are involved, the reduced mass results in lower inertia and kinetic energy. Since the density of NbC is very close to that of iron, gravity segregation should be rather low when dispersing solid NbC particles in melts of iron-based alloys. This, likewise, applies for spin casting processes where higher density particles segregate outwards and lighter density particles segregate inwards.

The Young's modulus of NbC is one of the highest amongst the refractory metal carbides, yet lower than that of WC. Hence, components made with NbC will show a somewhat higher elastic deflection under mechanical loading, compared to WC. On the other hand, contact stresses under a given load will be lower in NbC. Thermal stresses induced between NbC and metallic binder alloys can also be expected to be lower than for WC. This is because of the larger coefficient of thermal expansion which is closer to that of typical metallic binders, as well as to the lower Young's modulus of NbC.

Due to its metallic character, NbC has relatively good thermal and electrical conductivity. Its thermal conductivity increases at elevated temperatures. Frictional heat generated in tribological contacts can thus be efficiently conducted away. The reasonably good electrical conductivity allows processing of NbC by, for example, electrical discharge machining (EDM). It also helps avoid the build-up of substantial static electricity in tribo-contacts with electrical insulators, such as for instance, polymer-based composites.

Table I. Comparison of Basic Physical Properties of Niobium and Tungsten Carbide Published in the Literature [1]

	Melting point (°C)	**Density (kg/m^3)**	**Young's modulus (GPa)**	**Shear modulus (GPa)**	**Vickers hardness (GPa)**	**CTE (ppm/K)**	**Thermal conductivity (W/m.K)**	**Specific heat (J/g·K)**	**Electrical resistivity (μΩ·cm)**
NbC	3,520	7,780	380-480	214	17-22	6.6	14	0.351	35
WC	2,870	15,630	620-720	262	24-30	5.5	84	0.203	20

One of the most crucial properties with respect to wear resistant applications is the material hardness. From literature data and current experience, it is evident that the hardness of stoichiometric NbC is below that of tungsten carbide, Table I. However, its hardness is still far superior to most minerals and technical alloys, Figure 1, so that sufficient resistance against abrasive wear in such tribo-contacts should be available. On the other hand, finishing operations when manufacturing NbC tools, are expected to be easier than those for tungsten carbide tools.

The exact hardness value of these carbides is influenced by several parameters, such as the level of porosity, indentation load [7] and temperature [8,9]. An increase in each of these parameters results in a decrease of the measured hardness value. Considering the temperature dependence of hardness, a two-stage behavior can be observed. In the lower temperature range, hardness decreases moderately with increasing temperature. In the higher temperature range, this decrease becomes significantly steeper. The transition between the two regimes occurs in the temperature interval of 500-800 °C for WC [8]. NbC exhibits this transition at a higher temperature interval at around 900 °C [10]. This can result in a higher hot-hardness of NbC as compared to WC, which is of relevance for metal cutting operations. Recent hot-hardness measurements on NbC- and WC-based materials confirm this trend [11].

Contrary to WC, NbC can exist as sub-carbides, like Nb_6C_5 or Nb_4C_3, over a wide range of carbon stoichiometry, according to the Nb-C binary phase diagram shown in Figure 6 [12]. Carbon deficiency in the range of NbC to $NbC_{0.8}$ has a significant influence on the physical properties of the material. With increasing carbon deficiency in that range, elastic moduli [13], lattice constant [14], density [14], heat capacity [15] and magnetic susceptibility [16] decrease. Yet, hardness strongly increases with increasing carbon deficiency in NbC, as shown in Figure 7, [17] exceeding the hardness level of WC. In summary, the properties of NbC can be tailored by adjusting the carbon deficiency in the compound.

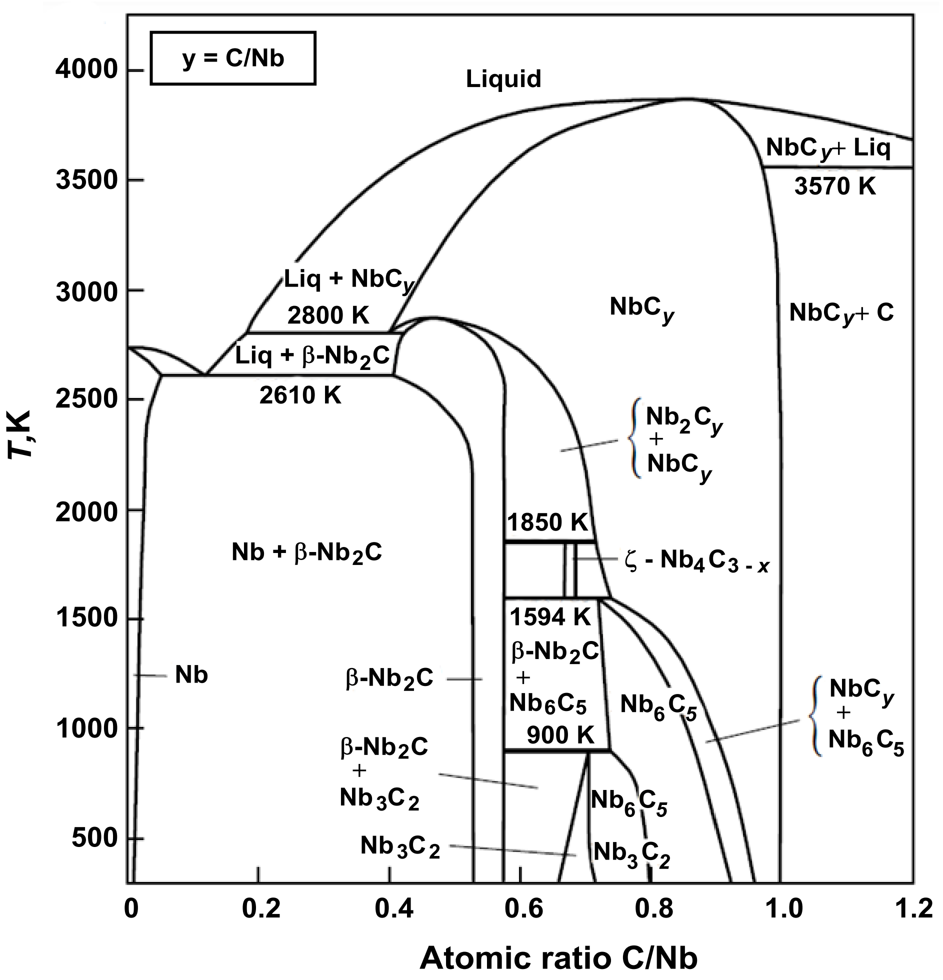


Figure 6. Binary Nb-C phase diagram indicating the existence of various sub-carbides [12].

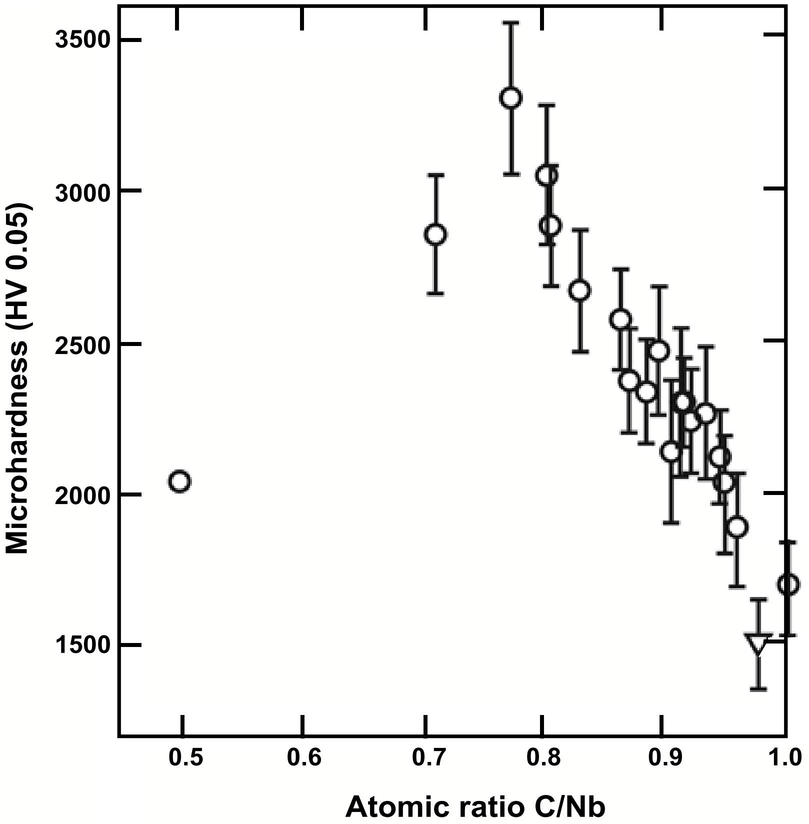


Figure 7. Microhardness of NbC as a function of C/Nb ratio in the compound [17].

The solubility of a carbide compound in a contacting metal at high temperature is a very important property with respect to the wear performance of the carbide in such hot tribo-contacts with that metal. The solubility of NbC in metals, such as iron, cobalt or nickel has been reported to be very low in contrast to the rather high solubility of tungsten carbides in these metals [18,19]. The solubility of NbC in austenite is shown in Figure 8, based on an established solubility product [20]. In this plot, equilibrium solubility isotherms of niobium and carbon are indicated for various temperatures. Only when the carbon content is extremely low, does niobium have a reasonably good solubility. In a hot tribo-contact scenario, NbC should dissociate into solute niobium and carbon according to the stoichiometric ratio. The intersection of the stoichiometry line with the solubility isotherm defines the maximum solubility of NbC in a tribo-contact situation at that specific temperature. Carbon, already present in an iron-based alloy, further limits the solubility of NbC to extremely low values. The solubility of tungsten carbide in austenite is several orders of magnitude larger than that of NbC [21]. Accordingly, WC-based components bear the risk of readily dissolving into iron-based alloys in hot tribo-contacts, whereas NbC-based tools will suffer very limited material loss by dissolution into the chips under the same conditions. Consequently, a protective coating, blocking the dissolution, is not necessary on NbC components.

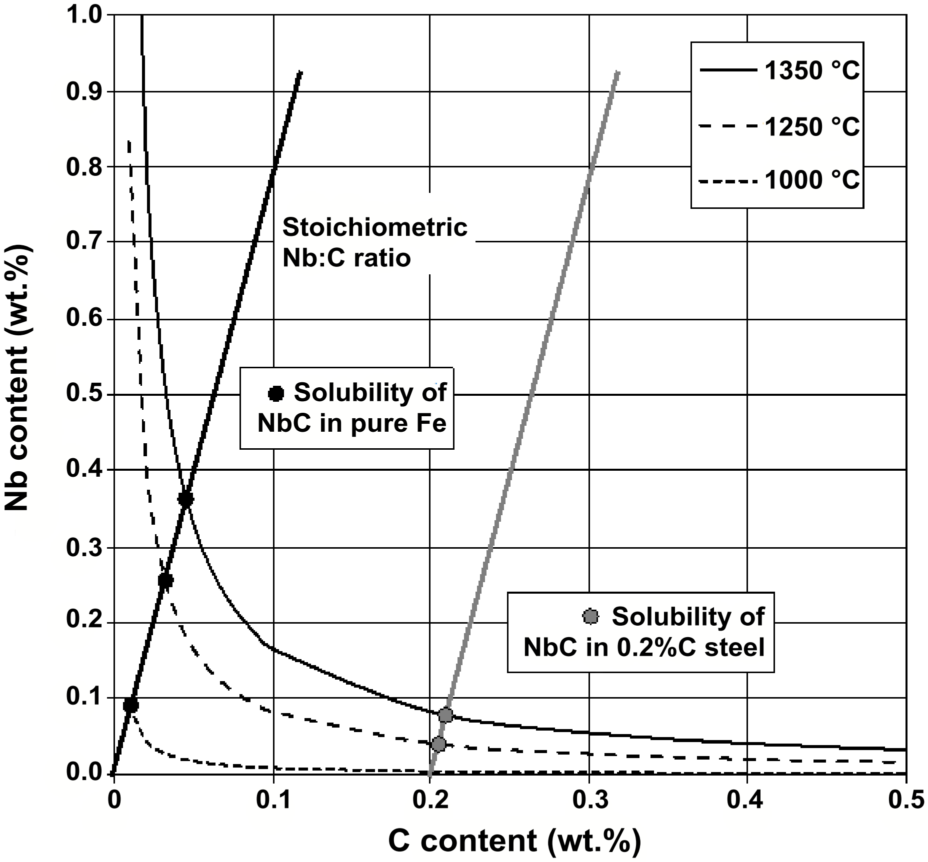


Figure 8. Solubility of NbC in austenite based on the solubility product log [Nb][C] = 3.4 – 7920/T where T is the absolute temperature; [Nb] and [C] are concentrations in wt.% [20].

Another chemical reaction that can lead to material loss in tribo-contacts is tribo-chemical or oxidative wear. The frictional work dissipated in the micro-asperities (hot spot temperatures) enhances this reaction with the surrounding atmosphere. Oxide layers form on the surfaces of the friction partners and are worn away as a result of relative movements between the bodies leaving oxide debris in, or close to, the wear track. NbC oxidizes when exposed to air at increased temperature, forming Nb_2O_5 and other block structure oxides ($Nb_{3n+1}O_{8n-2}$). The rate of oxidation increases significantly above 500 °C. However, the oxide does not form a passivating and protective layer. Nb_2O_5 and its polymorphs are also generated by tribo-oxidation on NbC and influence the friction and wear behavior, as well as having a microhardness in the range 500-650 HV 0.2. Tungsten carbide easily oxidizes, even in low energy tribo-contacts operated in an ambient environment [22], forming amorphous tungsten oxide debris, which tends to sublimate at temperatures above 800 °C. In contrast, Nb_2O_5, owing to its melting point of 1522 °C, forms a stable reaction layer on NbC.

Definition of NbC-based Materials for Tribological Performance Testing

Pure NbC

Although NbC is not likely to be used binderless for technical applications, it is still important to characterize the tribological performance of the pure material without having side effects from other constituents. Therefore, NbC was produced from a commercially available high purity niobium pentoxide (Nb_2O_5) powder (CBMM grade HP311) by the process described above [2]. The granulometry of the NbC powder was $d_{50} = 3.86$ µm and $d_{90} = 18.12$ µm. This powder was then hot-pressed by Fraunhofer IKTS (Dresden, Germany) without the use of sintering additives at 2150 °C under 50 MPa (4 h, 10 K/min) reaching an average density of 7.68 g/cm³. The microhardness of the sintered NbC averaged 1681 ± 92 HV 0.2.

NbC-Co and NbC-Fe_3Al Hard Metals

Since pure NbC is rather brittle, the addition of a metallic binder is necessary for use in technical applications. One of the most established binders in hard metals is cobalt. Consequently, it was chosen as a binder for NbC hard metals using 8 vol.% and 12 vol.%, respectively. The powders and the process conditions for the NbC bearing hard metals are given in references [2,24]. Some important details are as follows. The cobalt bonded NbC hard metals were spark plasma sintered (SPS) using a stoichiometric $NbC_{1.0}$ and commercially available NbC powder (Treibacher 100, Austria; Fisher Sub-Sieve Size (FSSS) = 1.18 µm) and cobalt powder (Umicore grade Co-HMP, Belgium; FSSS = 0.55 µm). The measured powder raw density was 7.60 g/cm³. NbC grades made from this $NbC_{1.0}$ powder (denoted as "T" in the following) had a granulometry of $d_{50} = 1.72$ µm and $d_{90} = 3.78$ µm using the Fraunhofer calculation model.

A second, sub-stoichiometric powder was used for producing $NbC_{0.88}$-12Co (denoted in the diagrams as "H1" in the following). Combustion analysis revealed a C:Nb ratio of 0.88 for this NbC powder. The powder had a granulometry of $d_{50} = 1.47$ µm and $d_{90} = 7.42$ µm (using optical data of SiC and MIE-model). The measured powder raw density was 7.37 g/cm³ with a carbon content of 9.95 ± 0.28 wt.% or $NbC_{0.87}$, thus being lower than that of stoichiometric NbC.

The granulometric values of the currently used NbC powders do not reflect the sub-micron size of the primary NbC particles, as these tend to agglomerate, Figure 9. However, methods of deglomerating such NbC powders are under development.

The University of Leuven (KU Leuven, Belgium) densified the powder mixtures of cobalt or Fe_3Al bonded NbCs to discs of ∅ = 56 mm by spark plasma sintering (SPS, type HP D 25/1, FCT Systeme, Germany). A pulsed electric current was applied with pulse/pause duration of 10/5 ms throughout all the experiments. The powder mixture was poured into a cylindrical graphite die with an outer diameter of 56 mm and sintered for four minutes at 1,280/1,300 °C. The conditions of densification are detailed in references [2,23,24] and summarized in Table II. Graphite paper inserts were used to separate the graphite die/punch set-up and the powder mixture.

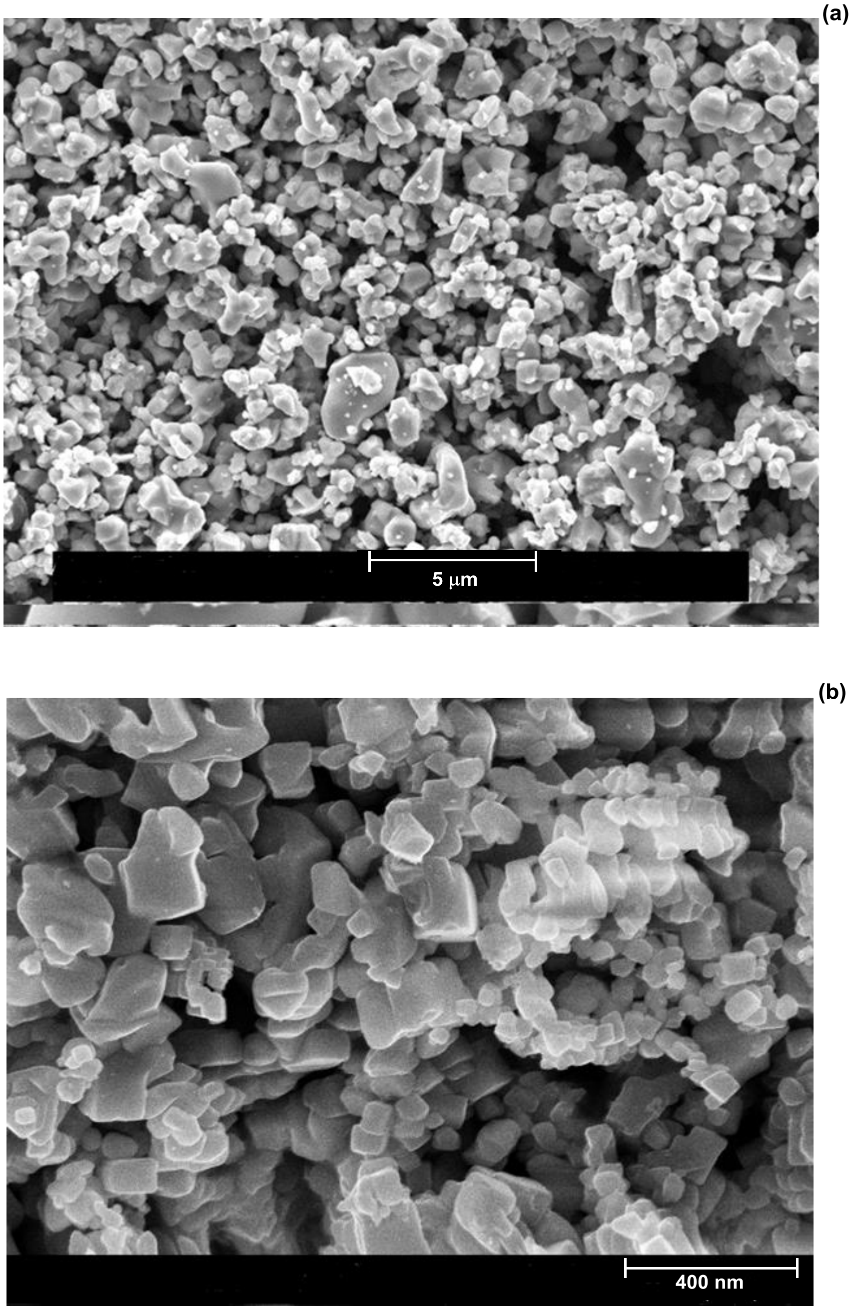


Figure 9. Morphology of NbC powders; (a) Treibacher NbC100, (b) NbC H1.

The intermetallic compound Fe_3Al represents an attractive alternative to cobalt, because it is composed of low cost elements and undergoes no phase transitions, except order-disorder transformations. N_2-atomized Fe_3Al powder (-325 mesh obtained by AGH University of Science and Technology, Krakow, Poland) was used for producing the NbC-12Fe_3Al samples via the same sintering process as was applied for the NbC-Co hard metal. Table II compiles the mechanical properties of all the NbC-based hard metals tested.

Table II. Properties of NbC-based Hard Metals

Property	**Temperature**	**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), time and pressure	-	-	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)
Phase composition		XRD	NbC	NbC + fcc-Co + Nb_2C	NbC + fcc-Co + Nb_2C	NbC + Fe_3Al + (Al_2O_3)	NbC + fcc-Co
		EBSD		NbC	NbC	NbC + Fe_3Al	NbC + Co
Binder (Vol.-%)		-	0	8	12	12	12
Density (g/cm^3)	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 HV 0.2	RT		1,681 ± 92	1,451 ± 54	1,453 ± 41	1,632 ± 50	1,765 ± 130
HV 0.5	700 °C		539 ± 20	-	734 ± 60	553 ± 30	-
Wear rate k_v (0.1 → 10 m/s) (10^{-6} mm^3/N-m)	RT	ISO 20808	0.2 → 0.5	1.8 → 0.6	3.9 → 0.4 →1.0	3 → 0.4 → 3	2 → 0.7
	400 °C		0.7 → 0.5	2.5 → 1.0	8.0 → 1.0	10 → 1.0	2 → 0.5 → 2
P.V value (0.1 → 10 m/s) (MPa.m/s)	RT		2 → 90	1 → 80	1 → >100	1 → 40	1 → 70
	400 °C		0.3 → 50	0.25 → 40	0.5 → 75	0.5 → 32	3 → 45

HP = Hot pressing; SPS = Spark plasma sintering

Metal Matrix Composites and Hard Metals by Casting

Metal matrix composites (MMCs), based on an iron-based alloy matrix reinforced by NbC or mixed NbCs, have the potential of greatly enhancing the wear resistance of parts subjected to dry sliding and abrasive wear occurring in closed and open tribo-systems [25-27]. The metallic binder in sintered hard metals ranges from >5 vol.% up to 25 vol.%. Castings can basically cover a much wider range of NbC hard phase contents from >5 vol.% up to 75 vol.%. The Fe-NbC ferroalloy, Figure 4, produced by CBMM as such is in fact an MMC. In the current investigation Fe_3Al-NbC MMC was considered, thus allowing a comparison with NbC-Fe_3Al hard metal. This MMC can be produced in the same metallurgical process used for Fe-NbC ferroalloy. Iron-aluminide formation is an exothermic reaction that may be integrated into the alumino-thermic reaction typically used for reducing oxides in the synthesis of Fe-NbC alloys. The formation of Fe_3Al in the alumino-thermic reaction is achieved by adding a defined excess of aluminum. The resulting Fe_3Al-NbC ferroalloy can be remelted, eg. in an induction furnace, and further be purified using a slag prior to casting [28].

The values for microhardness and elastic modulus of metallurgically synthesized NbC, shown in Table III, are comparable to those of NbC generated by the powder metallurgical route. The elastic modulus of the intermetallic Fe_3Al matrix is similar to that of conventional iron alloys. Microprobe and EDX analysis of the NbC particles in the Fe_3Al-NbC MMC revealed a sub-stoichiometric composition of $NbC_{0.70}$, whereas combustion analysis (ELTRA CS-800) of leached hard phase indicated $NbC_{0.94}$. The mismatches underline the necessity to develop appropriate analytical procedures for NbC bearing materials. Based on the phase diagram [12], such a stoichiometry may be composed of Nb_4C_3, Nb_3C_2 as well as mixtures of these, or of ζ-Nb_4C_{3-x}, Figure 6.

Table III. Properties of a Fe_3Al-NbC Metal Matrix Composite

Property	Intermetallic phase by XRD and EBSD (area-% by EBSD), balance NbC	Volume fraction hard phase (Vol.-% NbC)	Stoichiometry (by combustion analysis of leached grains)	Microhardness* (GPa)			E modulus (GPa)		Microhardness (MPa)		
				NbC	Metallic matrices		NbC	Matrix	NbC	Metallic matrices	
Method	-	ASTM E562-11		Nano-indentor* XP (Egilent)					Vickers HV 0.05		
Fe_3Al-NbC (AD5258)	19% Fe_3Al, 19% Fe_3AlC	54.0 (61.3 EBSD, 75% XRD)	$NbC_{0.94}$#	17.2 ± 0.8	6.3 ± 0.4	3.6 ± 0.2	362 ± 16	216 ± 14	17,330 ± 863	3,610 ± 254	6,340 ± 437

* Berkovich Indenter (CSM, 45 Hz, 2 nm), hardness for a penetration depth of 500 nm, values according to ISO 14577;
# 10.8 ± 0.4 wt.-%C or $NbC_{0.94}$ by combustion analysis; whereas microprobe spot analysis of NbC grains revealed $NbC_{0.70}$.

Microstructural Characterization

The microstructure of pure NbC analyzed by FESEM (Field Emission SEM) is shown in Figure 10(a). The microstructure reveals dense sintering along the NbC grain boundaries. The microhardness averaged 1681 ± 92 HV 0.2. The HP-NbC did not, however, reach the theoretical density due to a reaction between the natural Nb_2O_5, present on the surfaces of the NbC grains, with NbC and significant grain growth which occurred as a consequence of the very high hot-pressing temperatures. The dark spots visible in Figure 10(a) are pores of 1–3 μm in size and are responsible for the reduced microhardness as compared to literature data. Vickers indentations made into the sintered carbide lead to the development of cracks particularly originating from the indent corners. The pronounced crack formation is indicative of a rather brittle material, Figure 10(b).

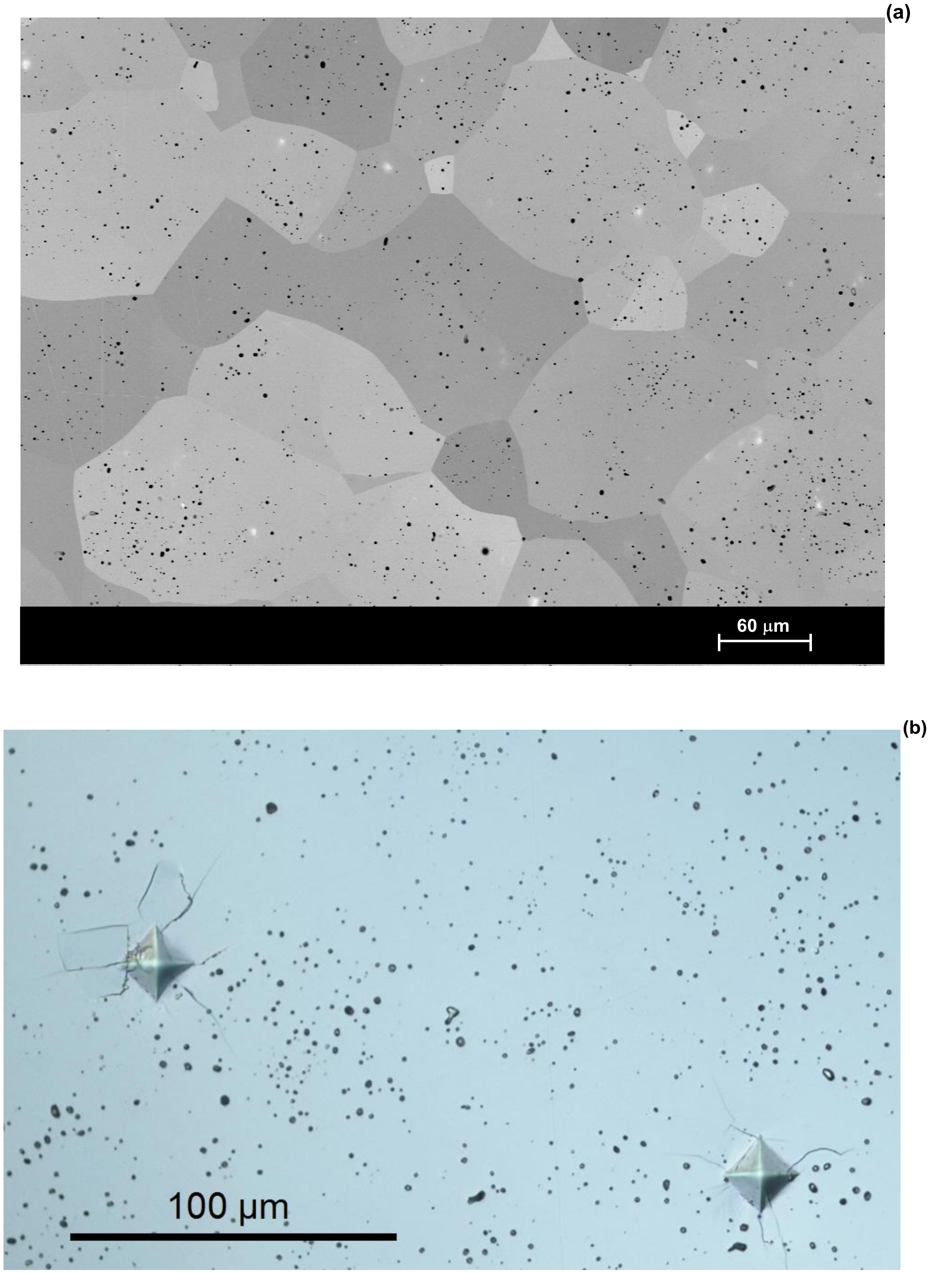


Figure 10. (a) Microstructure of pure NbC showing porosity inside the grains, (b) Vickers indents developing cracks at the corners (indentation load 5 kg).

The FESEM image taken with an SE detector and the SEM image of the metal-bonded NbC hard metals, Figure 11, revealed larger islands (situated deeper due to preparation) of the different metallic binders representing local inhomogeneity of the binder distribution. All metal-bonded NbC grades showed porosity-free NbC grains contrary to the pure NbC samples. Vickers indents made into the metal-bonded NbC samples led to less intense cracking as compared to pure NbC, as shown in Figure 12. This is indicative of an increased toughness and is likely to be due to the metal binder.

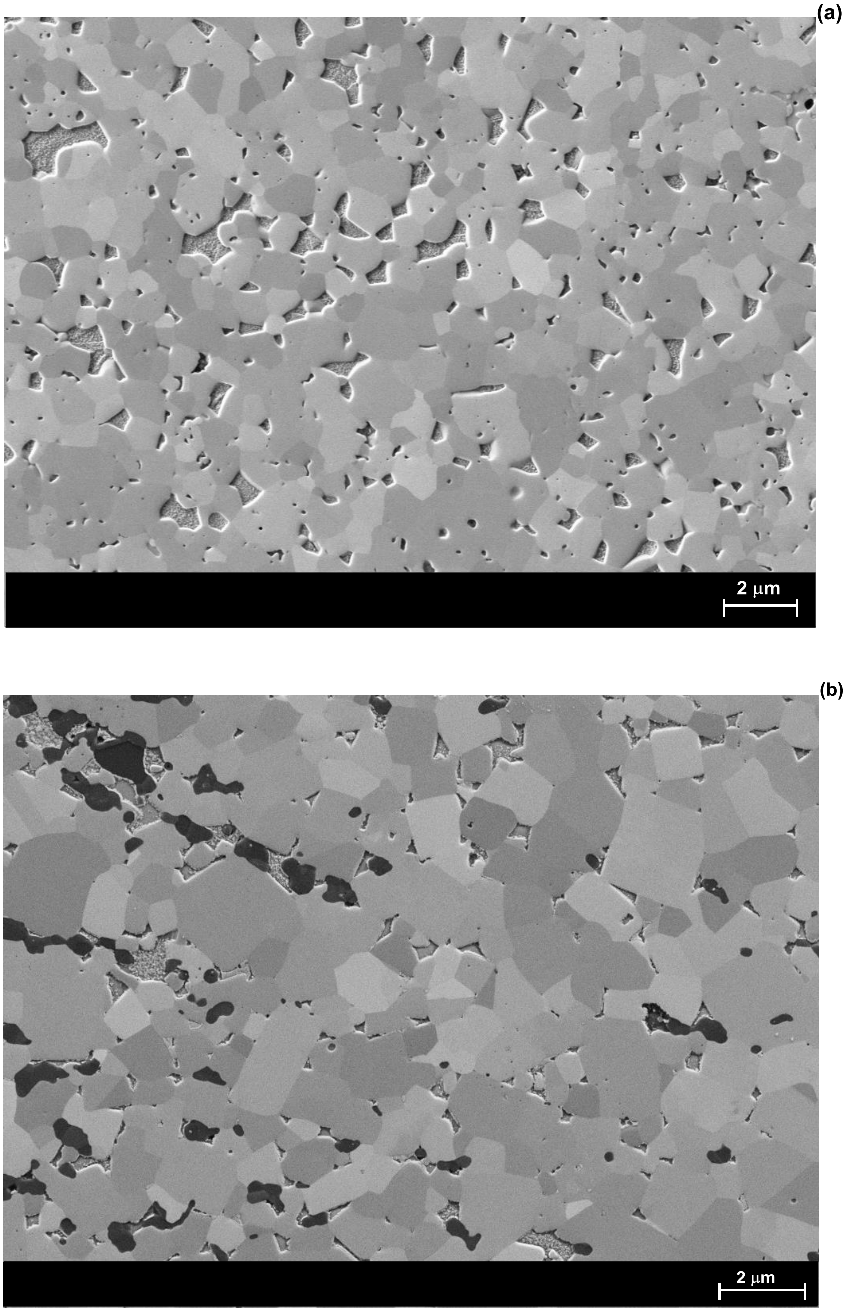


Figure 11. (a) Microstructure of NbC-8Co, (b) of NbC-12Fe_3Al.

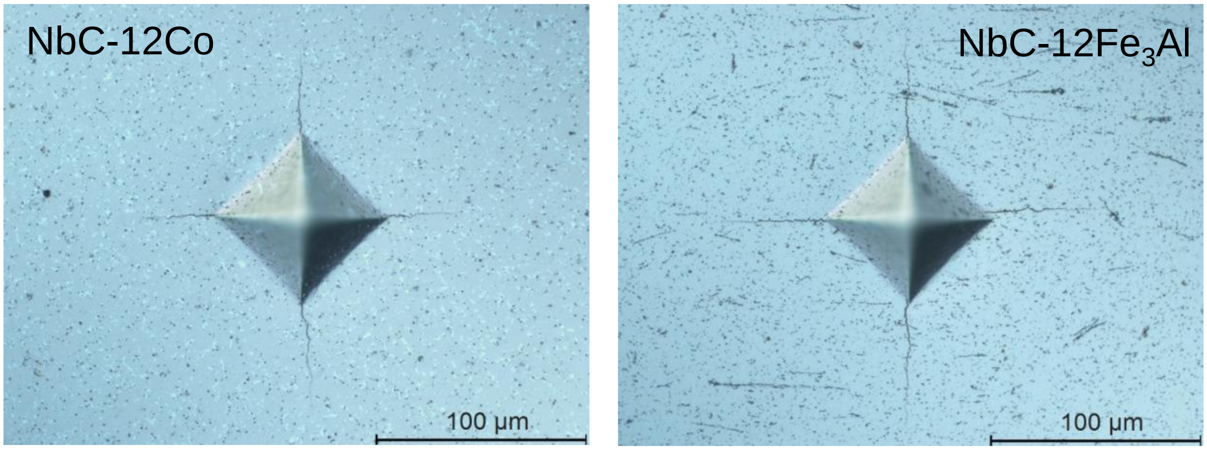


Figure 12. Microstructure of NbC (T) hard metal grades with 12% metal binder.
Indents were made with a load of 5 kg.

The microhardness of pure and metal-bonded NbC is shown as a function of indentation load in Figure 13. Pure NbC, ie. without metal binder achieves, as expected, the highest hardness values of around 1900 HV 0.2 without showing a great influence of the process (hot-pressing versus SPS). The hardness steeply declines with increasing indentation load to a stable level of around 1400 HV. The strong load influence on the microhardness of NbC is well established in the literature and similarly applies for WC, W_2C, V_8C_7 and Mo_2C [13]. The effect is due to plastic deformation via disloacation movements at room temperature under indentation loading. In cubic carbides, the motion of dislocations occurs along the {111} planes in the direction ⟨110⟩.

In the cobalt bonded NbC hard metals, the average microhardness is 1412 ± 51 HV 0.2 for NbC-8Co (T). Despite the increased amount of binder phase in NbC-12Co (T), the average microhardness is similar at 1410 ± 13 HV 0.2. Overall, the microhardnesses of the cobalt bonded NbC from the stoichiometric NbC "T" powder is less sensitive to load. The microhardness of $NbC_{0.88}$-12Co (H1) hard metal is 1712 ± 130 HV 0.2 which is clearly superior to that of the hard metals containing stoichiometric NbC. This is in agreement with the behavior shown in Figure 7 [17]. A second factor causing the higher hardness may be the finer particle size of the H1 powder. The hardness of the sub-stoichiometric $NbC_{0.88}$-12Co (H1) is also less sensitive to the indentation load, dropping to around 1500 HV 5. $NbC_{0.88}$-12Co (H1) at loads above 1 kg is the hardest NbC grade, Figure 13.

The microhardness of NbC-12Fe_3Al reaches values of 1632 ± 50 HV 0.2 and is considerably higher than that of cobalt bonded NbC, even using the same stoichiometric NbC "T" powder. Furthermore, NbC-12Fe_3Al hard metal had a significantly higher hardness than the other metal bonded NbC grades at indentation loads over 1 kg, as seen in Figure 13. The microhardness of NbC can be tailored through the stoichiometry and the type of binder.

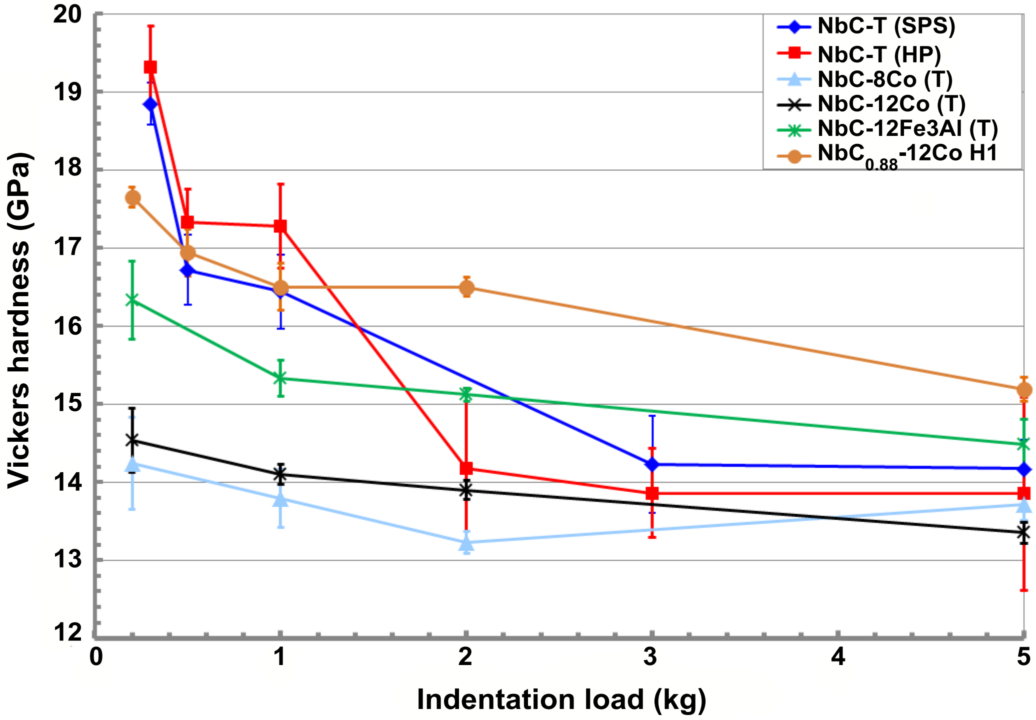


Figure 13. Microhardness as function of indentation load for pure and metal bonded NbC hard metal grades.

The phase composition of the Fe_3Al-NbC MMC was determined by EBSD to be 19.5%Fe_3Al and 19.5%Fe_3AlC with the balance being 61%NbC hard phase. This agrees quite well with the hard phase content of 54% as determined by ASTM E562-11 and 75% measured by X-Ray Diffraction (XRD). The XRD measurement also confirmed the presence of the three crystalline phases. The procedure for preparing the microstructures is described in detail in reference [28]. The microstructure, Figure 14, shows a rim of $Fe_3Al(C)$ surrounding individual NbC particles. More detailed analysis indicated a carbon-enriched interphase zone. This carbon is replenished from NbC and dissolved into the surrounding Fe_3Al matrix. The microhardness of carbon-enriched Fe_3Al phase is significantly higher than that of the Fe_3Al phase. The presence of Fe_3AlC interphase also indicates a metallurgical bonding of NbC to the Fe_3Al matrix, which supports the transmission of tribological shear stresses between hard phase and matrix. Microprobe analysis revealed the C:Nb ratio in the NbC particles to be sub-stoichiometric at around 0.70, compared to the combustion analysis of 0.94 (see Table III).

Vickers indents (HV 0.05) were positioned within the NbC particles of the Fe_3Al-NbC MMC, Figure 15. The typical crack pattern found in the nearly stoichiometric NbC particles of the hard metal samples showing cracks originating from the corners of the indent was not observed here. Some shallow cracks are oriented parallel or perpendicular to the sides of the indent. In some indents the material appears to show some plasticity. These features suggest that the sub-stoichiometric NbC grains should have a rather high toughness.

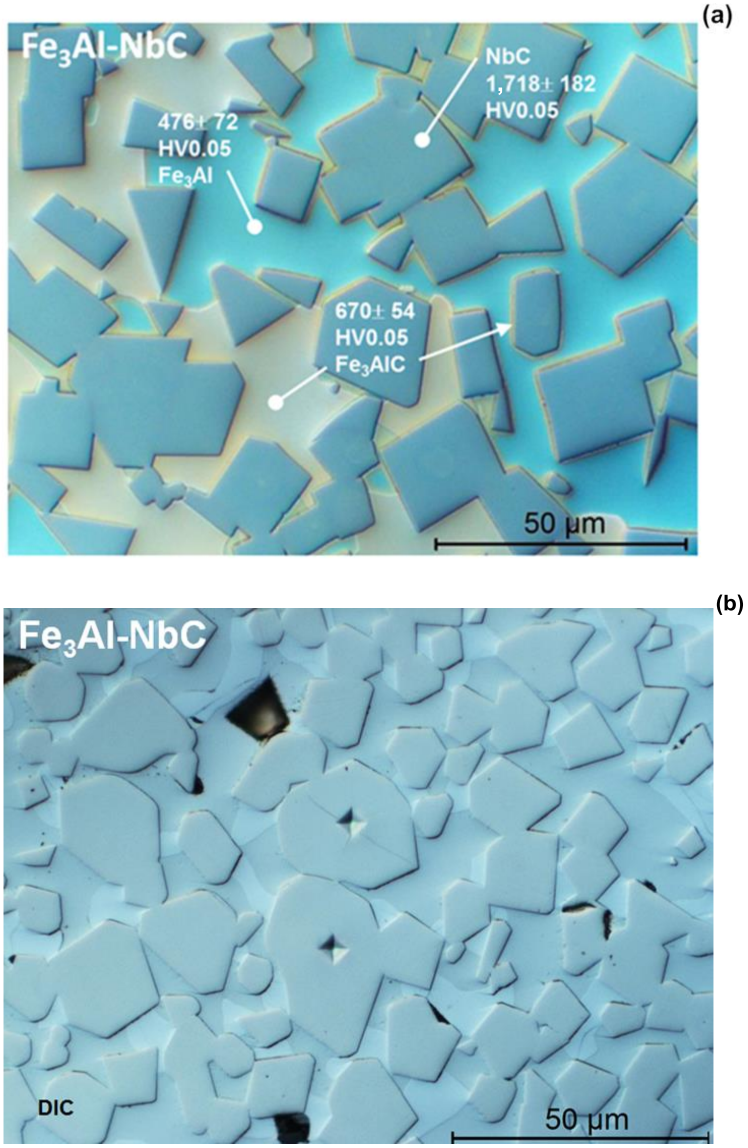


Figure 14. Microstructure and microhardness of the Fe_3Al-NbC metal matrix composite; (a) light optical microscopy, (b) LOM of indented NbC grains.

Nano-indentation using a Berkovich indenter revealed an elastic modulus of 362 ± 16 GPa for the melt grown NbC particles. The microhardness for an indentation depth of 500 nm was measured to be 18.8 ± 1.1 GPa, whereas the Vickers microhardness of such NbC particles was determined to be 1718 ± 182 HV 0.05, Table III. The elastic modulus of the $NbC_{0.88}$-12Co (H1) was also 10% lower than for the stoichiometric NbC grades, Table II. Thus, the elastic indentation modulus of sub-stoichiometric NbC is lower than that measured by the resonance method (ASTM E1875) or nano-indentation on stoichiometric NbC grades, Tables II and III, produced by carburization of niobium oxide. In comparison to stoichiometric NbC, having an elastic modulus of 477 GPa, the elastic modulus was reduced to 405 GPa for $NbC_{0.88}$ (measured by 4-point bending bars) and to ~365 GPa for the melt grown NbC (measured by nano-indentation), as can be seen from Table II and Table III.

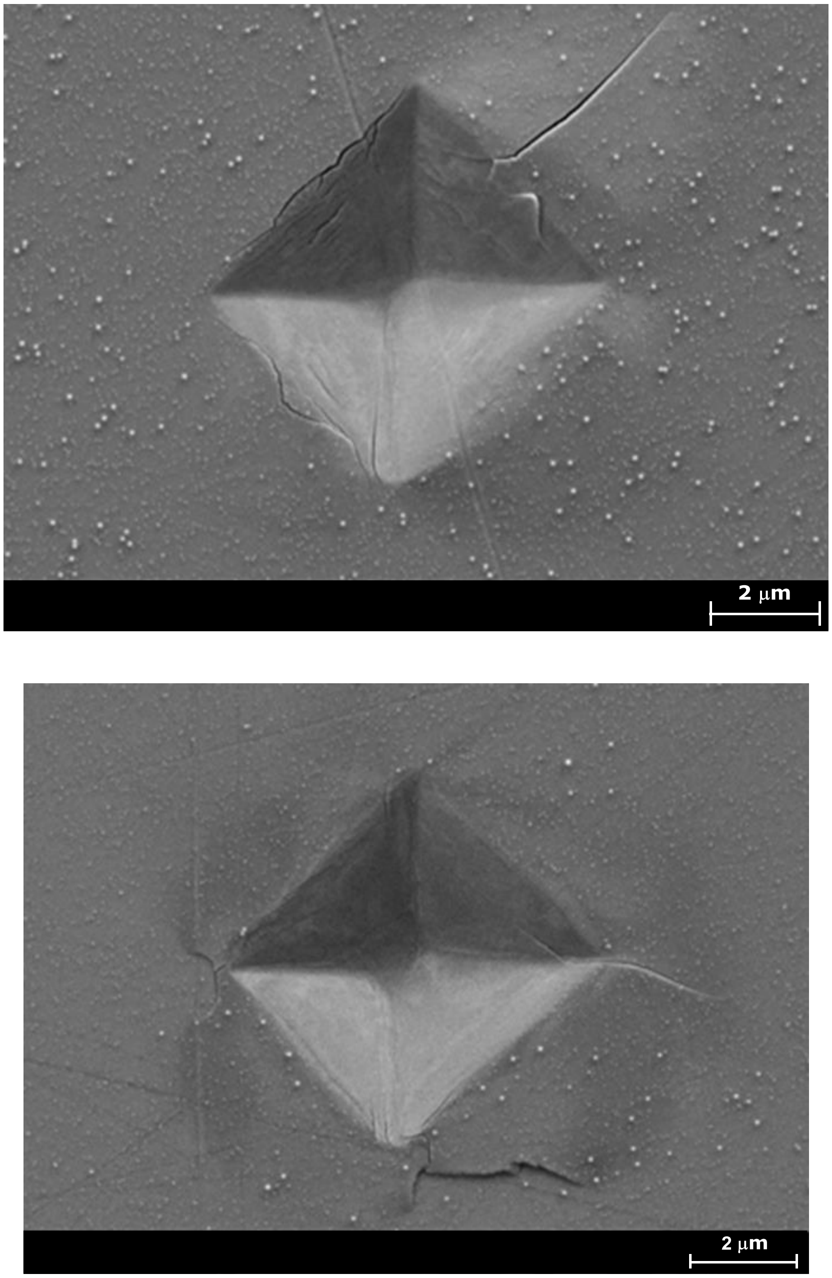


Figure 15. SEM analysis of Vickers indents in melt grown NbC particles of Fe_3Al-NbC MMC material.

Tribological Behavior of NbC-based Hard Materials

Friction and wear are complex system properties depending on many variables. Therefore, the tribological performance of carbides can only be reliably judged using specific tests simulating a defined tribo-contact condition. Such simulations have been performed for many hard materials, however, for NbC, no reliable tribological data could be found in the literature. Consequently, an extensive test program using a wide range of operating conditions has been set up to benchmark pure NbC, as well as NbC-based hard metals and MMCs against other established hard materials

The tribometers used for unidirectional sliding are proprietary developments of BAM and the details are disclosed elsewhere [29]. They comply with ASTM G99 (DIN 50324) and with DIN EN 1071-13:2010. The wear volumes of stationary and rotating specimens were calculated from stylus profilometry and the wear scar diameters were determined by using ASTM D7755-11 or DIN 51834-3. The wear rate *kv* is defined as the ratio of volumetric wear to the product of normal load F_N and the sliding distance *s*. The coefficient of friction (CoF) and the total linear wear of both tribo-partners were recorded continuously. One test per combination of parameters was performed, because the testing philosophy at BAM is to screen over a wide range of operating conditions, rather than doing repeated tests. Repetitions can be done, however, for specific test conditions. The tribological data of WC-, Cr$_3$C$_2$- and (Ti,Mo)(C,N)-based materials evaluated under the same test conditions were available from references [30,32,33] for benchmarking.

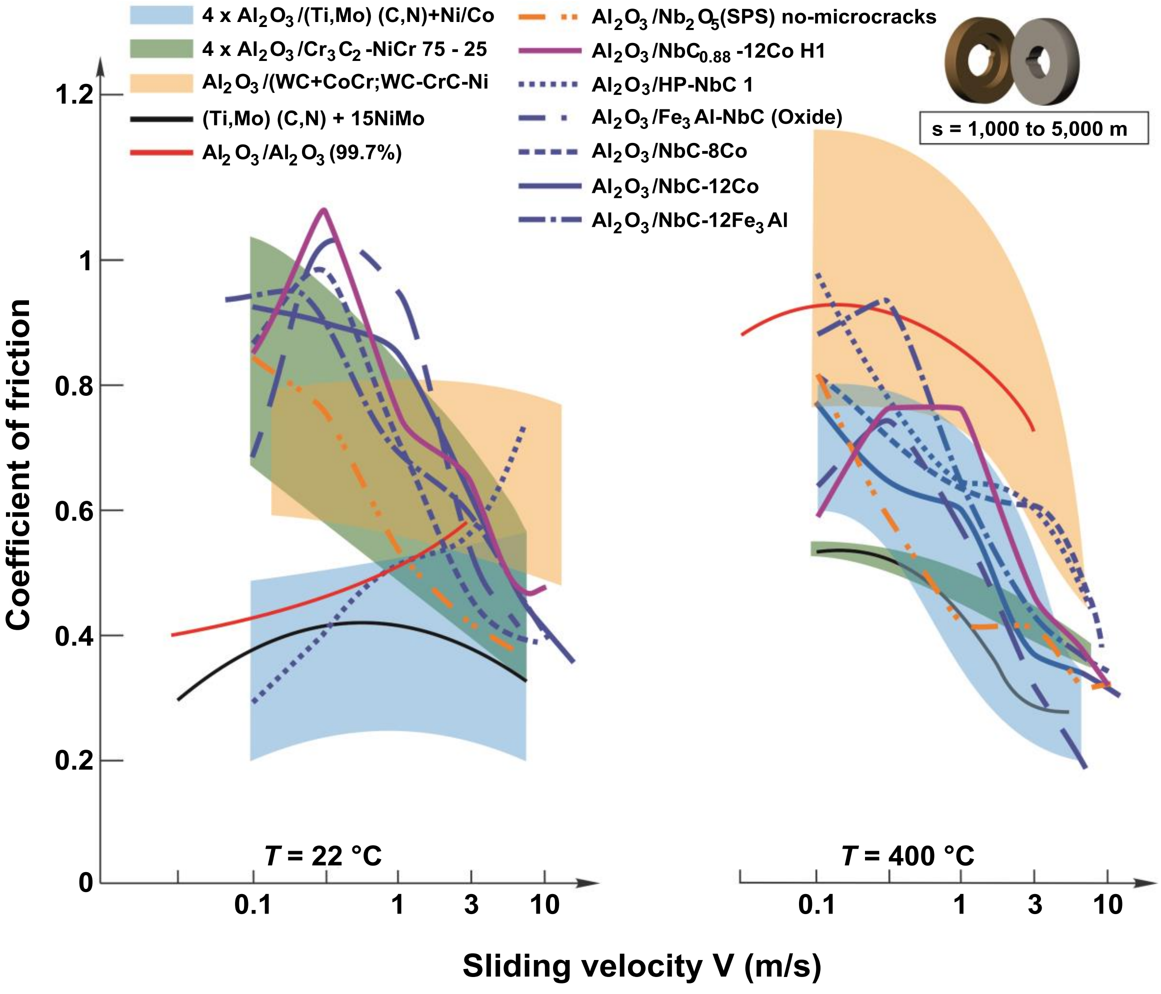


Figure 16. Coefficient of friction of NbC-based hard metals and Fe$_3$Al-NbC (MMC) compared for different ceramics and hard metals under dry friction at RT and 400 °C.

Unidirectional Sliding (Room Temperature and 400 °C)

Sintered alumina (99.7%) bodies were used as stationary disc shaped toroids (with R_1 = 21 mm and R_2 = 21 mm) using specimens with polished surfaces (R_{pk} = 0.019 mm), which were pressed against the planar surfaces of the rotating NbC-based materials. A normal force of 10 N was applied, resulting in an initial Hertzian contact pressure P_{0max} of approximately 660 MPa. The sliding distance was 5000 meters. Experiments were performed at 23 °C (RT) and 400 °C in air (relative humidity at RT approximately 35%) with sliding speeds of 0.1, 0.3, 1.0, 3.0, 7.5-8.0 and 10-12 m/s. The resolution limit of the wear rate for the rotating specimen corresponds to about 10^{-8} $mm^3/N \cdot m$.

The frictional level of different NbC grades and the Fe_3Al-NbC MMC displayed in Figure 16 compares well with different WC-based or Cr_2C_3–based hard metals or monolithic alumina [30]. At room temperature (RT), the friction of binderless HP-NbC_1 increased with increasing sliding speed having values of around 0.3 at low sliding speeds and reaching a level of 0.8 at high sliding speeds, similar to monolithic alumina, whereas all metal bonded NbCs presented an opposite trend. Friction decreased with increasing sliding speed. It thus qualifies NbC for traction and frictional applications such as clutches or brake rotors rather than for low friction bearings, Figure 16. Metal bonded NbC grades showed an opposite trend to pure HP-NbC as the coefficient of friction decreased with increasing sliding speed at RT, Figure 16 [34]. At low sliding speeds the value can reach unity, while at high sliding speeds it drops to a level of 0.4. This behavior is quite similar to that of Cr_2C_3–based hard metals. The friction behavior of the Fe_3Al-NbC MMC is very similar to that of the NbC-based hard metals.

At 400 °C, the coefficient of friction of all NbC and hard metal grades decreased with increasing sliding speeds above values of approximately 0.2, but values were on average lower as compared to WC grades. The friction of NbC grades at high sliding speeds was lower at 400 °C than at RT. Low friction at high sliding speeds is a favorable property for cutting tools, reducing cutting forces, thus achieving a given cutting performance at reduced machine power.

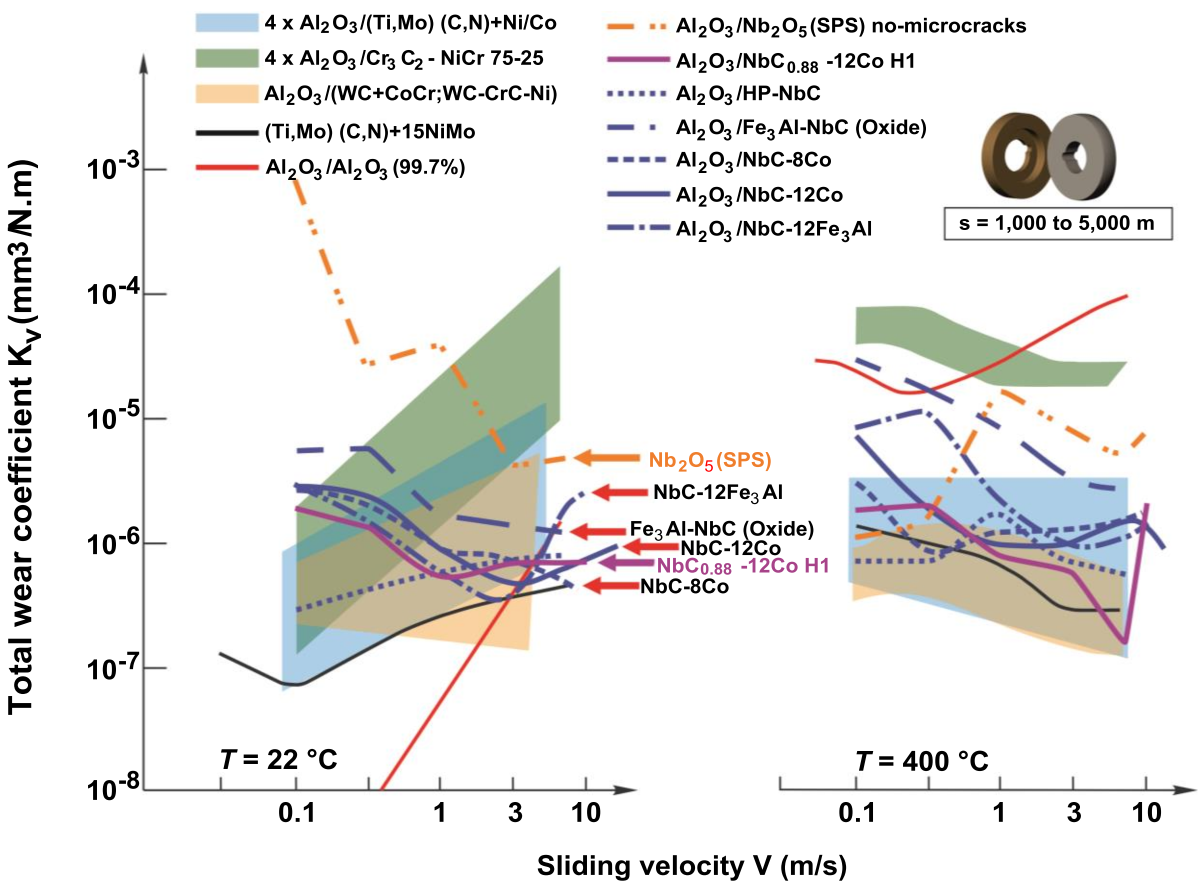


Figure 17. Total wear coefficients of NbC-based hard metals and Fe_3Al-NbC (MMC) compared to different ceramics and hard metals under dry friction at RT and 400 °C.

In comparison to other hard metals, binderless HP-NbC exhibited a particularly high wear resistance especially at RT, which is more or less independent of sliding velocity, Figure 17 [30]. The wear resistance of HP-NbC at RT is one of the highest and compares well with that of self-mating alumina (Al_2O_3): it compares also regarding its evolution with sliding speed. At RT the metal bonded NbC grades displayed a rather constant evolution of the wear rate with increasing sliding speed, Figure 17 [2]. The wear rates of the metal bonded NbC grades decreased with sliding speed by one order of magnitude to low wear rates at high sliding speeds. For a sliding speed of 8 m/s at RT, the wear rate range of $k_v = 4.4 – 7.8 \cdot 10^{-7}$ $mm^3/N \cdot m$ of the NbC-8Co rotating disc was outstandingly low in comparison to all other ceramics and hard metals. The wear rates of the rotating discs made from NbC-12Co reached values of $k_v = 9.6 \cdot 10^{-7}$ $mm^3/N \cdot m$ at RT at 12 m/s sliding speed.

At room temperature the wear rates of the Fe_3Al-NbC MMC are slightly higher than those of the NbC-bearing hard metals and decrease with increasing sliding speed, Figure 17. It is also apparent that metallurgically synthesized or sintered NbC bearing materials tribologically compete with WC and Cr_3C_2 bearing hard metals or cermets (Ti,Mo)(C,N), especially at high sliding speeds. It is beneficial for machining applications that coefficients of friction and wear rates decrease with increasing sliding speed.

At 400 °C, the dry sliding wear resistance of tribo-active materials ($Ti_{n-2}Cr_2O_{2n-1}$-phases, (Ti,Mo)(C,N)), HP-NbC and thermally sprayed Cr_2O_3 or WC-based hard metals ranged between 10^{-6} mm³/N·m and 10^{-7} mm³/N·m on a level of mixed/boundary lubrication. The wear resistance of HP-NbC under dry sliding is better than that of Cr_3C_2 and better than, or similar to, that of WC-based systems. At 400 °C, the Co-bonded NbC hard metals showed lower wear rates than the Fe_3Al-bonded NbC hard metals and MMC. This can be attributed to the well-known effect of Co_3O_4 formed by tribo-oxidation thus lowering the wear rate [35].

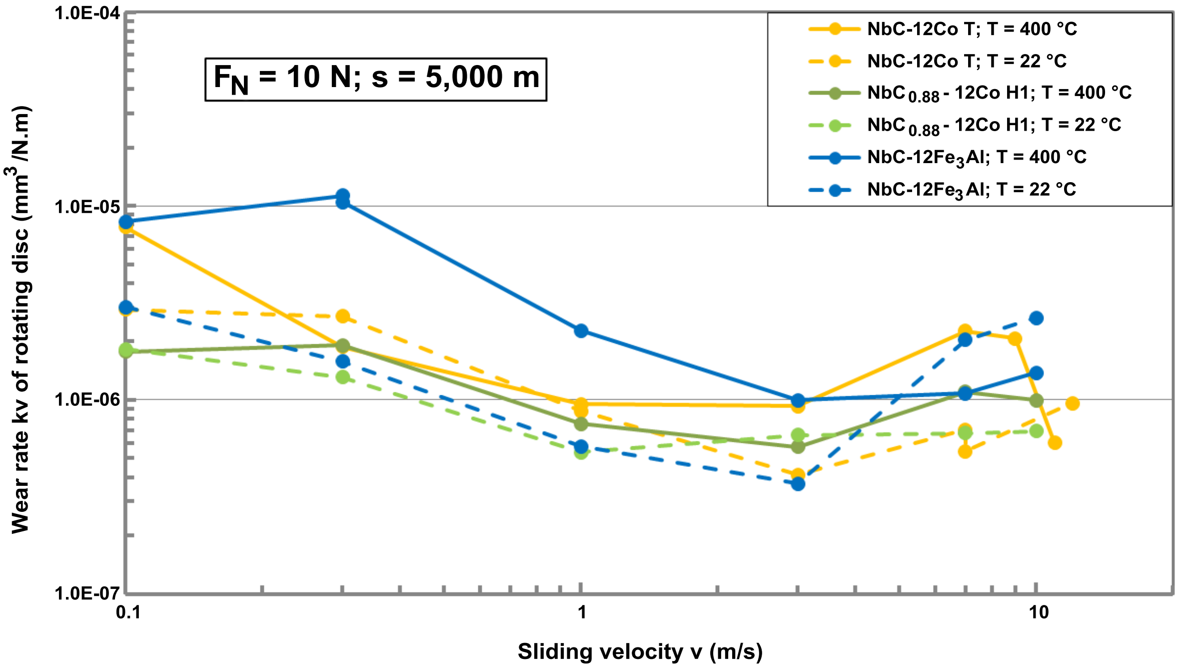


Figure 18. Wear rates of rotating discs of different NbC grades under dry sliding conditions.

Figure 18 indicates that the wear rates of the rotating discs (counterbody) made from different NbC grades decreased with increasing sliding speed and depend slightly on speed and temperature (RT and 400 °C). Consequently, the operating window of NbC in tribo-systems is wide. NbC thus represents an exceptional tribo-material offering such a large operating window in terms of sliding speed, ambient temperature and load carrying capacity under dry sliding conditions.

The morphology of the plateaus in the wear tracks is smooth for the discs slid at RT and 7.5 m/s. At 400 °C, the tribo-oxidation is beneficial to fully smoothen out the wear tracks [2,35]. For closed tribo-systems under dry sliding conditions, NbC is a favorable material because no wear particles visibly agglomerated on the wear tracks. The observation that no agglomerates were found on the wear tracks conforms to the low wear rates.

Table II summarizes the load carrying capacity, expressed as P·V values (contact pressure times sliding velocity), displayed in Figure 19, for all NbC grades. At room temperature the values increased from 1-2 MPa·m/s at 0.1 m/s up to 100 MPa·m/s at 8.0 m/s [1] because tribo-oxidation was enhanced with increasing sliding speed (or generated frictional heat) and stable, non-volatile

Nb_2O_5 was formed. In contrast the P·V values at 400 °C ranged more or less over the same level as measured at RT. The NbC grades exhibited a high wear resistance under dry sliding associated with exceptional load carrying capacity. Normally, P·V values [30,31] of dry sliding tribo-couples decrease with increasing sliding speed. The NbC-based materials are coming close to tribo-active materials [32,33] such as $Ti_{n-2}Cr_2O_{2n-1}$ phases, (Ti,Mo)(C,N) having slightly lower P·V values or maximum frictional heat flows.

The wear resistance of Co- and Fe_3Al-bonded NbC hard metals is highest at RT and high sliding velocities. Several factors are responsible for the wear resistance of NbC. Firstly, NbC has a very high melting point (3,522 °C). Secondly, Nb_2O_5 is relatively soft having a hardness of only 500-650 HV 0.2 and a melting temperature of 1,512 °C without sublimating. On the contrary, WO_3 formed by tribo-oxidation on WC starts sublimating above 750-800 °C and cannot serve for wear protection. Furthermore, it has to be taken into consideration that the modulus and hardness of NbC are less temperature dependent and its toughness increases with temperature.

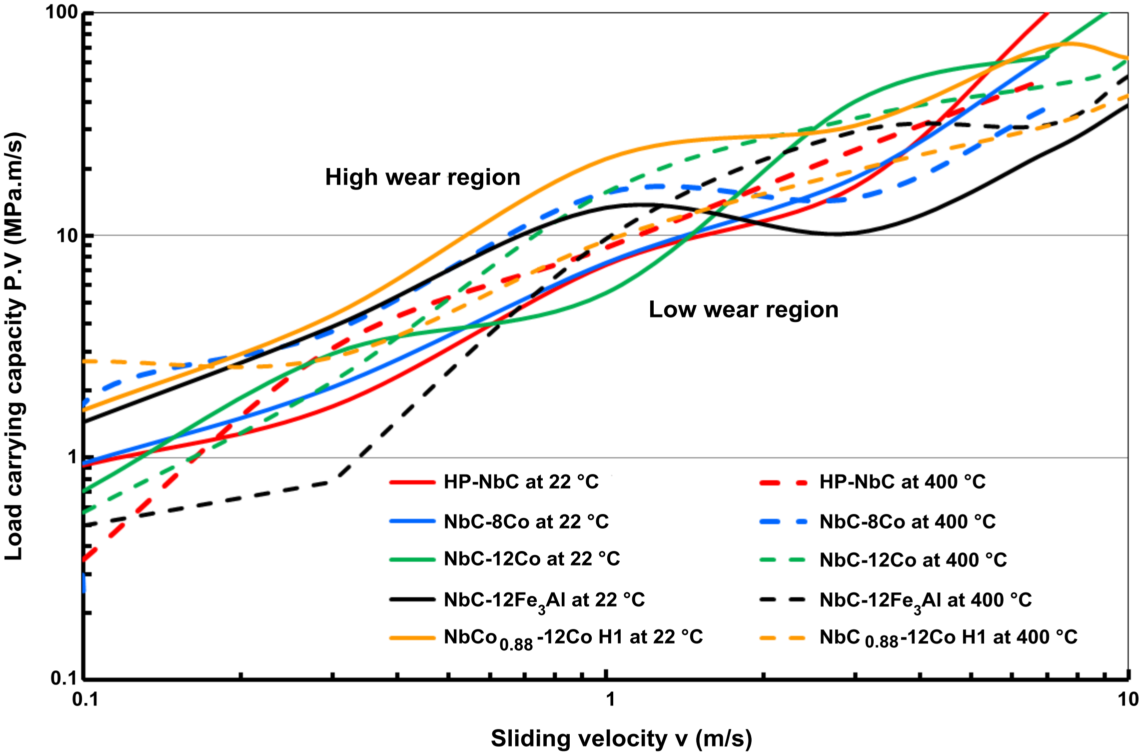
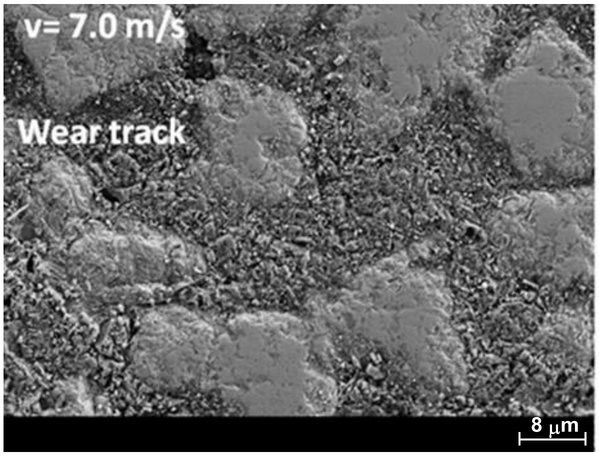
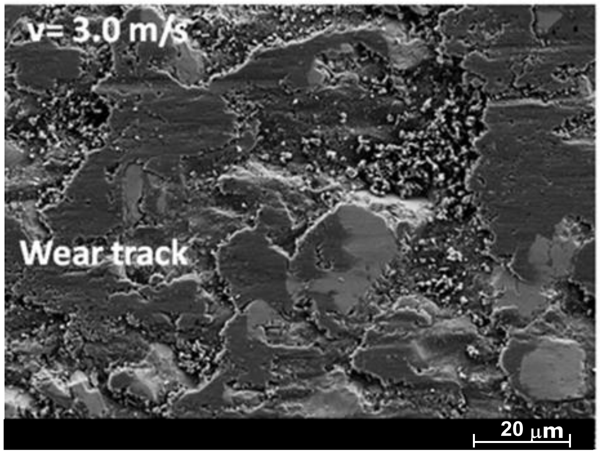
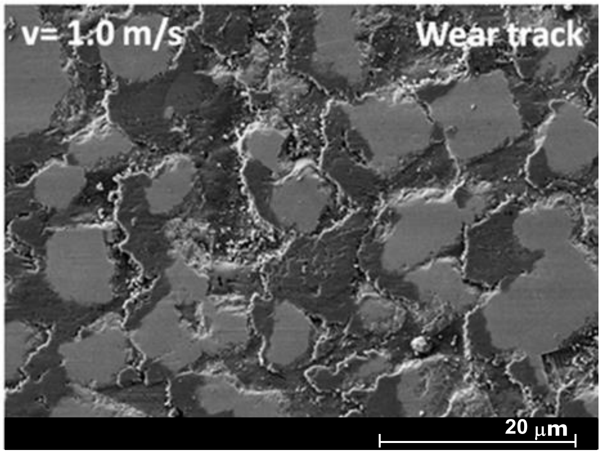


Figure 19. Load carrying capacity (maximum frictional power loss) of NbC-based materials as a function of sliding velocity under dry sliding conditions at room temperature and 400 °C.

Figure 20 shows wear tracks present on Fe_3Al-NbC MMC samples after sliding against alumina over 5000 m distance. The wear debris was removed from the wear tracks in order to better reveal the NbC grains. The micrographs clearly show NbC particles embedded in the matrix. There are no indications of NbC particle extraction because the carbon-enriched Fe_3AlC interface between particle and matrix withstands shear forces, Figure 14. Fragmentation of NbC particles was not observed. One can thus conclude that the wear behavior of the composite is principally controlled by the wear behavior of the NbC hard phase.


v= 7.0 m/s
Wear track
8 μm


v= 3.0 m/s
Wear track
20 μm


v= 1.0 m/s
Wear track
20 μm

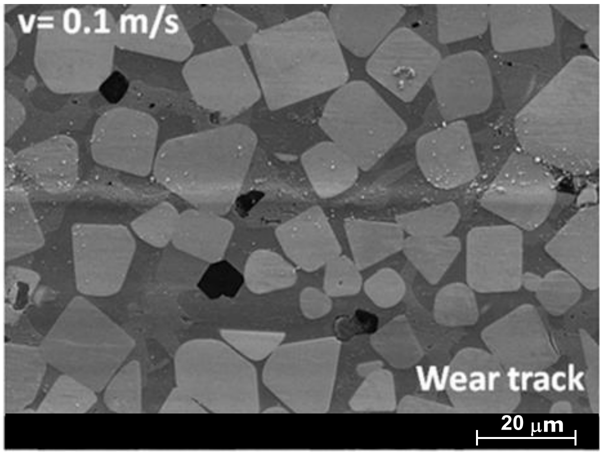


Figure 20. Morphology of RT wear tracks of Fe_3Al-NbC MMC after sliding against alumina over 5,000 m distance.

Oscillating Low-amplitude Sliding (Room Temperature – Different Relative Humidities)

The polished ball ($\varnothing$ = 10 mm; alumina 99.7% or 100Cr6H equivalent SAE E52100) in the oscillating tribometer is fixed at the top of a lever with an integrated load cell for the measurement of the friction force. The ball (non-rotating) is positioned on a disc that is fixed on a table, oscillating at ν=20 Hz with a stroke of Δx=0.2 mm. It is loaded by a dead weight acting as a normal force (F_N = 10 N) perpendicular to the sliding direction. The tests were run under three relative humidity levels of 2%, 50% and 98% up to one million cycles. The sensitivity of a couple against the impact of tribo-oxidation induced by humidity can be effectively quantified under dry oscillation.

The tribological profile (K_v versus CoF) is displayed in Figure 21 for alumina and, in Figure 22, for steel counterbodies. The arrows indicate an increasing relative humidity. The degree and trend of this sensitivity depends on the counterbody material being alumina or 100Cr6 steel. For alumina counterbodies all NbC-based materials behave in a similar manner. Against a polished alumina ball, Figure 21, the tribological profiles of steel and the ceramic samples, including WC-6Ni and pure HP-NbC, as well as cobalt and Fe_3Al bonded hard metals, are sensitive to relative humidity. The presence of cobalt (NbC-8Co, NbC-12Co) and Fe_3Al binders (NbC-12Fe_3Al) in NbC grades increases the sensitivity of their frictional behavior to relative humidity, when compared to binderless NbC. The coefficient of friction decreases under increasing relative humidity.

Ferrous alloys such as 100Cr6 steel, Figure 22, subjected to dry oscillation at RT exhibit tribo-oxidative [36] formation of Fe_2O_3 which may be hydrolyzed to α-, ß- or γ-FeOOH and $Fe(OH)_2$. Particularly, in comparison to polished WC-6Ni, the wear resistance of NbC grades under dry oscillation is high having K_v values of 10^{-6} $mm^3/N\cdot m$. The wear rates of binderless NbC (HP-NbC1) and cobalt bonded NbC grades behave in a similar manner under dry oscillation.

A direct comparison between WC-6Ni and HP-NbC1 is difficult because the nickel binder in WC-6Ni (6.4 wt%Ni + 0.5 wt%Co) has a beneficial role in terms of tribo-oxidation (formation of double oxides). Furthermore, the WC grain size being around 2 µm is much smaller than that of HP-NbC and the surface roughness of WC-6Ni with R_{pk} = 0.013 µm was also smoother than the one of HP-NbC with R_{pk} = 0.143 µm.

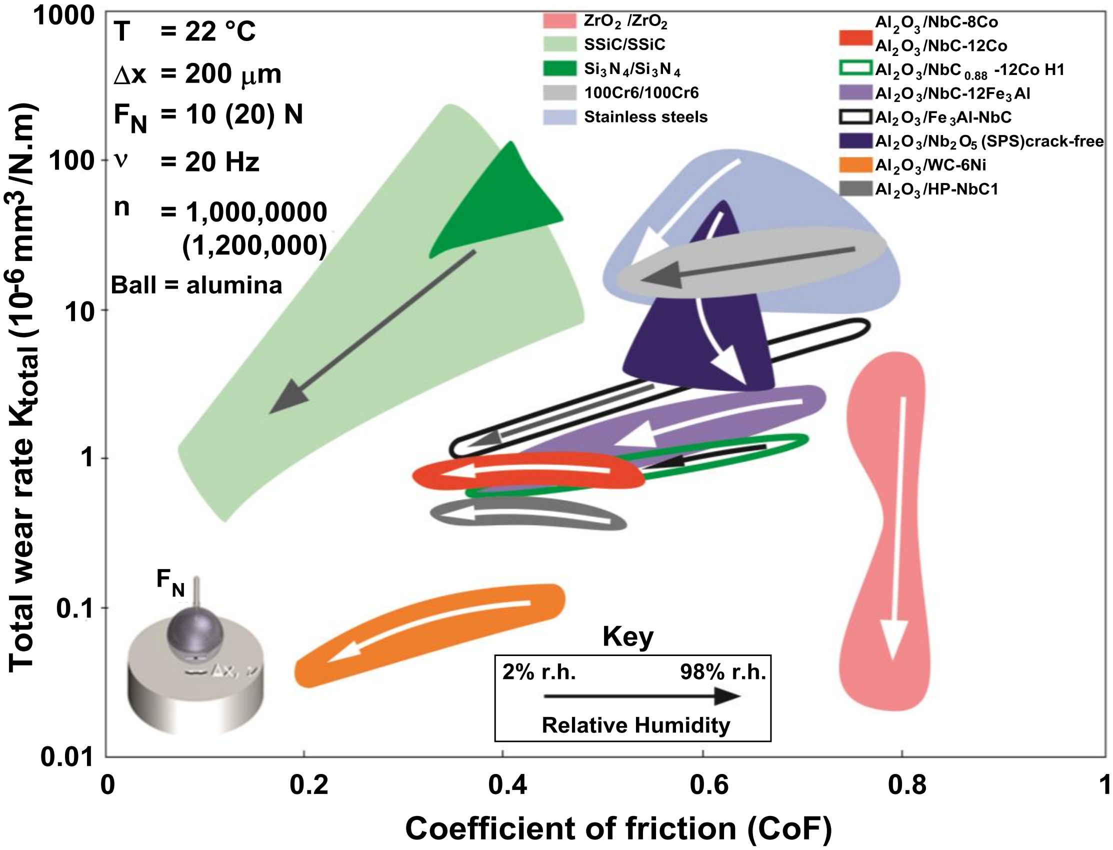


Figure 21. Total wear rate with the associated coefficient of friction of hard materials vs alumina counterbody under dry oscillation and different relative humidity levels.

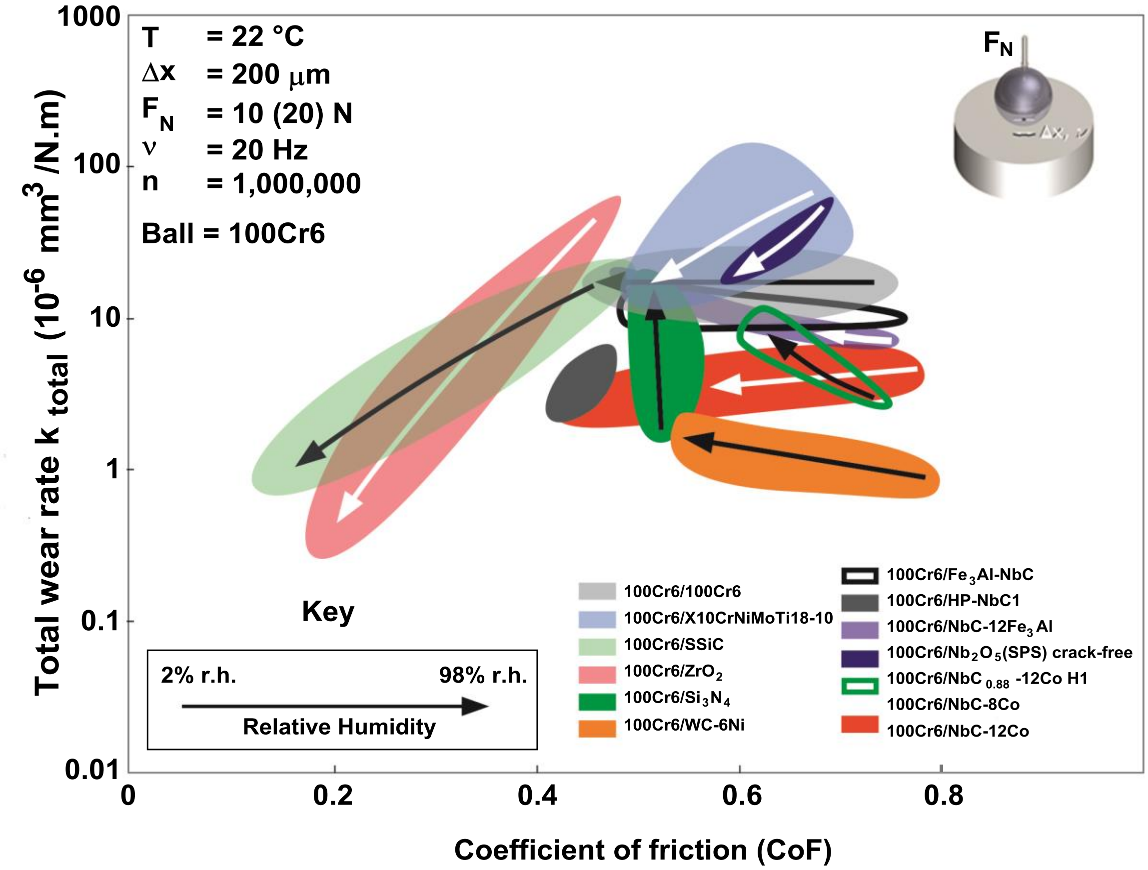


Figure 22. Total wear rate with the associated coefficient of friction of hard materials vs. 100Cr6 steel counterbody under dry oscillation and different relative humidity levels.

Conclusions

The potential of NbC as a hard material with respect to applications in mineral and metal processing has been investigated. NbC has a very high hardness which strongly depends on the stoichiometry (C:Nb ratio) in the material. By adjusting the stoichiometry, the hardness of NbC can be tailored to cover the entire range of other established transition metal carbides. Particular intrinsic advantages of NbC are its lower density that is very close to iron-based alloys, its low solubility in hot metals and its extremely high melting point. This allows the addition of NbC to liquid iron melts without significant gravity segregation effects. Moreover, NbC has a very low chemical wear rate under hot contact conditions with metals.

NbC can be processed via powder metallurgical processing using various metal binders, such as cobalt, nickel, molybdenum, iron aluminide, or stainless steel. It can also be produced in pyro-metallurgical processes, either by in-situ primary precipitation in iron-based melts, or by addition of an NbC containing ferroalloy. These processing routes are able to cover a wide range of hard phase compositions, with NbC particles ranging from sub-micron to several tens of microns in size.

NbC itself, as well as hard metals or metal matrix composites containing NbC, were all shown to have a pronounced intrinsic wear resistance. Stoichiometric or sub-stoichiometric NbCs have, under dry sliding at RT and 400 °C, a pronounced intrinsic wear resistance associated with an exceptional high load carrying capacity, either as a hard metal or as a metal matrix composite. They can easily compete with ceramics, "tribo-active" materials and existing hard metals based on these properties. Thus, NbC qualifies for the group of tribological materials with enhanced wear resistance.

Tribological properties can be tailored through adjusting stoichiometry and/or binder content. The dry sliding wear resistance of the present Fe_3Al-NbC with ~60% NbC was close to that of known NbC-based hard metals and the wear resistance of the sub-stoichiometric $NbC_{0.88}$-12Co (H1) was at the lower end of values for the stoichiometric NbC grades. The NbC grains are metallurgically bonded into the Fe_3Al matrix by a metallurgical interphase. Thus, no grain pull-outs or fragmentations were seen in the wear tracks. Hence, NbC-based materials are expected to show excellent performance in mineral processing.

Remarkably, at increased sliding speeds the wear rate further decreases to outstandingly low values. Wear rates of NbC grades at 400 °C generally remained low, regardless of the applied sliding speed. The low wear rates of NbC were associated with high load carrying capacity (P·V value), which further increases at higher sliding speeds. Under dry oscillation, the wear resistance of pure NbC was insensitive to relative humidity, both for steel and alumina counterbodies, whereas the coefficient of friction of metal-bonded NbC grades was reduced with increasing relative humidity due to the effect of cobalt and Fe_3Al binders.

The low solubility of NbC in metals, its extremely high melting point, as well as the high P·V value are ideal prerequisites for cutting tool materials. Furthermore, the available levels of hardness, elastic modulus, strength and toughness are sufficient to support the loads prevailing at the cutting edge of a tool. From a tribological point of view, the cobalt binder in NbC hard metals can be substituted by intermetallic Fe_3Al.

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