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Effect of nano addition on the microstructures and mechanical properties of Ti(C, N)-based cermets

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Abstract

The influence of nano TiC and TiN additions on the mechanical properties of Ti(C, N)-based cermets was studied. A cermet with proper amount of TiC and TiN additions, which had more than twice the transverse rupture strength (TRS) of a typical cermet, was manufactured. The microstructures of the prepared cermets with nano additions were studied further by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX). It was found that in the cermets with nano additions, the amount of smaller grains without obvious rim phase and those with ‘‘white core–black rim’’ increased greatly. In addition, the volume fraction of binder phases reduced apparently. Some smaller ceramic particles were also found to be inlaid in the rim of the larger ceramic grains and kept partial coherent with the larger grains. It was the firm joint between them and the reduction of the average size of the grains that led to strengthening and toughening of the cermet with nano additions.

Keywords: B. Nanocomposites; B. Microstructure; C. Mechanical property; Ti(C, N)-based cermet

1. Introduction

Recently, Ti(C, N)-based cermets attract much attention from researchers because of their excellent wear-resistance, high hardness at high temperature, perfect chemical stability, very low friction coefficient to metals, superior thermal deformation resistance [1–3]. They compare favourably 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]. They show a 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 of their other properties.

In 1998, the new concept of ‘‘nano materials engineering’’ was put forward formally at the fall symposium sponsored by the American Materials Research Society, the aim of which was to shorten the cycle of basic research and development research [5]. At present, nano synthesis technology has been applied widely to develop new materials with higher properties and to improve the properties of conventional materials. Some stage research results have been achieved in the fields such as nano coating material, high strength structural material, macromolecular-based nano composite, magnetic material, optical material, high dielectric material and bionic material [6,7].

Nanocomposite ceramics have also been studied extensively since the late eighties of last century when Japanese scholar Niihara reported that the mechanical properties of ceramics could be improved by adding a few nanometer additions to the ceramics [8–12]. Nowadays in the field of ceramics, it is widely accepted that the mechanical properties of micrometer ceramics matrix can be improved greatly by adding nano additions. However, the method

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Table 1
Mean particle sizes and the oxygen contents of raw powders

Powders	TiC (nm)	TiC (μm)	TiN (nm)	TiN (μm)	Ni	Mo	WC	Cr_3C_2	C
Particle size (μm)	<0.1	2.58	<0.1	14.89	2.3	2.80	0.72	1.80	5.5
O_2 content (mass%)	2.47	0.77	7.51	0.36	0.22	0.10	0.56	0.14	–

has not been used in the field of cermets. Therefore, in the present study, Ti(C, N)-based cermets with nano TiC and TiN additions were prepared by vacuum sintering, and the microstructures and properties of these cermets were also studied.

2. Experimental

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 all Ti(C, N)-based cermets in the present study are 33 wt.% TiC–10 wt.% TiN–32 wt.% Ni–16 wt.% Mo–6.9 wt.% WC–1.5 wt.% C–0.6 wt.% Cr_3C_2. TiC and TiN are mixture of micro and nano powders, the detail percentages of which are shown in Table 2. With respect to A, B, C and D cermets, both of the weight ratios of nano TiC to micro TiC and that of nano TiN to micro TiN are 0%:100%, 20%:80%, 60%:40%, 100%:0%, respectively.

These powders were dispersed homogeneously and mixed in a planetary ball-mill for 12 h at a speed of 150 rpm (rotations per minute). The slurries were dried at 353 K in an infrared stove, then sieved and pelletised. After that, the powders were pressed at 300 MPa for 30 s in a DAKE press. The green compacts were sintered at 1723 K in vacuum for 1 h. The vacuum was controlled at 10^{-2}–1 Pa during liquid sintering.

The hardness and transverse rupture strength (TRS) at room temperature were measured. The microstructures were observed by a JSM—5600LV scanning electron microscopy (SEM) in backscattered electron (BSE) mode. Thin slices of the specimens were polished to 20 μm thickness. The disks for the TEM investigation were thinned to electron transparency by ion-milling in a Gatan691 miller. A JEM—2000FX II transmission electron microscopy (TEM) was used to study the microstructure in more detail, and a INCA energy dispersive X-ray analysis (EDX) in combination with TEM to fulfil element microanalysis.

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

Cermet	TiC (nm)	TiC (μm)	TiN (nm)	TiN (μm)	Ni	Mo	WC	Cr_3C_2	C
A	0	33	0	10	32	16	6.9	0.6	1.5
B	6.6	26.4	2	8	32	16	6.9	0.6	1.5
C	19.8	13.2	6	4	32	16	6.9	0.6	1.5
D	33	0	10	0	32	16	6.9	0.6	1.5

3. Results

3.1. Mechanical properties and porosity

The porosity, hardness and transverse rupture strength at room temperature of the cermets with different nano TiC and TiN additions are summarized in Table 3.

Cermet B with the weight ratio of nano ceramic powders to micro ceramic powders equal to 20%:80% shows the highest TRS and hardness. On the contrary, cermets C and D show very low TRS and hardness.

Table 1 shows that the oxygen contamination of nano TiC and TiN powders is higher than that of other micro powders. When the amount of the added nano powders was too much, the oxygen contamination couldn't be reduced completely during sintering, resulting in the decrease of the surface energy of solid γ_{SV}. The wetting angle can be determined by the following equation [13]:

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

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

Thereby it can be determined from formula (1) that the residual oxygen on the surface of the ceramic grains would increase the wetting angle and accordingly reduced the wetting of the ceramic grains by liquid metal during sintering, resulting in low density of the sintered cermets. In addition, the bad wettability also made the liquid metal phase effusing toward the surface and consequently reduced the properties of the cermets greatly.

Fig. 1 shows the fracture images of cermets A and B, both of which consisted of ceramic grains, concavities formed by the removal of ceramic grains, tearing ridges formed by the tearing of the metal phase, dimples along the expanding paths of the tearing ridges, which also included some small concavities with ceramic grains as the core formed during

Table 3
Mechanical properties and porosities of cermets with different nano TiC and TiN additions

Cermet	Weight ratio of nano powder to micro powder (%/%)	TRS (MPa)	Hardness (HV)	Porosity (%)
A	0:100	1831.6	1219	≈0
B	20:80	2884.7	1251	≈0
C	60:40	519.5	766	>2.0
D	100:0	138.6	563	>2.0

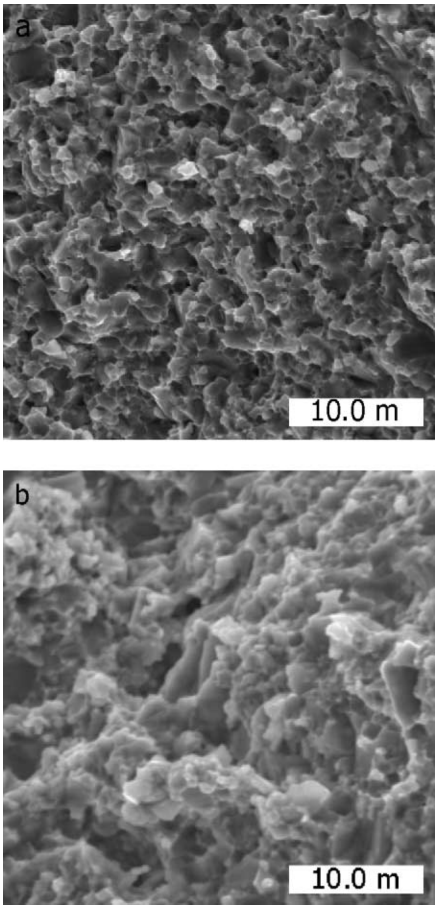

Fig. 1. Fracture appearance of Ti(C, N)-based cermet: (a) cermet A with no nano addition added; (b) cermet B with nano additions added.

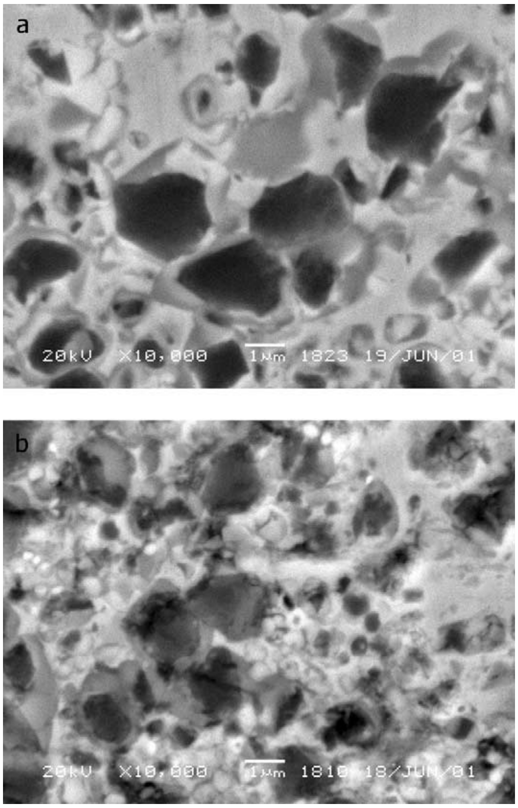

Fig. 2. Microstructure of Ti(C, N)-based cermet: (a) cermet A with no nano addition added; (b) cermet B with nano additions added.

fracture, and a few ceramic grains, resulting from cleavage fracture. The removal of ceramic grains resulted from weak interface coalescence between the grains and the metal phase. More tearing ridges, less intergranular fracture, more dimples, and greater plastic deformation occurred in cermet B, with moderate amount of nano TiC and TiN additions added, than in cermet A, with no nano addition. Obviously, the nano additions strengthened and improved the TRS of the cermets. It can be determined further that when the cermets could be densified completely, the addition of nano powders could improve the mechanical properties of the cermets greatly.

3.2. Microstructure

The microstructures of cermets A and B were observed using backscattered electrons in the SEM, as shown in Fig. 2. There exist three kinds of grains in the two cermets: one has ‘‘black core-white rim’’ structure, which is well known as the typical structure of conventional cermets, the second has ‘‘white core–black rim’’ structure and the third has no obvious rim phase.

Cermet A with no nano TiC and TiN additions has the typical microstructures mainly consisting of large ceramic grains with ‘‘black core-white rim’’ besides a few small ceramic grains with ‘‘white core–black rim’’.

However, in the cermet B with nano TiC and TiN additions, the amount of the small grains with ‘‘white core–black rim’’ increased greatly while the amount of the large grains with ‘‘black core-white rim’’ decreased slightly. In addition, some small grains without clear rim were observed. The volume percentage of the metal binder was much less than that in cermet A.

It was proved to be difficult in observing the true microstructures of cermets C and D, in which nano additions were beyond 60 wt.% of the amount of TiC and TiN, because they couldn’t be densified by vacuum sintering and had many micro-cracks. In addition, the appearances of the two cermets were rough, which should be attributed to the poor wetting of ceramics grains by liquid metal during sintering, resulting in the effusion of liquid phases to the surfaces of the cermets.

To elucidate the characteristics of the microstructure of the cermets with nano additions in detail, TEM observations were performed, as shown in Fig. 3. Clear interface between the core and rim phase exists, which mainly results from the different contents of Mo and W between the two phases [14]. The larger grains were surrounded by thicker rim phases (grain 1 in Fig. 3), and some smaller grains were inlaid in the rim phases. A part of small grains hadn’t obvious rim (grain 2 in Fig. 3) while other part of small grains had very thin rim

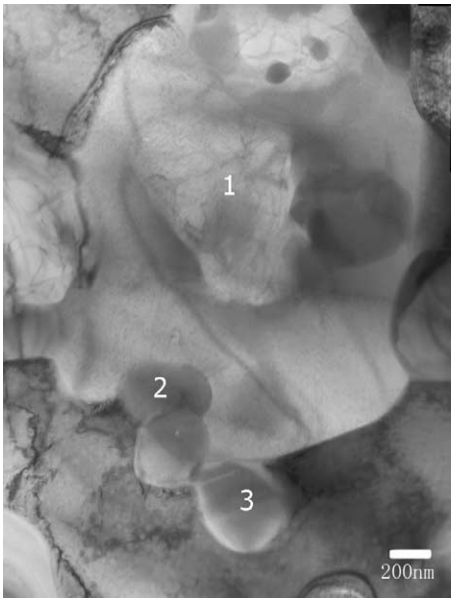

Fig. 3. TEM micrograph in bright field of cermet B with nano additions.

(grain 3 in Fig. 3). Clearly the forming mechanisms and characteristics of the grains with different appearances were different.

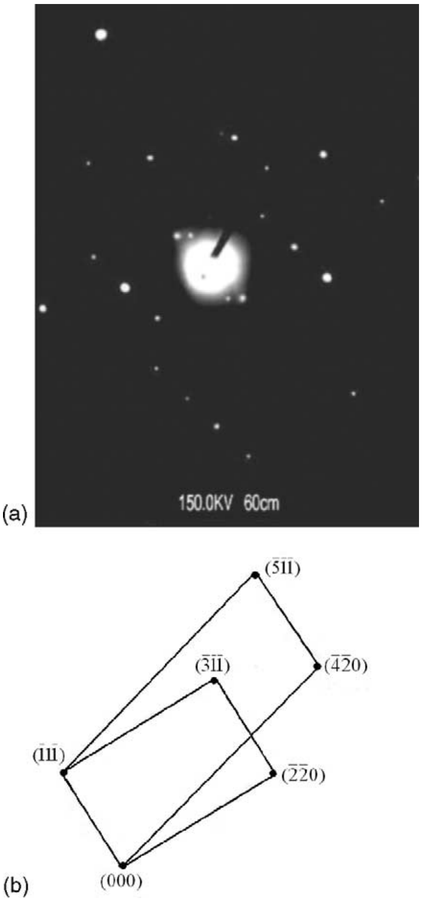

Fig. 4. Diffraction pattern showing the orientation relationship between grains of cermet B with nano additions: (a) diffraction pattern; (b) determination of diffraction pattern.

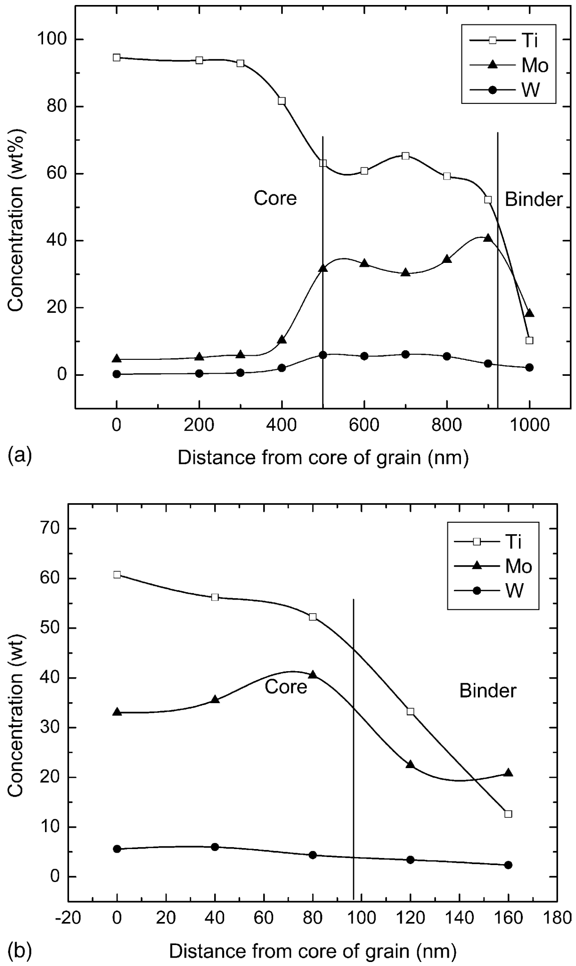

Fig. 5. Distribution of elements in different grains of cermet B with nano additions (from core to binder): (a) grain 1 with core-rim structure; (2) grain 2 without obvious rim phase.

Grain 1 and 2 chosen by the diaphragm of TEM, selecting area diffraction analysis was performed, as shown in Fig. 4.

The larger grain 1 with typical core-rim structure and the smaller grain 2 without obvious rim were measured quantitatively by EDX in combination with TEM. The distributions of the main elements in grain 1 are shown in Fig. 5(a). Nearly only Ti was detected in the core which was the remaining TiC during sintering. (In fact, when the cermet was sintered at high temperature, the TiC core has become Ti(C, N) in the final sintering stage by the diffusion of nitrogen toward TiC core). The distributions of the main elements in grain 2 are shown in Fig. 5(b). Besides Ti atom, some Mo and W atoms also existed in the core.

4. Discussion

4.1. Microstructure

In the case of Ti(C, N)-based cermet, as temperature increases, WC and Mo_2C dissolve into TiC in a solid state.

During liquid phase sintering, the rim phase (Ti, Mo)(C, N), which is in equilibrium with the liquid, precipitate on Ti(C, N) grains due to the dissolution of small grains and reprecipitation on large ones (Ostwald ripening) [15,16]. On the other hand, at the high temperature N atoms, resulting from the decomposition of TiN, substitute partially C atoms, consequently (Ti, Mo, W)C becomes (Ti, Mo, W)(C, N). In addition, N atoms diffuse easily to the core and substitute partially C atoms of TiC to form Ti(C, N) [17].

It can be determined that before liquid phase appears, larger TiC grains do not dissolve completely. The grains with ''black core-white rim'' are formed by dissolution and precipitation of (Ti, Mo, W)C around the solid-dissolved (Ti, Mo, W)C with remaining TiC core. The great change in composition of Fig. 5(a) suggests the difference between the solid-dissolved (Ti, Mo, W)C and TiC core. On the contrary, during solid state sintering, smaller TiC grains dissolve completely by counter diffusion of carbides and TiC, forming the solid-dissolved (Ti, Mo, W)(C, N). During liquid phase sintering, (Ti, Mo, W)(C, N) precipitate around the solid-solution (Ti, Mo, W)(C, N). Because the difference between the composition of (Ti, Mo, W)(C, N) formed during liquid phase sintering and that during solid state sintering is minor, the grains without obvious rim phase are formed. Fig. 5(b) suggests there is no clear composition grads within the small ceramic grain. In addition, during the later stage of liquid phase sintering, (Ti, Mo, W)(C, N) relatively poor in Mo and W continue to precipitate around the formed (Ti, Mo, W)(C, N), resulting in some grains with ''white core–black rim''.

Because there were large amounts of big TiC ceramic grains in cermet A made from coarse powders, there are many grains with ''black core-white rim'' in its microstructures. However, there were an amount of fine particles besides coarse powders in cermet B, so there existed not only larger grains with ''black core-white rim'', but also smaller ones with ''white core–black rim'' and that without obvious rim in cermet B with nano additions added.

4.2. Properties

Fig. 4 shows the orientation relationship between grains of cermet B. Some smaller grains inlaid in the rim of the larger grains kept partial coherence with the larger ones. The strong joint between them led to the cracks deflecting during the fracture and a limitation of their extension. Moreover, the smaller grains existing in the rim phase resulted in many dislocation groups inside the larger ones. The dislocation groups could be pinned by the smaller grains themselves, which also hindered the cracks extension and led to their deflection. As a result, the fracture energy was improved and thus cermet B with nano additions was strengthened.

In addition, it could be determined from Fig. 2 that the average grain size in cermet B is reduced. Gurland have studied the influence of the grain size on the strength of hardmetals, which is expressed as [18]:

$$\sigma^2 = K\frac{f^{2/3}}{d} \tag{2}$$

Here, σ represents the axial stress; K denotes a constant; and f and d denote the volume percentage and the mean grain size of WC, respectively.

The theory also applies to Ti(C, N)-base cermet, because both of Ti(C, N)-based cermet and WC–Co hardmetals belong to the same category. Clearly, the fining of the grains in cermet B would improve the strength of the cermet.

5. Conclusions

1. The amount of the nano additions have great influence on the properties of the sintered Ti(C, N) cermets. When the amount of nano additions is too high, the cermet cannot be densified by vacuum sintering, because the high oxygen content adsorbed on the surface of the powders reduce the wetting of the ceramic grains by liquid metal during liquid phase sintering.
2. When nano TiC and TiN additions accounted for 20 wt.% of the amount of TiC and TiN, the cermets could be densified by vacuum sintering, and the mechanical properties were improved greatly. The transverse rupture strength and the hardness of the cermets produced reached 2885 MPa, 1251 HV, respectively.
3. The microstructures of the cermets with nano additions showed that the grains without obvious rim phase and those with ''white core–black rim'' increased greatly, and the volume fraction of metal binder decreased markedly. However, no obvious trend was found for the amount of larger ones with ''black core-white rim'' as a function of nano additions.
4. Some small grains were found to be inlaid in the rim phase of larger grains and keep partially coherent with these larger ones. It was the firm combination between them and the reduction of the average size of grains that led to the strengthening and toughening of cermets.

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