ISSN 2179-3956

TriboBR
Second International Brazilian
Conference on Tribology - TriboBR-2014
2014

NIOBIUM CARBIDE (NbC) AS WEAR RESISTANT HARDMETAL IN OPENED AND CLOSED TRIBOSYSTEMS*

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Abstract
The tribological and mechanical properties of binderless and metal-bonded niobium carbides (8 or 12 vol.-% of Cobalt, 12 vol.-% of Fe_3Al) are presented. Rotating disks made of niobium carbide bearing hard metals were mated against alumina (99.7%) under unlubricated (dry) unidirectional sliding tests (0,1 m/s to 12,0 m/s; 22°C and 400°C) as well as in oscillation tests (f= 20 Hz, Δx= 0,2 mm, 2/50/98% rel. humidity, n= $10^5/10^6$ cycles). Microstructure and phase compositions were determined as well. The tribological data obtained were benchmarked with different ceramics, cermets, hard metals and thermally sprayed coatings, where NbC bonded with 8% and 12% Co presented above 8 m/s the lowest wear rates so far in such a benchmark. Binderless NbC (HP-NbC1) and the metal bonded NbCs exhibited low wear rates under dry sliding associated with high P·V load carrying capacities. NbC-based hard metal bonded with 12 vol.-% of Fe_3Al resulted in a higher hardness level than for 12 vol.-% cobalt. The tribological profile established revealed a strong position of NbC bearing materials under tribological considerations and for closed tribosystems against established reference tribo-couples.
Keywords: Sliding; Friction; Wear; Ceramic; Oscillation; NbC; Niobium carbide; Cobalt; Fe_3Al; Hard metal; Strength; Modulus; High temperatures.

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* *Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.*

ISSN 2179-3956

1 INTRODUCTION

Historically, tungsten carbide (WC) has dominated the market for wear resistant materials including cutting tool materials. Hard metals and tungsten carbide stand synonymously with wear resistance.

Approximately 80% of the global tungsten production is mined in China, yielding an annual total of 75.000 tons. Niobium, a refractory metal like tungsten, offers a possibility in partially or even fully substituting tungsten in hard metals, thermally sprayed coatings, claddings and wear resistant castings. The monocarbide NbC has a melting point of 3.520°C in comparison to the 2.870°C of WC.

Although niobium carbide has been well known for decades, knowledge of its property profile remained limited. Its poor sintering ability and very high sintering temperatures may explain why little research has been done on this material. These obstacles can now be overcomed by either hot pressing, high-frequency induction heated sintering or by plasma-spark sintering (SPS). On the other hand, demand for niobium has increased significantly over the last 45 years to a volume of ~85.000 tons, particularly as a micro-alloying element in high strength structural and automotive steels, stainless steels and alloys for petrochemical industry. In such alloys, niobium forms dispersed micro- or nano-sized niobium carbide precipitates, controlling the microstructure and thus improving mechanical properties [1,2] and the resistance against hydrogen embrittlement.

Yet, mechanical and particularly tribological properties of NbC remain largely unexplored. From an a priori contemplation, NbC is expected to be superior to WC in cutting tool applications, because at 1.225°C NbC is nearly insoluble in Cr, Ni, Co or Fe [3,4], whereas WC is fully soluble under the same conditions. The high solubility of WC in these metals is responsible for the chemical wear of WC.

Recent studies [5] on hot-pressed (binderless) NbC (HP-NbC1) indicated, that pure niobium carbide has a high intrinsic wear resistance, when benchmarked against different ceramics, cermets, hard metals and thermally sprayed coatings. HP-NbC as such is quite brittle. Consequently, the addition of cobalt binder will improve properties, such as toughness and strength [6].

2 EXPERIMENTAL PROCEDURE

The binderless and metal bonded NbCs were elaborated using stoichiometric NbC powders. Different types of test samples for tribological and mechanical testing were prepared from disks by means of electrical discharge machining (See Figure 1). The planar surfaces of the tribological samples were finished by lapping or by polishing. The powders for densification of binderless (HP-NbC1) and cobalt as well as Fe_3Al bonded NbC were pure and essentially free of tantalum. The non-commercial powder for HP-NbC1 had a carbon content of 11,45±0,65 wt.-% carbon. The details of the mechanical and metallurgical features for hot-pressed and binderless NbC (HP-NbC1) using NbC powder (d_{90}= 18,12 µm) from CBMM are disseminated in reference [5]. A commercial powder from Treibacher AG (NbC100, Austria; FSSS= 1,18 µm; 11,4±0,7 wt.-%.carbon) was used for the metal bonded NbCs.

The route of preparation of the NbC grades are detailed in the references [5-7] as well as the 4-point bending strengths. Application of SPS technology allowed reducing the sintering temperature (from 2.150°C for hot-pressing to 1.280°C) and sintering time

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TriboBR 2014
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(from 4 h to 4 min.), as will be shown in the present paper. The Figure 2 presents the microstructures and the phase composition by X-ray diffraction (XRD).

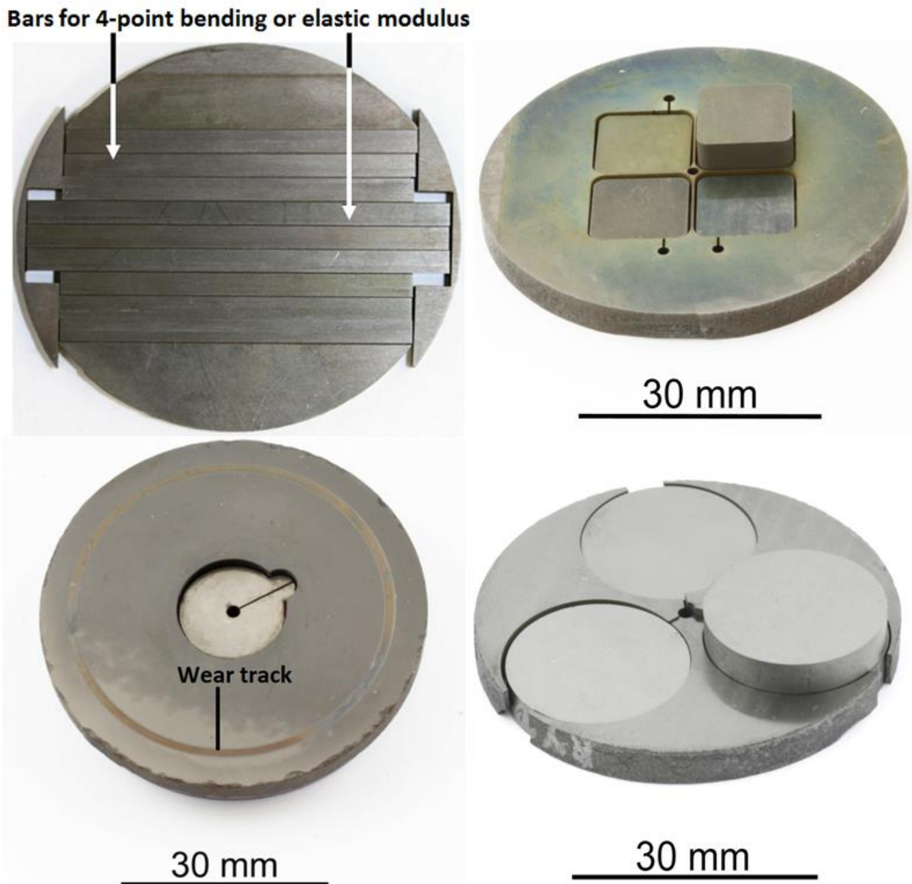

Figure 1. Different samples machined by electro-discharge from disks; top: left for mechanical testing and right for cutting inserts; bottom: left for continuous and right for oscillating sliding.

Bonding NbC with cobalt resulted in an average micro-hardness of 1.412 ± 51 HV0.2 for NbC-8Co and 1.410 ± 13 HV0.2 for NbC-12Co. Micro-hardness is considerably higher in NbC-12Fe_3Al (1.633 ± 50 HV0.2) and in HP-NbC1 (1.681 ± 92 HV0.2) [5-7]. When performing HV5 measurements the Fe_3Al as intermetallic phase bonded NbC-12Fe_3Al appears to have a higher hardness (1.448 ± 32 HV5) than the binderless HP-NbC1 (1.380 ± 35 HV5) as seen in references [5-7]. NbC-based hard metal bonded with 12 vol.-% of Fe_3Al resulted in a higher hardness level than for 12 vol.-% cobalt at any indentation load. The NbC grades showed a strong load influence of micro-hardness for binderless NbC, which is well established in literature and similarly applies for WC, W_2C, V_8C_7 or Mo_2C [7]. The effect is due to plastic deformation at room temperature under indentation via dislocation movements. In cubic carbides [8], the motion of dislocations occurs along the {111} planes in the direction ⟨110⟩.
The WC-6Ni (E204; C7P) used for comparison in the oscillating tests was from Sandvik Hard Materials and had a micro-hardness of 1.482 ± 40 HV 0.2.

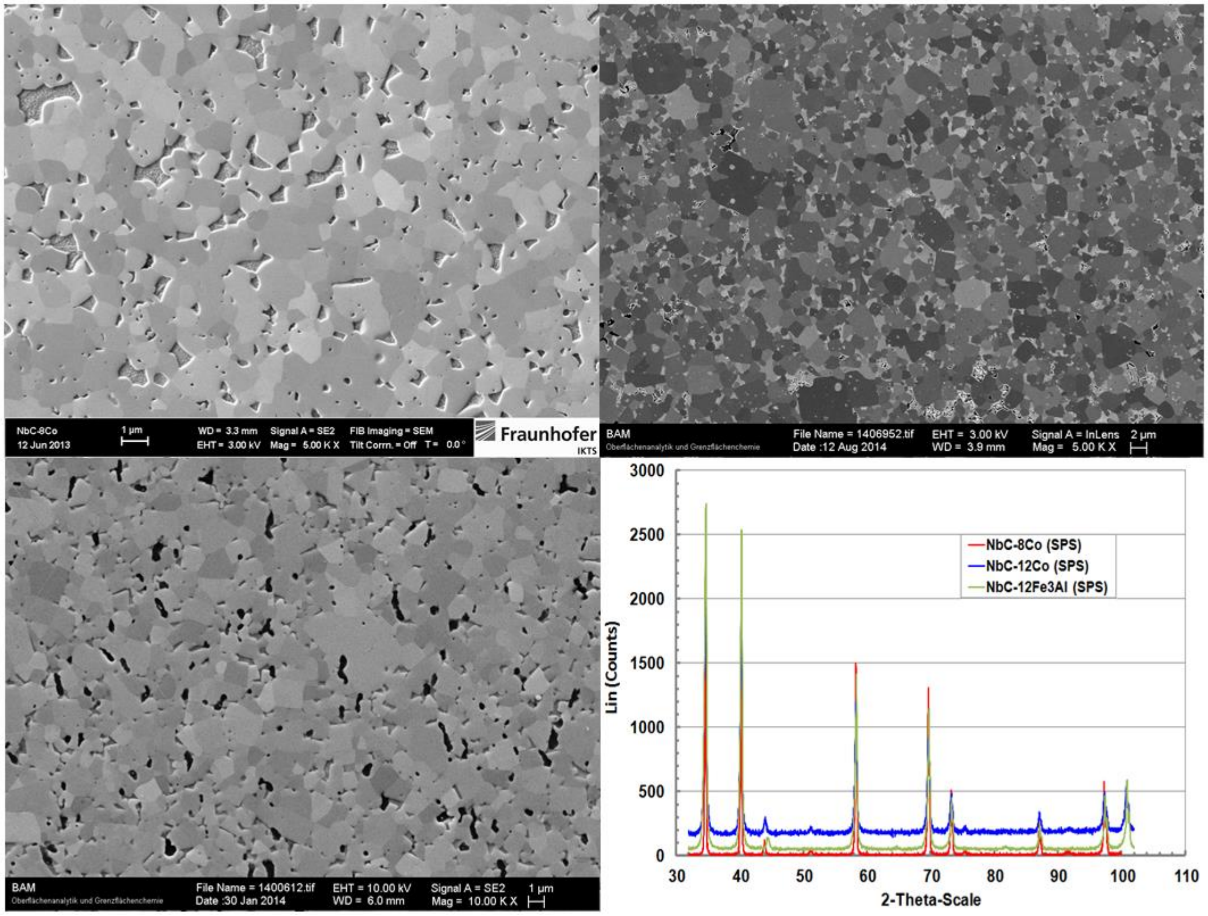

Figure 2. Microstructure of NbC-8Co (FESEM, top left), of NbC-12Co (top right) and of NbC-12Fe_3Al (SEM, bottom left) and XRD diffraction diagrams (bottom right) of bonded NbCs (NbC-8Co, NbC-12Co and NbC-12Fe_3Al)**.**

The tribometers for unidirectional sliding [9,10] and oscillating [11] sliding are proprietary developments of BAM and the details are disclosed elsewhere. They comply with ASTM G99 (DIN 50324) and with DIN EN 1071-13:2010. Sintered alumina (99,7%) bodies were used as stationary spherical (toroids with R_1= 21 mm and R_2= 21 mm) specimens with polished surfaces (R_{pk}= 0,019 µm), which were pressed against the planar surfaces of the rotating NbC. The polished balls (∅=10 mm; alumina 99.7% or 100Cr6H= SAE E52100) oscillated on top of a disk in the oscillating tribometer. The wear volumes of stationary and rotating/oscillating specimen were calculated from stylus profilometry and the wear scar diameters by using ASTM D7755-11. The wear rate k_v is defined as the ratio of volumetric wear to the product of load F_n and the sliding distance s. The coefficient of friction (CoF) and the total linear wear of both tribo-elements (specimen) 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, except at specific points.

3 TRIBOLOGICAL RESULTS

The following tribological data under dry friction were compared with homologous results issued from the tribological data base TRIBOCOLLECT of BAM for thermally sprayed

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ISSN 2179-3956

coatings [10,12], self-mated ceramics, ceramic composites [13] and steels as well as mated with stationary specimen in alumina. The tribological characteristics of these materials are summarized in [14]. The colored areas indicate the ranges established with different grades of the indicated material system.

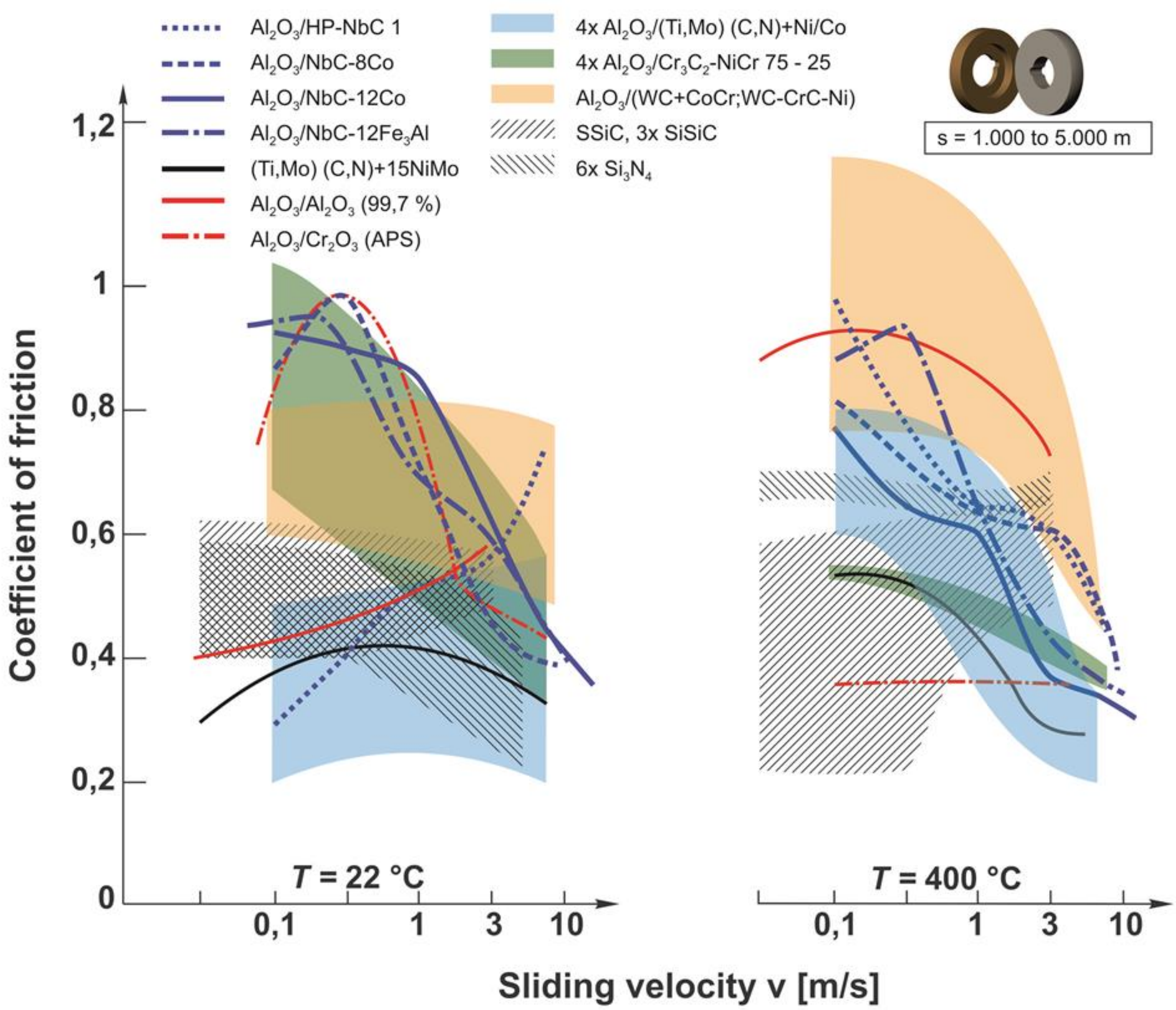

Figure 3. Coefficient of friction of HP-NbC1 and of cobalt or Fe_3Al bonded NbCs compared to different ceramics and hard metals [9,12,14] under dry friction at RT and 400°C.

3.1 Dry Sliding

The frictional level of NbC grades in Figure 3 compares well with different tungsten carbide based or Cr_2C_3–based hard metals or monolithic alumina and thus qualifies these for traction & frictional applications rather than for low friction bearings. At RT, the friction of HP-NbC1 increased with increasing sliding speeds, whereas metal bonded NbCs presented an opposite trend, where the tribo-oxidation of the binders dominated. At 400°C, the friction decreased for all NbC grades and hard metal grades with increasing sliding speed, but were on average lower than those for WC grades. The friction of NbC grades at high sliding speeds was lowest at 400°C. Low friction at high sliding speed is a favorable property for a cutting tool, reducing the cutting forces, thus achieving a given cutting performance at reduced machine power.

Figure 4 illuminates the total wear rate (sum of stationary (Al_2O_3) and rotating (NbC) specimen). HP-NbC1 comprised a particularly high wear resistance, especially at RT, which is more or less independent of sliding velocity. The wear resistance of HP-NbC1 at RT and low speeds is one of the highest. The metal bonded NbC grades at RT displayed a rather constant evolution of the wear rate with increasing sliding speed. The wear rates of the metal bonded NbCs decreased with sliding speed by one order of magnitude to low wear rates at high sliding speeds. At 8 m/s at RT, the wear rates k_v of the rotating disk in NbC-8Co were outstandingly low with k_V= 4,4/7,8·10^{-7} mm³/N·m, when compared to all other ceramics and hard metals. The wear rates of the rotating disks made from NbC-12Co reached values of k_V= 9,6·10^{-7} mm³/N·m at RT and 12 m/s.
At 400°C, the dry sliding wear resistances of tribo-active materials ($Ti_{n-2}Cr_2O_{2n-1}$-phases, (Ti,Mo)(C,N)), binderless HP-NbC1, metal bonded NbCs and thermally sprayed Cr_2O_3 or WC-based hard metals ranged between 10^{-7} mm³/N·m to 5·10^{-6} mm³/N·m on a level known from the regime of mixed/boundary lubrication. Wear resistance under dry sliding of NbC grades is better than that of Cr_3C_2 and similar to or better than that of WC-based systems.
The load carrying capacity expressed as P·V values (contact pressure times sliding velocity), for all NbC grades increased at room temperature from 1-2 MPa·m/s at 0,1 m/s up to 100 MPa·m/s above 8,0 m/s, because tribo-oxidation was enhanced with increasing sliding speed (or generated frictional heat). In contrast at 400°C, the P·V values ranged more or less on the same level as at RT. It is remarkable that the P·V values, or μ·P·V, of these NbC grades increase with increasing sliding speed. NbC presented an unusually high load carrying capacity [6,7].
Normally, the P·V values [15] of dry sliding couples decreased with increasing sliding speed. Triboactive materials [10,12], like $Ti_{n-2}Cr_2O_{2n-1}$ and (Ti,Mo)(C,N), represent the nearest neighbor to NbC grades having slightly lower P·V values or maximum frictional heat flows. It has to be taken into consideration that NbC has a very high melting point (3.522°C). Hot-pressed Nb_2O_5 is relatively soft and likely formed by tribo-oxidation on the NbC, having a hardness of only 500 HV0.2 and has a melting temperature of 1.512°C without sublimating. In contrast, WO_3 formed by tribo-oxidation on WC begins to sublimate above 800°C.
As can be seen in Figure 4, the wear resistance of cobalt and Fe_3Al bonded NbCs at RT and high sliding velocities are the highest. The high melting point of NbC and of Nb_2O_5, when compared with WC and the sublimation of WO_3, represent a tribological advantage under high temperature conditions at the cutting edge of a tool according to the shown wear resistances.
The wear tracks of HP-NbC1 obtained at RT and 400°C are represented in reference [5]. NbC is a beneficial material for closed tribosystems under dry sliding, because no wear particles visibly agglomerated in the wear tracks. The observation, that no agglomerates were found in the wear tracks is in line with the low wear rates of 10^{-6} mm³/N·m.

ISSN 2179-3956

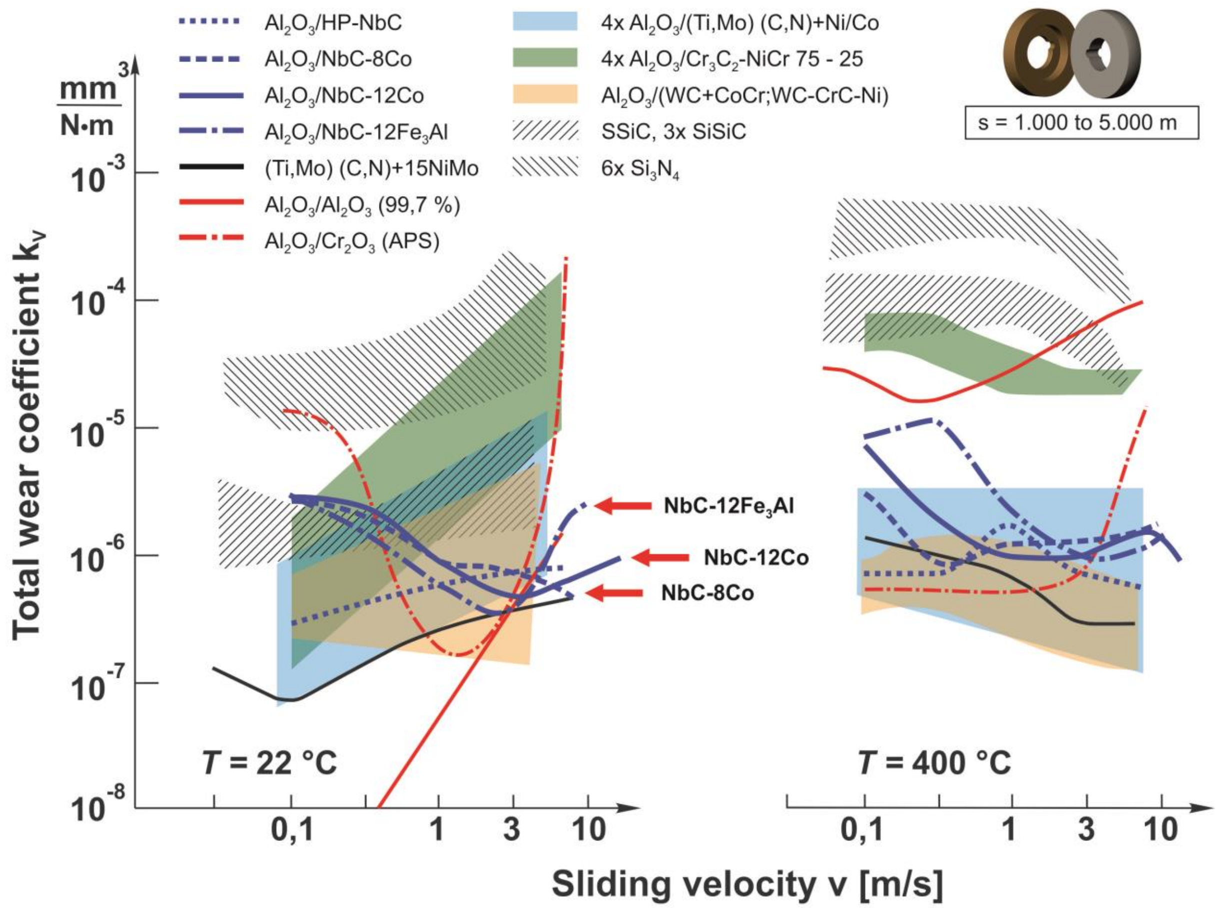

Figure 4. Total wear rates (right) of HP-NbC1 and of cobalt or Fe_3Al bonded NbCs compared to different ceramics and hard metals [9,12,14] under dry friction at RT and 400°C

3.2 Dry Oscillation

The tribological profile (wear rate as "K_V" versus coefficient of friction as "CoF") is displayed separately for polished counterbodies of alumina in Figure 5 and for ball bearing steel (100Cr6, SAE E52100) in Figure 6. The arrows indicate the effect of increasing the relative humidity from 2% to 98%. The tribological profiles of steels and the ceramic samples including WC-6Ni, HP-NbC1 as well as cobalt and Fe_3Al bonded NbCs are sensitive to relative humidity. The degree and the trend depend on the counterpart either in the case of the polished alumina ball (∅= 10 mm) or of the polished 100Cr6 (∅= 10 mm). In contrast, the wear rates and coefficients of friction of binderless NbC (here: HP-NbC1) are practically insensitive to relative humidity when oscillating against 100Cr6. In 100Cr6 steel or other ferrous alloys, tribo-oxidative [16] formation of Fe_2O_3 and/or hydrolyzed to α-, β- or γ-FeOOH and $Fe(OH)_2$ dominate under dry oscillation at RT. Generally, and 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} mm³/N·m.

ISSN 2179-3956

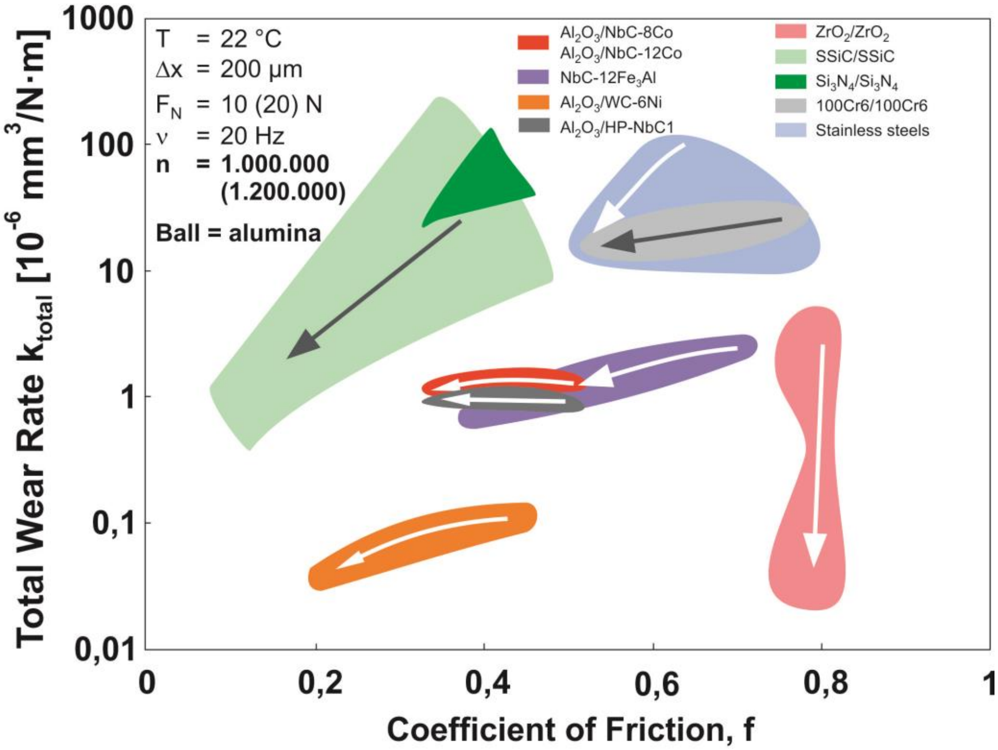

Figure 5. Total wear rates with the associated coefficient of friction of (balls= alumina) dry oscillation of different materials with the influence of the relative humidity

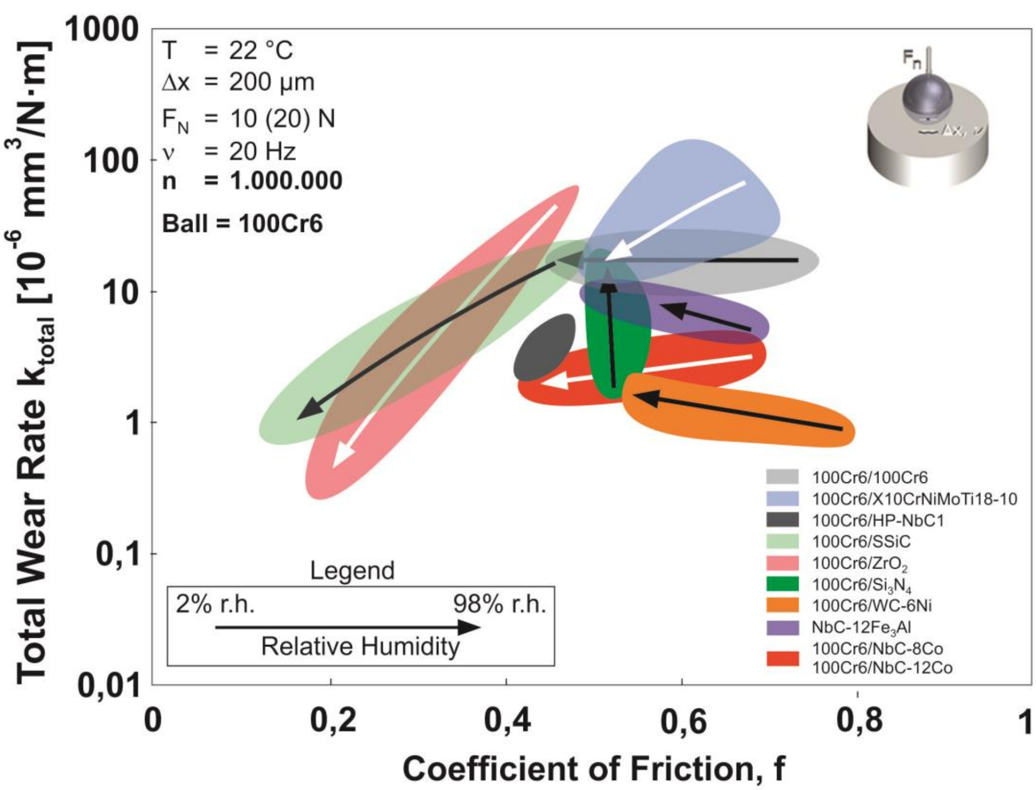

Figure 6. Total wear rates with the associated coefficient of friction (balls= 100Cr6) under dry oscillation of different materials with the influence of the relative humidity.

ISSN 2179-3956

The wear rates under dry oscillation of binderless NbC (HP-NbC1) and the cobalt bonded NbC grades are quite similar.
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. The coefficient of friction decreases under increasing relative humidity. The wear rates remain unchanged for cobalt bonded NbC. The Fe_3Al binder further enhanced the influence of relative humidity on friction.

4 CONCLUSIONS

The wear resistance presented by binderless NbC and NbC grades bonded by cobalt or ironaluminide (Fe_3Al) can easily compete with that of ceramics, “triboactive” materials and hard metals. Thus NbC qualifies as a member of the group of tribological materials with enhanced wear resistance. The room temperature wear rates of different NbC grades are low and less sensitive to increasing sliding speed. Remarkably, increasing sliding speeds to 8,0 m/s and above decreases the wear rate down to outstandingly low values of k_V of 2-7·10^{-7} mm³/N·m. The wear rates at 400°C of NbC grades generally remained below 10^{-6} mm³/N·m, regardless of the applied sliding speed. The low wear rates of NbC were associated with high load carrying capacities (P·V-values), in excess of 100 MPa·m/s. The P·V values increase with increasing sliding speed. Under dry oscillation, the wear resistance of binderles NbC was insensitive to relative humidity for bearing steel (100Cr6=SAE E52100) as well as alumina counterbodies, whereas the coefficient of friction of metal bonded NbC grades was reduced with increasing relative humidity indicating the impact or cobalt and Fe_3Al binders. The low solubility of NbC in metals [3,4] and the high P·V values are an ideal prerequisite for cutting tool materials. Furthermore, the achieved level in hardness and elastic modulus as well as the actual level in strength and toughness are sufficient to support the load at the cutting edge.

Acknowledgements

The assistance of Ms. Christine Neumann and Mr. Norbert Köhler for performing the tribological tests and profilometric analysis as well as of Mr. Steffen Glaubitz for the mechanical testing is gratefully acknowledged. Many thanks are addressed to Ms. Sigrid Binkowski, Ms. Sigrid Benemann and Mr. Maximilian Scheibe for carefully performing metallography, recording optical and SEM micrographs, as well as XRD. The authors are deeply indebted to Dr. Shuigen Huang from KU Leuven (Belgium) for producing the disks. The authors are grateful to Companhia Brasileira de Metallurgia e Mineração (CBMM), São Paulo, Brazil, for supporting this intensive test campaign.

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** Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.*

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