ELSEVIER

Ceramics International 30 (2004) 2111–2115

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of carbon content on the microstructure and mechanical properties of Ti(C, N)-based cermets

Yong Zheng[a,b,*], Wenjun Liu[b], Shengxiang Wang[b], Weihao Xiong[c]

[a] College of Physics Science and Technology, Wuhan University, Wuhan 430072, PR China
[b] College of Materials Engineering, China Three Gorges University, Yichang 443002, PR China
[c] College of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

Received 28 July 2003; received in revised form 13 August 2003; accepted 28 November 2003
Available online 10 March 2004

Abstract

Three series of Ti(C, N)-based cermets with various carbon content were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX) and X-ray diffractometry (XRD). Hardness (HV) and transverse rupture strength (TRS) were also measured. A lower carbon content resulted in the aggregation of ceramic grains because the absorbed oxygen of the powder mixture could not be outgassed completely, and then the ceramic grains could not be well-wetted by liquid metal during sintering. On the contrary, too high carbon content resulted in the formation of graphite phase. An increased carbon content decreased the dissolution of tungsten, titanium and molybdenum in the binder phase. The volume fraction of the binder is not much influenced by the carbon content. The highest hardness and TRS were found for the cermet with 1.5 wt.% carbon addition, which was characterized by fine grains and moderate thickness of rim phase.

Keywords: B. Microstructure; C. Hardness; D. Carbon; Ti(C, N)-based cermet; Transverse rupture strength

1. Introduction

Ti(C, N)-based cermets have been used in Japan and Sweden as cutting tools. At present, Ti(C, N)-based cermets are attracting much attention from researchers in other countries because of their excellent wear-resistance, good high temperature hardness, perfect chemical stability, very low friction coefficient to metals, superior thermal deformation resistance [1–3]. They compare favorably in the following respects with conventional WC-based hardmetals: high cutting speeds at moderate chip cross-sections, high wear-resistance, high surface quality of the mechanical workpiece [4]. It has shown great potential as a substitute for the commonly used WC-Co based hardmetals. However, cermets are less strong than the commonly used WC-Co based hardmetals. Efforts have been made to produce cermets with a higher strength without losing too much in their other properties. Such efforts are especially necessary in China, because most equipment in China is not advanced and has a lower running stability than that of advanced equipment. The basic approach for improving the strength of the cermet is to control its microstructure.

In general, Ti(C, N)-base cermets are manufactured by sintering pressed compacts to dense bodies at a temperature where a liquid phase is formed. This results in a complex microstructure with hard carbonitride grains embedded in a tough binder phase (see Fig. 1) [2]. The carbonitride grains generally consist of a Ti(C, N) core surrounded by a rim that in addition to the Ti(C, N) contains heavier elements, such as Mo, W, Ta and others. An enrichment in the heavier elements is often found in the rim at the epitaxial core/rim boundary [5]. This is referred to as the inner rim. The continuous Ni-based binder phase is the residual of the liquid phase formed during the sintering process.

It has been known that the carbon content in Ti(C, N)-base cermet influences the stability of carbide and nitride [6,7]. Consequently, the solubility of these carbides and nitrides in the binder phase varies with the content of carbon. The aim

---

* Corresponding author. Tel.: +86-717-6392060; fax: +86-717-6394655.
E-mail address: yzheng_only@263.net (Y. Zheng).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.11.016

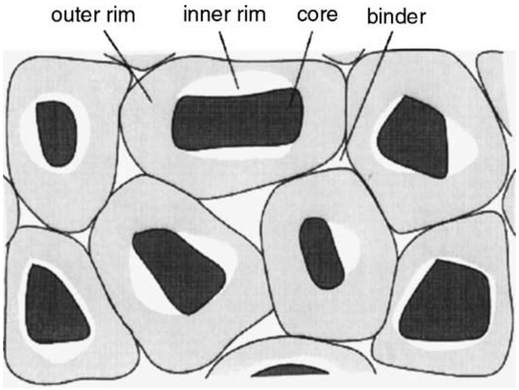

Fig. 1. Schematics of a typical cermet microstructure.

of this paper was to investigate in what ways the microstructure and properties are influenced by the carbon content. The present study would be advantageous to improving the strength of Ti(C, N)-based cermet.

2. Experimental procedure

The mean particle sizes measured by the sedimentation method and the oxygen contents determined by TC-136 oxygen–nitrogen analyzer are summarized in Table 1.

The compositions of the three cermets with different carbon content considered in the present study are given in Table 2.

These powders were dispersed homogeneously and mixed in a planetary ball-mill for 12 h at a speed of 150 rpm. The slurries were dried at 353 K in an infrared stove, then sieved and palletized. After that, the powders were pressed into the shapes of test specimens for the transverse rupture strength (TRS) of ceramics at 300 MPa for 30 s in a DAKE press. The green compacts were sintered at 1683 K in vacuum for 1 h. The vacuum was controlled at a residual pressure of 10^{-2} to 1 Pa during liquid sintering.

The hardness and TRS at room temperature were measured. The microstructures were observed by a JSM-5600LV scanning electron microscope (SEM) in backscattered electron (BSE) mode, and the distribution of the elements was determined by energy dispersive X-ray analysis (EDAX; Noran Vantage 4015) in combination with the SEM. The quantitative analysis of the BSE images was fulfilled using VMS2000 image processing system. After grinding into powder, the oxygen content of the sintered cermets was determined by TC-136 oxygen–nitrogen analyzer. The X-ray diffraction analysis of the specimens with different carbon contents was performed using Cu Kα radiation (D/MAX-YB X-ray diffractometer), and lattice parameters of main phases were measured by a standard procedure. A JEM-2000FXII transmission electron microscopy (TEM) was used to study the microstructure in more details.

Table 1
Mean particle sizes and oxygen contents of raw powders

	Powders					
	TiC	TiN	Ni	Mo	WC	C
Particle size (μm)	0.51	0.52	2.3	2.80	0.72	5.5
Oxygen content (wt.%)	1.21	1.10	0.22	0.10	0.56	–

Table 2
Composition design of the experimental materials (wt.%)

Cermet	TiC	TiN	Ni	Mo	WC	C
A	33	10	32	16	8.5	0.5
B	33	10	32	16	7.5	1.5
C	33	10	32	16	6.5	2.5

3. Results and discussion

3.1. Microstructure

The microstructure was observed using backscattered electrons in the SEM (see Fig. 2). The three cermets showed a typical microstructure consisting of hard core, rim phase and binder phase. It was found that the grain size was affected by the carbon content. The grains of the cermet with 1.5 wt.% carbon addition were the smallest of the three cermets.

The grains of the cermet with 0.5 wt.% carbon addition were the biggest of the three cermets. The microstructure showed that aggregation occurred. Clearly, the hard carbonitride grains were not wetted by metal phase completely, so they agglomerated during sintering due to contacting each other.

Some gaseous species always adsorb on the surface of the powders. Because TiC and TiN have higher oxygen affinity, O_2 is the main gaseous species existing on the surface of these ceramic grains, which reduces the surface energy of them, γ_{SV} [8]. During the sintering of the compacts in vacuum, several gaseous species are formed. The oxygen of the powder mixture, probably as chemisorbed or chemically bonded oxygen, has reacted with carbon present in the mixture as carbides or free carbon before the liquid phase appears. It is reduced to CO, which is given off into the atmosphere. With increasing temperature the rate of reaction increases gradually until it reaches a maximum at 1100 °C [2,7,9]. The more completely the oxygen is desorbed, the higher the surface energy γ_{SV}. The wetting angle can be determined by the following equation [8]:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

where θ is the wetting angle, γ_{SV} is the surface energy of solid, γ_{SL} is the solid–liquid interfacial energy, and γ_{LV} is the surface energy of liquid.

Clearly, if the adsorbed oxygen was not reduced completely, the surface energy of solid, γ_{SV}, would be lower.

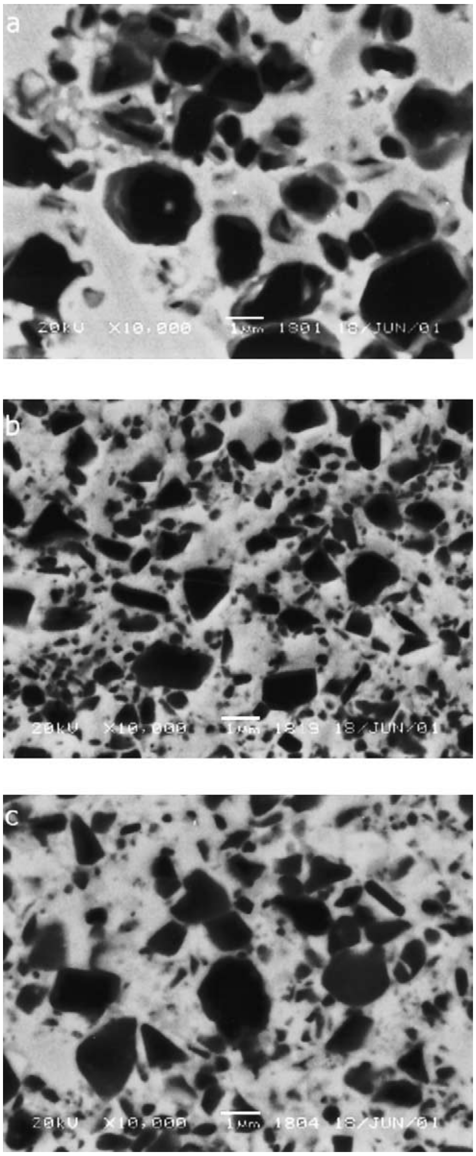

Fig. 2. Microstructure of Ti(C, N)-based cermets: (a) with 0.5 wt.% carbon addition; (b) with 1.5 wt.% carbon addition; (c) with 2.5 wt.% carbon addition.

Thereby from formula (1) it can be determined that the residual oxygen on the surface of the ceramic grains increased the wetting angle and accordingly reduced the wetting of the ceramic grains by liquid metal during sintering, resulting in the aggregation of ceramic grains.

Table 3 shows the oxygen contents of the sintered cermets. The oxygen content of cermet A with 0.5 wt.% carbon addition is much higher than that of the cermets B and C.

Table 3
Oxygen contents of the sintered cermets

	Cermet		
	A	B	C
Oxygen content (wt.%)	0.42	0.05	0.04

Table 4
Effect of the carbon addition on the volume fraction of the binder

Addition of carbon (wt.%)	0.5	1.5	2.5
Volume fraction of binder (vol.%)	51.4	54.1	55.4

Through summarizing above results and analysis, it can be deduced that 0.5 wt.% carbon addition was not enough to degas the oxygen completely. When the carbon addition was 1.5 wt.%, the grains of the cermet were finer, nearly no aggregation appeared, and no abnormal phase was observed by TEM. When the carbon addition was 2.5 wt.%, the grains again became coarse, which was due to the increase of the ratio C:N. It has been reported that the formation energy of Mo_2N is positive at 900 °C [7]. This is to say, N in cermets can preclude the diffusion of Mo to Ti(C, N) during sintering above 900 °C. The development of the rim phase is inhibited. Hence, lower N content or relative higher C content results in coarse grains in Ti(C, N)-based cermets.

3.2. Content and composition of binder

A quantitative analysis was performed for the cermet shown in Fig. 2, and the contents of the binders were determined as shown in Table 4. The volume fraction of the binder showed small change with carbon content. It only increased slightly with increasing carbon addition.

The content of main alloy elements in the binders was determined, and the results are summarized in Table 5. Clearly, the addition of carbon had great influence on the solubility of alloy elements in binder. The content of main alloy elements decreased with increasing carbon addition.

During sintering, the following reactions occur at higher temperature in Ti(C, N)-based cermets:

$$\mathrm{TiC} \rightarrow \mathrm{Ni(Ti)} + \mathrm{Ni(C)} \tag{2}$$

$$\mathrm{Mo_2C} \rightarrow \mathrm{Ni(Mo)} + \mathrm{Ni(C)} \tag{3}$$

$$\mathrm{WC} \rightarrow \mathrm{Ni(W)} + \mathrm{Ni(C)} \tag{4}$$

It is deduced from the above reaction equations that increasing carbon addition made the reactions progressing towards the opposite direction, thereby reducing the solubility of these carbides in Ni phase, and accordingly resulting in an increase of the volume fraction of the rim phase enriched in Mo and W. The formation of the rim phase consumed Ti, Mo, W, and thereby compensated for the lower amount of titanium and tungsten dissolved in the binder. On the other hand, it has been reported that the inner rim phase is formed during solid state sintering [10]. Therefore, we may

Table 5
Effect of the carbon addition on the element content of the binder

Carbon addition (wt.%)	Ti	Mo	W
0.5	13.40	12.19	3.85
1.5	11.50	6.92	3.02
2.5	5.94	6.76	2.23

Table 6
Carbon addition vs. lattice parameters of Ni and TiC phases

Cermet	Addition of carbon (wt.%)	Lattice parameter of Ni phase (nm)	Lattice parameter of TiC phase (nm)
A	0.5	0.3581	0.4315
B	1.5	0.3574	0.4306
C	2.5	0.3570	0.4302

expect the amount of the rim phase to be given by the thermodynamic equilibrium at the solid state sintering temperature. The thermodynamic calculated results showed that the higher carbon content promoted the formation of tungsten- and molybdenum-rich phases [11], and accordingly resulting in the decrease of alloy elements in the binder, which is consistent with the present experimental results.

The lattice parameters of both TiC and Ni phases in the cermets with various carbon additions were determined from XRD data, and are summarized in Table 6. The lattice parameters of both TiC and Ni phases decreased with increasing carbon addition. During the sintering, both carbon and nitrogen atoms easily diffuse through the vacancies interstices of sublattice. The continuous Ti(C, N) solid solutions form by the counter diffusion of TiC and TiN. Mo_2C, WC and TiC dissolve into liquid Ni and reprecipitate onto large TiC particles to form the rim phase (Ti, W, Mo) (C, N). The crystal structures of these carbonitride phases were the same as that of TiC [12,13]. It can be determined that the variation of the lattice parameter of TiC is due to the variation of the dissolution of Mo and W level in carbonitride grains. The fact that the lattice parameter of TiC decreased with increasing carbon addition indicated that the dissolution of Mo and W in carbonitride grains increased with increasing carbon addition, while the lattice parameter of Ni decreased with increasing carbon addition indicating that the dissolution of Mo and W in Ni decreased with increasing carbon addition, which is consistent with the EDX data.

3.3. Mechanical properties

Table 7 shows the hardness and TRS at room temperature of specimens with different carbon additions.

Cermet with 1.5 wt.% carbon addition showed the highest TRS. The finer grain size, the moderate thickness of rim phase and the lower solid solubility of alloy elements in the binder are the explanations of this TRS behavior. When the carbon addition was 2.5 wt.%, the TRS of the cermet decreased. To explain this phenomenon, TEM observation was carried out for the cermet. The microstructure is shown in Fig. 3. It was found that small amount of graphite phase was present in some areas of the binder, which resulted in the reduction of TRS. The cermet with 0.5 wt.% carbon addition showed the lowest TRS and hardness, which resulted from the bad wettability because of too low carbon addition.

Table 7
Mechanical properties of cermets with different carbon additions

Cermet	Addition of Carbon (wt.%)	TRS (MPa)	Hardness (HRA)
A	0.5	691.0	87.2
B	1.5	1011.5	89.1
C	2.5	997.1	88.9

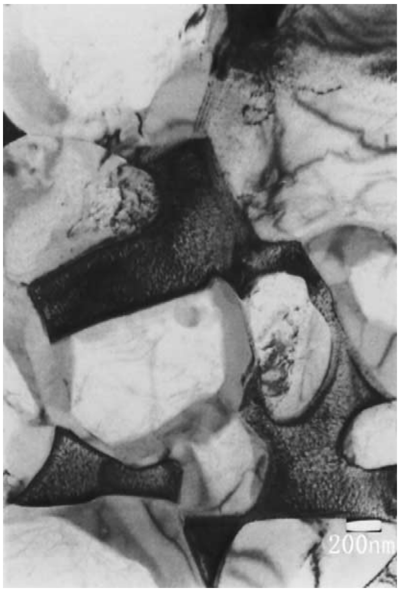

Fig. 3. TEM micrograph in bright field of the cermet with 2.5 wt.% carbon addition.

4. Conclusions

1. When the carbon addition in Ti(C, N)-based cermets is too low, the absorbed oxygen of the powder mixture can not be degassed completely, so the ceramic grains cannot be well wetted by liquid metal during sintering. On the contrary, when carbon addition is too high, graphite is present in the microstructure.
2. A higher carbon addition decreases the dissolution of tungsten, titanium and molybdenum in the binder phase. The volume fraction of the binder is not much influenced by the carbon content. To some extent, the dissolution of some alloy elements in the binder phase can be controlled by the carbon addition in cermet materials.
3. The highest hardness and TRS were found in the cermet with 1.5 wt.% carbon addition, which was characterized by fine grains and moderate thickness of rim phase.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China under project no.

50104006, the Hubei Province Natural Science Foundation of China under project no. 2000J032 and the Education Bureau Science Foundation of Hubei Province of China under project no. 2001D67002.

References

[1] D. Moskowitz, L.L. Terner, TiN improves properties of titanium carbonitride-base materials, Int. J. Refrac. Met. Hard Mater. 5 (1986) 13–13.

[2] J. Zackrisson, H.O. Andren, Effect of carbon content on the properties of (Ti, W, Ta, Mo) (C, N)-(Co, Ni) cermets, Int. J. Refrac. Met. Hard Mater. 17 (1999) 265–273.

[3] H. Matsubara, Application of hard and ultra-hard materials, J. Jpn. Inst. Metals 29 (12) (1990) 1008–1018.

[4] L. Chen, W. Lengauer, K. Dreyer, Advances in modern-containing hardmetals and cermets, Int. J. Refrac. Met. Hard Mater. 18 (2000) 153–161.

[5] A.H. Heuer, J.S. Sears, N.J. Zaluzec, Analytical electron microscopy of phase separated Ti/Mo cemented carbides, in: E.A. Almond, C.A. Brookes, R. Warren (Eds.), Proceedings of International Conference on the Science of Hard Materials, vol. 2, Rhodes, Adam Hilger, Briston and Boston, London, 1986, pp. 321–334.

[6] S. Kang, Stability of N in Ti(CN) solid solutions for cermet applications, Powder Metall. 40 (2) (1997) 139–142.

[7] Y. Zheng, Research on a composite of fine grained Ti(C, N)-based cermet, Ph.D. Thesis, Huazhong University of Science and Technology, Wuhan, China, 2002.

[8] C. Kenneth, S.-Y. Russell, A. Figueredo, Theoretical and experimental studies of ceramic: metal wetting, MRS Bull. 4 (1991) 46–52.

[9] L. Chen, W. Lengauer, P. Ettmayer, Fundamentals of liquid phase sintering for modern cermets and functionally graded cemented carbonitrides (FGCC), Int. J. Refrac. Met. Hard Mater. 18 (2000) 307–322.

[10] H.-O. Andren, Microstructures development during sintering and heat-treatment of cemented carbides and cermets, Mater. Chem. Phys. 167 (1–3) (2001) 209–213.

[11] S. Jonsson, Phase relations in quarternary hard materials, Ph.D. Thesis, Royal Institute of Technology, Stockholm, Sweden, 1993.

[12] M. Ehira, A. Egami, Mechanical properties and microstructures of submicron cermets, Int. J. Refrac. Met. Hard Mater. 13 (1995) 313–319.

[13] Y. Zheng, W.H. Xiong, Effect of powder particle size on the properties and microstructure of Ti(C, N)-based cermet, Rare Metals 20 (1) (2001) 47–51.