Densification and tribological profile of niobium oxide

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ABSTRACT

The origin of the intrinsic wear resistance of NbC-based materials is investigated through an assessment of the tribological performance of fully dense, crack-free spark plasma sintered Nb_2O_5 (here as a reduced polymorph: monoclinic $Nb_{12}O_{29}$ or $NbO_{2.416}$). The most likely wear mechanism on NbC is the tribo-oxidation to Nb_2O_5. The unlubricated (dry) friction and wear behavior of alumina (99.7%) mated against rotating disks of crack-free niobium(V)oxide (Nb_2O_5) under unidirectional sliding (0.03–10 m/s; 22 °C and 400 °C) and oscillation ($f=20$ Hz, dx=200 mm, 2/50/98% rel. humidity, $n=10^5/10^6$ cycles) will be presented. The microstructure and mechanical properties of the crack-free Nb_2O_5 are assessed. The tribological data obtained are benchmarked with different NbC grades, ceramics, cermets and thermally sprayed coatings.

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1. Introduction

Niobium carbide has, more recently, attracted attention for the purposes of wear protection, because it has shown an outstanding level of wear resistance [1] and represents a strategic alternative to tungsten carbide. Niobium oxides are formed on the surface of NbC by oxidation and/or tribo-oxidation. The tribological properties of niobium oxide are, thus far, unexplored. The aim of the present paper is to explore the contribution of niobium oxide to the tribological profile of niobium carbide by using monolithic niobium oxide specimens. The tribological properties of different NbC grades are shown for comparison from reference [1]. Niobium oxides are formed as films by tribo-oxidation on NbC. Thus, the contribution of niobium oxide to the tribological profile of niobium carbide by using monolithic and crack-free niobium oxide is of scientific interest and has model character. A similar approach was performed by Woydt [2] in order to quantify the contribution of monolithic Magnéli-type phases of titania (Ti_nO_{2n-1}, $4 \leq n \leq 19$) on the tribology of titanium based coatings and (Ti,Mo)(C,N) based hard metals. Surface analysis results proving the formation of specific oxides do not generate any tribological data. By synthesis of monolithic Magnéli-type phases of titania or of slightly sub-stoichiometric Nb_2O_5 in the present paper generates experimental data on the tribological profile of oxides, which are similar to those

triboxidatively formed. They are model substances to prove, if the tribo-oxidatively formed oxides have a contribution to the tribological behavior of the NbC or non-oxide cermets.

Nb_2O_5 has a melting point of 1522 °C without any tendency to sublimate. On the other hand, niobium oxide appears immediately after the extraction processes with attractive costs and can also be converted to niobium carbide by carbothermal reduction and carburization. Niobium(V)oxide is fully REACH-registered and no notifications for H341 (suspected of causing genetic defects), H350 (may cause cancer when inhaled), H351 (suspected of causing cancer) or H360 (may damage fertility or the unborn child) were filed to date.

2. Crystal structures of pentavalent niobium as binary oxide

The ideal or undistorted structure of Nb_2O_5 can be broken up into two groups of octahedron. The blocks are composed of NbO_6-octahedra arranged in groups of 3×3 and 3×4, sharing octahedron edges with each other. These blocks enable different local arrangements within the crystal. Unshared block corners define tunnels of tetrahedral sites in a kind of "defect". Grühn et al. [3] also showed the presence of 2×5 blocks in Nb_2O_5 using TEM.

In consequence, many different polymorphic modifications of Nb_2O_5 exist in the stoichiometry range as NbO_x between $2.40 < x < 2.50$, as shown in the binary phase diagram of Naito et al. [4]. At least four different block-structures [5] of

stoichiometric Nb_2O_5 were identified by crystal structure determination and illuminate the polymorphism of Nb_2O_5 [6]:

$H-$, $M-$, $N-$ and $T- Nb_2O_5$.

The crystallographic density of monoclinic and stoichiometric $N-Nb_2O_5$ (or $\alpha-Nb_2O_5$) is 4.55 g/cm³. The $H-Nb_2O_5$ ("Hochform" or high temperature phase) has a crystallographic density of 4.52 g/cm³, but is sub-stoichiometric as $Nb_{28}O_{70}$. The crystallographic density of tetragonal $M-Nb_2O_5$ (denoted as "β") determined by Mertin et al. [7] was 4.4 g/cm³ and consists of 4×4-blocks of NbO_6-octahedra. The crystallographic density of $T-Nb_2O_5$ determined by Kato [8] et al. at 5.236 g/cm³ and by Holtzberg [6] et al. at 5.17 g/cm³ (denoted as $\gamma-Nb_2O_5$) is greater than that of $\alpha-Nb_2O_5$. $\zeta-Nb_2O_5$ is another monoclinic phase reported by Laves [9] et al. with a crystallographic density of 5.29 g/cm³, which is homolog to the "$B-Nb_2O_5$" reported by Schäfer [10] et al. Stoichiometric and monoclinic Nb_2O_5 is the member with $n=9$ of a possible series of structural homologs [11] expressed by $Nb_{3n+1}O_{8n-2}$. Based upon this principle, these homologs will only arise when n is odd. Hypothetical sub-stoichiometric phases as structural homologs to Nb_2O_5 can be assumed to have the same symmetry and unit cell dimensions when $n=7$ and $n=5$, which results in the compounds $Nb_{22}O_{54}$ ($NbO_{2.454}$) and $Nb_{16}O_{38}$ ($NbO_{2.375}$). This complicates the phase analysis by diffraction techniques.

$Nb_{22}O_{54}$ ($n=7$, $NbO_{2.45}$) and $o-Nb_{12}O_{29}$ ($n=4$, orthorhombic, $NbO_{2.42}$) are two examples of reduced Nb_2O_5 and share a common motif [12] of symmetry-equivalent 4×3 blocks of corner sharing NbO_6 octahedra, whereas 3×3 blocks are also present in $Nb_{22}O_{54}$. Grühn et al. [3,13] illuminated that in $Nb_{12}O_{29}$ the 3×4 blocks can be linked to an orthorhombic or monoclinic symmetry. Reduced Nb_2O_5 contains some fraction of reduced Nb^{4+} ($4d^1$ atoms), enabling electrical conductivity and paramagnetism, which allows it to be machined by electrical discharge machining.

3. Experimental

3.1. Materials

The high purity Nb_2O_5 powder (CBMM spec HP311 (AD4796), Brazil) had a granulometry of $d_{50}=28.44$ μm and $d_{90}=55.53$ μm. Disks of 60 mm in diameter and 5 mm in height were hot-pressed (HP) at 1350 °C for 1 h under 30 MPa to a density of 4.52 g/cm³. These disks had a black color and were electrically conductive (sufficient for EDM machining). Even transparent light micrographs could be made (see Fig. 1). The density of monoclinic and stoichiometric Nb_2O_5 (or $\alpha-Nb_2O_5$) as confirmed by XRD is 4.55 g/cm³. The hot-pressed Nb_2O_5 had transgranular cracks as shown in Fig. 1. This internal fracture and micro-cracking in the polycrystalline microstructure is explained by the mismatch in the

thermal expansion, when crystals with significantly different thermal expansion coefficients meet and form grain boundaries.

The average coefficients of thermal expansion [14] for monoclinic Nb_2O_5 in the three crystallographic room directions for describing the anisotropy are:

$a=+5.25 \pm 1$ ppm/K, $b=0 \pm 1$ ppm/K and $c=+5.87 \pm 1$ ppm/K as well as per volume $V=+11.2 \pm 2$ ppm/K.

In consequence, these hot-pressed samples were not tribologically characterized, because they had a pronounced network of micro-cracks, which cannot support shear stresses. This increases wear and will wrap a tentative or existing contribution of Nb_2O_5 to the wear resistance of NbC.

It is therefore likely to reduce the micro-crack formation by reducing grain size and by reducing the temperature for densification. The refinement of CBMM's optical grade OG350 powder was executed in a fluidized bed opposed jet mill (100 AFG) using ceramic wheels, resulting in a granulometry of $d_{10}=0.45$ μm, $d_{50}=5.1$ μm and $d_{90}=41.3$ μm. Disks of 56 mm in diameter and 5 mm in height were spark plasma sintered (SPS) in a graphite die/punch setup at 1075 °C for 6 min under 30 MPa to a density of 4.50 g/cm³. The microstructure of the SPS sintered Nb_2O_5 is crack-free as a result of a significant reduction in grain size. The micrographs, taken at several positions and all magnifications using LOM and SEM (see Fig. 2), revealed practically no defects or voids.

3.2. Phase composition

The crystallographic structure of crack-free Nb_2O_5 was determined by means of electron back scattering diffraction (EBSD). Depending on the metallographic preparation, 60–80% of the pattern (See Fig. 3) could be indexed by using EBSD as monoclinic $Nb_{12}O_{29}$ ($NbO_{2.4167}$; crystallographic density=4.5789 g/cm³), whereas the remaining difference could be assigned to a crystallographic structure pre-existing the data base. By using this crystallographic density, the crack-free Nb_2O_5 was SPS sintered up to 98.2% of the theoretical density. The stoichiometry of the initial $NbO_{2.50}$ was reduced to $NbO_{2.4167}$ during SPS in a vacuum (~ 8 Pa) and graphite dies. All present SPS sintered Nb_2O_5 specimen must be sub-stoichiometric, because they were black in color and electrically conductive. Reduced Nb_2O contains some fraction of reduced Nb^{4+} ($4d^1$ atoms) in order to accommodate the oxygen deficiency, thereby enabling electrical conductivity and becomes paramagnetic.

Scanning Transmission Electron Microscopy (STEM) still revealed some remaining micro-cracks that were not visible in LOM. In consequence, by avoiding these micro-cracks in future, further improvements of the four point bending strengths (See Fig. 7) are likely. Micro-domains, already seen by EBSD (See Figs. 2 and 3), were present in the grains. Micro-twins (See Fig. 4,
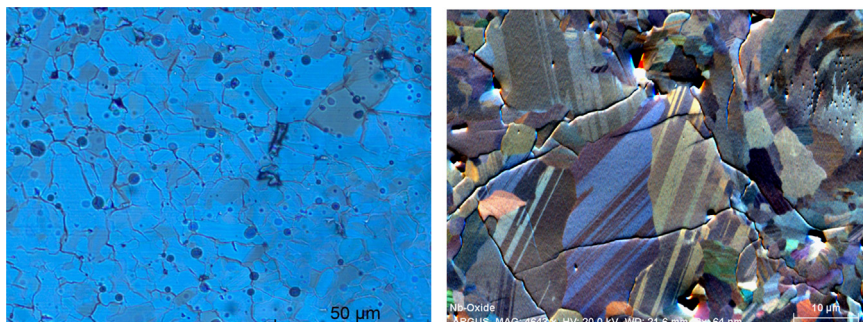

Fig. 1. Microstructure of Nb_2O_5 (Hot pressed 1 h under 30 MPa at 1350 °C, 10 K/min) with micro-cracks (left: transmitted optical light image; right: orientation contrast in color SEM using a force scattered detector).