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Influence of tantalum on the microstructure and properties of Ti(C,N)-Ni cermets

Melisha Naidoo [a], Oluwagbenga Johnson [b], Iakovos Sigalas [a,*], Mathias Herrmann [c]

[a] School of Chemical and Metallurgical Engineering, University of the Witwatersrand, 2050 Johannesburg, South Africa
[b] Department of Mining and Metallurgical Engineering, University of Namibia, Ongwediva Campus, P. O. Box 3624, Namibia
[c] IKTS, Fraunhofer Institute for Ceramic Technology and Systems, 01277 Dresden, Germany

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ABSTRACT

Several (Ti,Ta)(C,N) cermets were prepared from Ti(C,N) and Ta powder with or without Ni. For comparison, Ti(C,N) with Ni were also prepared. The mixed powders were sintered at 1400–1500 °C by FAST/SPS up to a density higher than 99% theoretical density. The addition of Ta delays densification of Ti(C,N)-Ni cermets due to the formation of intermetallic phases. During sintering, the Ta was incorporated into the Ti(C,N), forming solid solution, thus changing the core-rim structure of the Ti(C,N) cermets. On the other hand, the Ta additions result in grain refinement and improved hardness (from 16.1 GPa to 17.8 GPa) and fracture toughness (from 5.5 MPa.m$^{1/2}$ to 6.9 MPa.m$^{1/2}$).

1. Introduction

Titanium carbonitrides are widely used as the hard phase in sintered ceramic-metal (cermet) composites and protective coatings on conventional hard metal cutting tools. Their excellent and unique combination of physical properties such as high melting point, hardness, thermal conductivity, wear resistance and good chemical and thermal stability make this family of structural and wear-resistant materials particularly attractive for metal machining applications [1–6]. These materials, when used in cutting tool applications, ensure excellent chip resistance and tolerance control [7].

In the production of titanium carbonitride-based cermets, the starting materials are typically Ti(C,N) and a metal binder that is usually Ni, Co, or a combination of the two. Ti(C,N) cermets possess a fine-grained, stable microstructure, in which the equiaxed fine grains of the hard phase are embedded in the tough metallic binder. The typical microstructure of Ti(C,N)-based cermets display core-rim morphology, which enhances wetting of the carbonitrides to the metal binder and inhibits the coalescence and growth of the carbonitride grains during sintering [1,2,8]. Generally, the cores are partially dissolved raw particles on which the rim structures have grown through dissolution-reprecipitation processes. Typically the undissolved Ti(C,N) cores are responsible for excellent wear resistance, while crack interactions between the solid solution rim structure and the binder phase determine the cermets' toughness and integrity [9]. For industrially important cermets, additions of transition metal carbides have become standard practice during manufacturing. These additions form carbonitride solid solutions which improve the sinterability, high-temperature hardness, and thermal shock resistance of the hard phase.

The effect of Ta on Ti(C,N)-based ceramic materials and hard metals has been reported in the literature. Kang and co-workers [10] investigated the effect of TaC and other carbides on the microstructure and mechanical properties of Ti(C,N). They found that cubic carbide forming additives yielded a coarser microstructure than additives, forming hexagonal carbides. This was reflected in the mechanical properties in that the cubic carbide forming additives resulted in lower hardness and higher fracture toughness. Tret'yakov and Mashevskaya [11] reported on the effect of Ta in the Ti(C,N)-Ni-Mo-WC system. They found that addition of Ta increased the bending strength and explained this by the formation of a complex carbonitride phase of high strength. In a conclusive remark it was recommended to use complex Ta-containing carbonitride raw materials for manufacturing the mentioned alloys. Lindahl et al. [12] showed that this complex carbonitride phase is formed during liquid-phase sintering.

Rolander et al. [13] investigated the effect of tantalum additions on the properties of (Ti-W) (C,N)-Co cermets used during machining process. They found that Ta additions enhanced the materials' resistance to plastic deformation and consequently reduced flank wear during metal cutting. They suggested that Ta influenced the interfacial energies of the system, thereby giving a stronger hard phase skeleton which increased the materials resistance to plastic deformation. The present study evaluates the effect of tantalum addition on the microstructure-property relationship of Ti(C,N)-Ni cermets.

* Corresponding author.
E-mail address: Iakovos.Sigalas@wits.ac.za (I. Sigalas).

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2. Experimental

The powders used to obtain the (Ti,Ta)-carbonitride solid solution were $TiC_{0.7}$ $N_{0.3}$ (Grade B; 1.3 – 2 μm; H.C. Starck), Ta (1–5 μm; Speciality Metals (Pty) Ltd) and Ni (grain size: d_{50} = 25 μm; d_{90} = 50 μm; Alfa Aesar). Two kinds of cermets were prepared: a) $TiC_{0.7}$ $N_{0.3}$ and Ta (in a mass ratio of 60:40 wt%) with and without Ni binder (5, 10 wt%), and b) $TiC_{0.7}$ $N_{0.3}$ cermets containing Ni (10 wt%) only. The latter was done for comparison purposes.

The powder mixtures were wet milled in a Fritsch Pulverisette-5 ball mill, in isopropanol for 3 h, at a rotational speed of 300 rpm. Milling was performed using WC milling pots and 3 mm diameter grinding balls, with a 10:1 ball-to-powder weight ratio. Steric acid (3 wt%) was added to the initial powder mixture as a process control agent. The oxygen content of the starting TiCN powder was 0.6 wt% (TCH 600, LECO combustion analyzer). The materials were densified using a SPS furnace (model HPD 25/1, FCT Systeme GmbH, Germany) under vacuum, at a pressure of 30 MPa and a heating rate of 200 K/minute in graphite dies. Between 1300 K and 100 K below the final temperature the heating rate was reduced to 100 K/minute in order to avoid an overshooting of the sintering temperature. The isothermal holding time was 5 minute.

Samples were prepared for scanning electron microscopy (SEM), hardness and fracture toughness determination by cold mounting in resin, and preparing metallographically down to 1 μm. The microstructures were characterized by scanning electron microscopy (SEM) using a Philips XL 30 ESEM-FEG series, with an EDX detector. The phases present were determined by X-ray diffraction (XRD) using a Bruker AXS D2 phaser desktop powder diffractometer with monochromatic Cu Kα radiation produced at 30 kV and 10 mA, with a step size of 0.03 °2θ. Changes in the Ti(C,N) lattice parameter were determined from the interplanar spacing by a least squares fit.

Density was determined by Archimedes principle, and the hardness and fracture toughness were measured using Vickers indentation technique at an indentation load of 5 Kg. For toughness estimation, the radial crack length around the Vickers indentation was measured and the Shetty formula [14] was applied. At least five indentations were taken and the reported values were the average of the measured values.

3. Results

The sintering conditions and the density of the cermets are given in Table 1. The densities obtained for Cermets 1 and 2 were lower than for the other samples. Since these samples contained higher binder contents, a higher volume of the liquid phase was produced during sintering. Due to the applied pressure and the relatively high sintering temperature (1500 °C), the liquid phase was partially squeezed out. To avoid this, for Cermets 2 and 3 the amount of Ni binder was reduced to 5 wt% and the densification temperature was also reduced. Under these conditions, no liquid exudation was observed and full densification was obtained.

Fig. 1 shows the densification curves of Cermets 3–5. These curves display significantly different sintering behaviour as a result of the different starting compositions. For Cermet 5 (TiCN-Ta), densification started at approximately 1200 °C. The shallowness of the gradient indicated that the rate of densification was slow during the heating period. Therefore approximately 40% of the densification occurred during the isothermal sintering period. The addition of Ni to the cermet reduced the starting densification temperature, so that for Cermet 3 (TiCN-5Ni) and Cermet 4 (TiCN-Ta-5Ni) densification started earlier at approximately 900 °C and 1100 °C respectively. The rate of densification in these samples was much faster than for Cermet 5, which contained no Ni, as indicated by the greater gradients of the curves. Most of the densification of Cermets 3–5 took place during the heating up period as indicated by the piston displacement curves (Fig. 1). Conversely, the piston displacement curve for Cermet 5 without Ni binder indicated that nearly half of the densification took place during the isothermal sintering period at a 100 °C higher sintering temperature.

The results of the XRD analysis of the cermets are given in Fig. 2 (from International Centre for Diffraction Data (ICSD) card), and showed the absence of the Ta phase peak in Cermet 2 after sintering at 1500 °C. However, for Cermets 4 and 5 the Ta peak was still present but with a distinguishable shift in peak position to higher 2θ by 1.6°. This indicated that Ni and perhaps even Ti, C and N had dissolved into the Ta crystal lattice.

The lattice parameters of the sintered cermets showed an overall increase for Ti(C,N) (Table 2). The greatest increase was observed in the Ta-containing cermets, due to the dissolution of the Ta into the carbonitride with a higher ionic radius (TaC lattice parameter 0.445 nm [15]).

For Cermets 1 and 3, the lattice parameters were only slightly higher than that of the starting Ti(C,N) powder (0.4296 nm). These changes may be due to denitrification during sintering. Denitrification had been reported in literature to occur during reactions between the Ti(C,N) phase and the binder [16]. This was also confirmed by the microstructural observations (Fig. 3).

The microstructures of the different cermets are shown in Fig. 3. In general, the microstructures displayed typical core-rim morphology of Ti(C,N)-based cermets. However, the characteristics of the core-rim observed in terms of size and shape were different, depending on the composition of starting powders and the sintering temperature. In the Ta- free cermets, 1 and 3, the core and rim had differences only in the nitrogen-carbon ratio indicated by EDX. While the rim had an unchanged ratio, the core had reduced nitrogen content.

In the Ta-containing cermets, the core-rim structure is mainly attributed to the formation of the (Ti,Ta)(C,N) solid solution [17]. The micrographs also show strong grain growth at 1500 °C, which is less pronounced for the materials sintered at 1400 °C, and the Ni-free material.

The distribution of the binder phase (bright contrast) in the ceramic phase is different for the different cermets. The micrographs (Fig. 3) show good wetting behaviour for the Ni containing cermets, as is expected, whereas in Cermets 4 and 5 the binder formed more ball-like inclusions, indicating high dihedral angles between the two phases. The microstructure of Cermet 2 with tantalum was similar to the pure Ni cermet. The Ta binder phase in Cermet 2 was probably more brittle

Table 1
Composition and density of Ti(C,N)-based ball-milled cermets. The numbers in the sample's names correspond to the weight % of the additives; the balance is Ti(C,N).

Cermet number	Sample (wt% additive)	Sintering		Density (g/cm^3)	% Theoretical density	Open porosity (%)
		Temp (°C)	Time (min)			
1	TiCN-10Ni	1500	5	5.04	96.2	1.8
2	TiCN-36Ta-10Ni	1500	5	6.70	94.8	2.1
3	TiCN-5Ni	1400	5	5.10	99.5	0.4
4	TiCN-38Ta-5Ni	1400	5	6.92	99.0	0.4
5	TiCN-40Ta	1500	5	6.88	99.6	0.3