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Microstructure and mechanical properties of Ti(C,N)-Mo_2C-(Ni,Co) cermets as a function of their initial chemical composition

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Abstract

The effects of the chemical composition before sintering upon the sintered microstructure of different Ti(C,N)-Mo_2C-(Co,Ni) cermets are studied and analysed from morphological, structural and chemical points of vue. The microstructure is characterised by conventional and analytical TEM and SEM observations. The morphology is investigated by digital image analysis. The mechanical properties are determined by indentation tests and ultrasonic measurements performed at room temperature and by three point bend tests at high temperature. The observed microstructural variations are discussed in relation with the mechanical properties of these materials

Introduction

Two major factors motivate the development of new cutting tool materials : the permanent increase of machining rates and the increase of the mechanical properties of the materials to machine. The carbide or carbonitride based cermets have always find their application fields between the one of the high speed steels and the one of the ceramic inserts. The use of the HSS cutting tools is limited because of the loss of their mechanical properties with the increase of temperature whereas the use of ceramic inserts remains limited by their brittleness. The first association of a carbide phase with a metallic one for cutting tool applications was performed in 1923 [1] with the association of tungsten carbide with cobalt. The WC-Co grades have known numerous developments but are still largely used, particularly for the rough machining and for the interrupted cutting operations. The titanium carbonitride based cermets constitute a promising alternative but their use is today restricted to finishing operations. The cubic Ti(C,N) phases play a predominant role in controling the high temperature behaviour of these materials. The metallic phase has also a critical effect both on the sintering mechanisms and on the mechanical properties of the sintered cermets. The present paper is devoted to the Ti(C,N)-Mo_2C-Co and Ti(C,N)-Mo_2C-Ni systems. Two axis have been considered in these study. The first approach focuses on the relations between the initial composition and the sintered microstructures. The second one focuses on the relations between the sintered microstructures and the mechanical properties in a wide range of temperatures.

Materials

The elaboration of cermets involves processes commonly used both in the ceramic processing and in the powder metallurgy. In the present works, raw material powders have been mixed and milled by attrition in acetone. After an addition of a paraffin wax, the slurry was spray dried and granulated to allow the shaping process by uniaxial pressing. After a debinding treatment, the so-shaped samples were densified by a liquid-phase sintering step. Samples were sintered under a non-oxidising atmosphere at 1450°C with an isothermal dwell of 2 hours. During this isothermal treatment, a 60bars overpressure of argon was applied into the furnace in order to promote the densification.

grade	1	2	3	4	5	6	7	8	9	10	11	12
$TiC_{0.7}N_{0.3}$	87.2	80.6	75.6	90.4	80.3	.	.	.	.	90.9	87.2	80.5
$TiC_{0.5}N_{0.5}$	-	-	-	-	-	87.2	75.6	92.1	90.4	-	-	-
Mo_2C	6.4	6.4	6.4	3.2	13.0	6.4	6.4	1.5	3.2	3.0	6.4	13.0
Co	6.4	13.0	18.0	6.4	6.4	6.4	18.0	6.4	6.4	-	-	-
Ni	-	-	-	-	-	-	-	-	-	6.0	6.4	6.5

Table 1 : Initial compositions of the twelve considered grades of cermets (vol. %)

Twelve compositions (cf. table 1) were sintered and characterised in order to take into account the effects of the C/N ratio in the Ti(C,N) particles, of the Mo content and of the binder content (cobalt or nickel) on the microstructure.

Sintered microstructures

The typical microstructure of Ti(C,N)-Mo_2C-Co (or Ni) cermets after sintering can be seen on figure 1. The hard phase grains exhibit their characteristic core-rim structure and constitute a continuous skeleton. The metallic binder phase (light grey areas on SEM pictures) is located between the hard phase grains. This microstructure can be discussed in relation with the sintering mechanisms of these cermets. After milling and shaping, compacts are made of angular Ti(C,N) particles, and of Mo_2C and Co (or Ni) particles. During the heating, a solid state dissolution of the molybdenum carbide occurs in the metallic phase, as previously described by Yoshimura et al. [2] in nickel bound cermets.

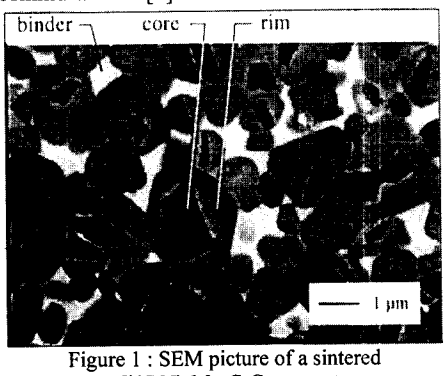

Figure 1 : SEM picture of a sintered Ti(C,N)-Mo_2C-Co cermet

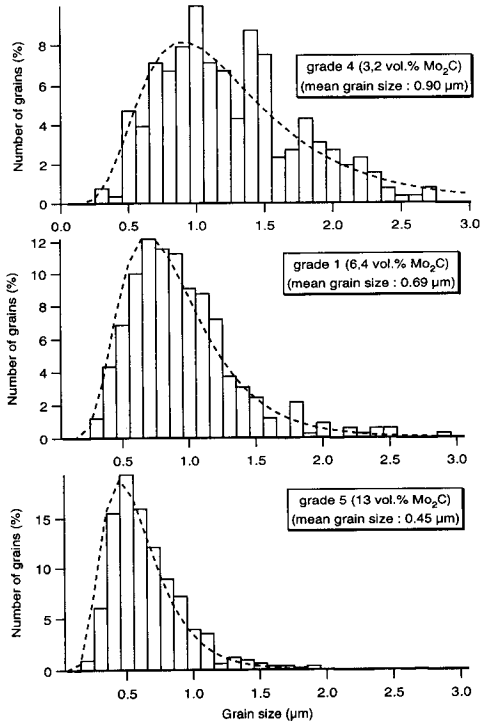

Figure 2 : Core-rim grain size distribution for three grades of cermets

At the sintering temperature, Ti(C,N) particles are embedded in a Co-Mo (or Ni-Mo) liquid phase. After the rearrangement step of the liquid-phase sintering, a dissolution-reprecipitation stage occurs in agreement with the Gibbs-Thomson thermodynamic law. In this second step, dissolution occurs at the solid/liquid interfaces of the small Ti(C,N) particles. Then transport mechanisms occurs by diffusion in the Co-Mo (or Ni-Mo) liquid phase. The precipitation of a (Ti,Mo) carbonitride phase takes place on the large particles at the liquid/solid interfaces, forming a (Ti,Mo)(C,N) rim around the initial Ti(C,N) core. From TEM observations performed on these cermets, and as previously observed by Laoui et al. [3] in nickel cermets, these rims grow epitaxially around the initial Ti(C,N) crystal and no significant variations of the lattice parameters can been measured between the Ti(C,N) cores and the (Ti,Mo)(C,N) rims. Only small misorientations are locally observed at the core-rim interfaces. Dislocations are located in the rims that can accommodate small lattice parameter mismatches between a core and its rim.

In order to quantify the effects of the initial composition variations on the sintered microstructures, image analyses were performed by digital processing. As can be seen on figure 2 for three cobalt cermets (grades 4, 1 and 5), the initial Mo content strongly affects the hard-phase grain size. This confirms the role of grain growth inhibitor played by the molybdenum, an element which was historically introduced to increase the wettability of the Ti(C,N) particles by the liquid metallic phase during sintering [4]. An increase of the initial Mo_2C content leads to a decrease of the hard-phase grain size but also to a decrease of the volumic fraction of (Ti,Mo)(C,N) rims in the material. This has to be related to the solubility variations of Ti(C,N) crystals in liquid Co-Mo alloys (or Ni-Mo alloys) when varying the Mo content in the metallic phase. Such variations in the initial Mo content also induce large modifications in the chemical composition of each phase. As indicated by Electron Dispersive Spectrometry analyses performed in TEM on the materials considered in figure 2, large differences can be measured between the compositions of the metallic binder phase of these three grades (cf. table 2). A large increase of the Mo content in this phase is measured between grades 4 and 5 (from 1.9 wt.% up to 27.1 wt.%). This result is good agreement with the regular lattice expansion (cf. table 2) which is measured in this binder phase by X-ray diffraction (XRD), due to the larger radius of Mo atoms compared with the Co ones. It must be noted from XRD and TEM observations that in this cermets the cobalt binder phase has a face cubic centered crystalline structure. As in the case of WC-Co hardmetals the expansion coefficient mismatch between the hard phase and the binder phase induces at room temperature large residual stresses in the metallic phase. The fcc to hcp transformation which characterises pure cobalt

cannot take place during the post-sintering cooling and the high temperature fcc structure is stabilised. Nevertheless the numerous stacking faults observed in this cobalt phase locally restore an hcp structure (cf. figure 3). Large differences are also observed in the (Ti,Mo)(C,N) rim phase since the Mo content varies from 7.8 at.% up to 30.0 at.% between grades 4 and 5 (cf. table 2). As a confirmation of TEM observations, no significant variations could be measured in the lattice parameter of the FCC structure of the hard phase grains when varying the Mo content.

grade \ characteristics	binder phase composition (at. %)			binder lattice parameter (Å)	rim phase composition (at. %)		core-rim lattice parameter (Å)
	Mo	Ti	Co		Mo	Ti	
grade 4 (3.2vol.%) Mo_2C	1.2	2.5	96.3	3.567	7.8	92.2	4.298
grade 1 (6.4vol.%) Mo_2C	10.1	2.5	87.4	3.580	13.5	86.5	4.297
grade 5 (13vol.%) Mo_2C	18.5	2.1	79.4	3.609	30.0	70.0	4.300

Table 2 : Chemical compositions determined by EDS and lattice parameters determined by XRD for the binder and rim phases of three cermet grades

Grades 1, 2 and 3 were chosen in order to measure the effect of a variation of the binder content on the microstructures and on the mechanical properties. Because of the variation of the initial Mo_2C/Co ratio a Mo enrichment in the binder phase is measured from grade 3 to grade 1 (cf table 3). Varying the initial cobalt content from 6.40 vol.% up to 18 vol.% results naturally in large modifications of the microstructure morphological parameters. In particular an important decrease of the carbonitride contiguity is measured from grade 1 to grade 3 that has large effects on the mechanical properties of cermets. In the present case this contiguity parameter is the ratio of the rim-rim contact surface and of the total rim surface measured by image analysis.

	binder phase composition (at. %)			carbonitride contiguity
	Mo	Ti	Co	
grade 1 (6.4vol.%Co)	10.1	2.5	87.4	0.731
grade 2 (13vol.%Co)	7.7	2.8	89.5	0.573
grade 3 (18vol.%Co)	6.9	2.0	91.1	0.342

Table 3 : Chemical composition determined by EDS of the binder phase and carbonitride contiguity determined by image analysis for three cermet grades

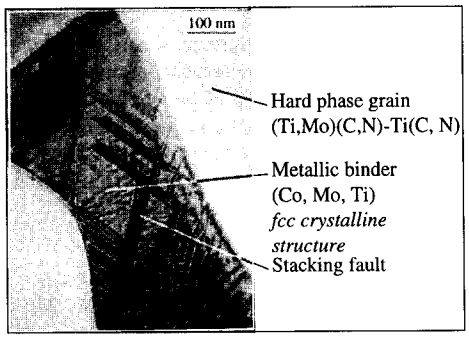

Figure 3 : Bright field TEM picture of the fcc cobalt phase of a Ti(C,N)-Mo_2C-Co cermet

Mechanical properties

Room temperature mechanical properties were investigated by classical ultrasonic pulse-echo measurements and by indentation tests. The Young's modulus E, the shear modulus G and the Poisson ratio ν were so determined from the measurements of the velocity of longitudinal (V_L) and transversal (V_T) ultrasonic waves (with 10MHz transducers) from relations [5] :

$$V_L = \sqrt{\frac{E}{\rho} \cdot \frac{(1-\nu)}{(1+\nu)(1-2\nu)}} \quad (1) \quad \text{and} \quad V_T = \sqrt{\frac{G}{\rho}} \quad (2)$$

where ρ is the density of the material.

The hardness (H_v) and the critical-stress intensity factor K_{1c} were measured from 30kg load Vickers indentation tests. The K_{1c} values were calculated from the measurements of the crack length induced by indentation following the Warren equation [6] :

$$K_{1c} = 0.087 \cdot 9.806 \cdot \sqrt{\frac{H_v \cdot P}{l_t}} \quad (3)$$

where H_v is the hardness (in kg/mm^2), P the load, and l_t the cumulative length of the four indentation cracks (in µm). The results of these investigations are summarised in table 4. Important variations are observed and can be related to the morphological and to the chemical evolutions of each phase (core, rim and binder) as a function of the initial composition. As an example, for the third first grades, the effect of an increase of the cobalt content on the Young's modulus can be seen on figure 4. From Young's modulus values of 480GPa for

TiC [7] and of 210 GPa for cobalt [8], and from the initial volumic fraction of the metallic and carbide-carbonitride phases the Reuss and Voigt limits can be calculated.

grade	1	2	3	4	5	6	7	8	9	10	11	12
E(GPa)	455	436	416	461	449	455	414	462	462	460	452	434
G(GPa)	189	180	171	192	185	188	169	192	192	192	188	179
ν	0.21	0.21	0.22	0.20	0.21	0.21	0.22	0.22	0.21	0.20	0.2	0.22
H_v (kg/mm^2)	1698	1589	1415	1711	1777	1735	1380	1660	1712	1575	1650	1725
K1c (MPa.m$^{1/2}$)	8.41	8.94	9.56	6.76	7.23	6.99	9.40	6.41	6.40	7.70	7.30	7.00

Table 4 : Room temperature mechanical properties of cermets.

Increasing the cobalt content leads to a decrease of the Young's modulus between the two calculated limits. Other important effects of increasing the Co content is the regular decrease of hardness and the increase of toughness. Such a behaviour is observed in cermets and hardmetals and is closely related to the increase of the mean free path of the binder phase. Increasing the Mo and N contents results in the refinement of the microstructures as observed from SEM observations. These observations confirm the important part taken by these two elements in grain growth inhibition during the sintering of Ti(C,N) based cermets.

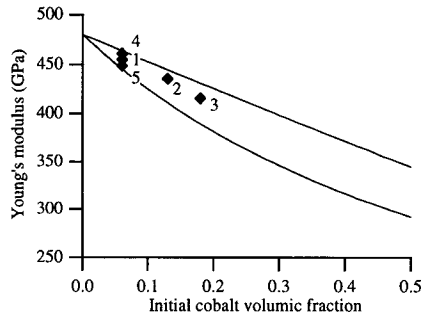

Figure 4 : Young's modulus variations as a function of the initial cobalt content.

The finest microstructure is observed for the grade 6 which is characterised by the highest Mo and N contents. Increasing the molybdenum content leads to higher Mo concentrations in the Co-Mo-Ti (or Ni-Mo-Ti) binder phase. Such an enrichment of this metallic phase results in an increase of the cermet hardness because of the hardening of the Co-Mo-Ti (or Ni-Mo-Ti) alloy. A detailed study of the high temperature plastic behaviour of these cermets has also shown important effects of these variations in the initial composition [9,10]. Creep mechanisms are directly influenced by the morphology and by the chemical composition of each phase in the material.

Conclusions

This study has shown the possibility to sinter Ti(C,N)-Mo_2C-Co cermets in a large range of compositions, particularly with different initial Co and Mo contents. The cobalt content variation essentially affects the morphological parameters of the microstructure because of their direct incidence on the volumic ratio between the hard phases and the metallic one. The molybdenum content variation results in important modifications of these morphological parameters but also in large variations of the chemical compositions of each phase. Such evolutions influence the mechanical properties of the sintered cermets in terms of hardness and toughness, but also in terms of resistance to plastic deformation at high temperature. At equivalent hard phase/metallic phase ratio, the Ti(C,N)-Mo_2C-Co cermets are characterised by a mechanical behaviour intermediate between the one of the Ti(C,N)-Mo_2C-Ni cermets and the one of the WC-Co hardmetals.

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