Microstructural evolution and characteristics during sintering of submicron Ti(C, N)‑based cermet [①]

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Abstract: Ti(C, N)‑based cermets were prepared with submicron powders. The microstructure evolution and character‑ istics during the sintering of cermet were studied by TEM, SEM, EDX and XRD. The forming mechanism of the struc‑ tures was also studied. There exist inner rim and outer rim between the hard cores and the binder. The inner rim is en‑ riched in Mo and W compared with the outer rim, and is formed during the solid sintering by counter diffusion of TiC, Mo_2C and WC. The outer rim is formed during the liquid sintering by Ostwald ripening mechanism.

Key words: submicron Ti(C, N)‑based cermet; microstructure; evolution; forming mechanism

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1　INTRODUCTION

The basic composition of Ti(C, N)‑based cer‑ mets is Ti(C, N) and Ni. It has been known that the addition of Mo or Mo_2C is necessary to ensure good wettability[1], and WC or other carbides are often added to improve the plasticity of hard grains and hot hardness of the cermets[2]. Ti(C, N)‑based cermets consist mainly of carbonitride grains and metal binder. The " core‑rim" structure within the hard grains is the typical microstructure of cermets. The carbonitride phase enriched Mo and W (the rim phase) has been found to surround the Ti(C, N) cores[3].

Because the cermet materials involve several dif‑ ferent raw powders, the microstructure evolution during the sintering is complex. Up to now, the for‑ mation mechanism of cermet microstructures hasn't been understood. Several researchers have reported results concerned with microstructure evolution dur‑ ing the sintering of cermets. Moskowitz et al[4,5] sug‑ gested Mo diffusion from liquid Ni to solid TiC parti‑ cles substituting Ti to form a unstable TiC‑Mo‑C solid solution, while Rudy[6] proposed the decomposition of (Ti, Mo) C solid solution to Ti‑rich and Mo‑rich(Ti, Mo) C solid solutions. And it was also suggested that the rim phase (Ti, Mo) (C, N), which is in equilibri‑ um with the liquid, precipitates on Ti(C, N) grains due to the dissolution of small grains and reprecipita‑ tion on large ones (Ostwald ripening) during sinter‑ ing[7,8]. It has been ambiguous for the rim phase to form. The microstructure is the most important de‑ terminant of mechanical properties of cermets, so it is worth studying the microstructure evolution and forming mechanism during the sintering of cermets.

2　EXPERIMENTAL

The cermets investigated were prepared from 33% TiC‑10% TiN‑32% Ni‑16% Mo‑6. 9% WC‑1. 5% C‑0. 6% Cr_3C_2 (mass fraction). The median sizes measured by SA‑CP3 powder size analyzer and the oxygen contents by TC‑136 oxygen‑nitrogen analyzer are summarized in Table 1.

These powders were dispersed homogeneously

Table 1　Particle size and oxygen content of main raw materials

Powder	Particle size/ μm	Oxygen content (mass fraction) / %
TiC	0. 51	1. 21
TiN	0. 52	1. 10
Ni	2. 30	0. 22
Mo	2. 80	0. 10
WC	0. 72	0. 56
Cr_3C_2	1. 80	0. 14
C	5. 50	–

and mixed for 12 h in a QM-1SP planetary mill with a mass ratio of ball to mixture being 5∶1, and the rotational speed being 150 r/min. The slurries were dried at 353 K in an infrared stove, then sieved and pelletised. Compacts were mechanically pressed at 300 MPa for 30 s in a DAKE presser. The green compacts were sintered in vacuum at different temperature for 1 h.

Thin slices of the specimens were polished to 20 μm in 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 microscope(TEM) was used to study the microstructure in more detail, and an INCA energy dispersive X-ray analysis(EDX) in combination with TEM was used to fulfill element microanalysis. The microstructures were observed by a JSM − 5600LV scanning electron microscopy (SEM) in backscattered electron mode. The X-ray diffraction analysis of the specimens sintered at various temperature were performed by CuK$_\alpha$ radiation (D/ MAX − YB X-ray diffraction apparatus).

3 RESULTS AND DISCUSSION

The microstructures of the specimens sintered at various temperature for different holding time are shown in Fig. 1.

The microstructures resulting from different sintering temperature and holding time are completely different. It is clear that the microstructure development goes further during the sintering. After 20 min sintering at 1 370 ℃, the microstructure shows aggregation among hard grains, and a great variety between different regions. The shapes of hard grains nearly don't change. There isn't obvious rim phase surrounding most of the hard grains, although some regions contain a few grains with thinner and incomplete rim phase surrounding their cores. After 120 min sintering at 1 370 ℃, the amount of small grains become less, and part of the hard grains have been spheric, indicating that a part of small grains and the angles of big grains have dissolved into the binder. In addition, most gains have thicker rim phase, whereas a few grains have only incomplete rim phase. Furthermore, in very few regions there is still the sign for the rim to form. At 1 410 ℃, the proportion of small grains decreases greatly. Obviously, the forming rate of the rim surrounding big grains increases obviously. The process has proceeded further and there has a core-rim structure throughout the specimen. However, the grains grow up slightly. At 1 450 ℃, there is an increase in rim thickness and the consequently larger grains appear.

Moskowitz et al[4, 5] have suggested that the surrounding complex carbonitride in the cermets is developed by the substitutional diffusion of Mo into TiC during sintering. However, this mechanism isn't consistent with our experimental observation
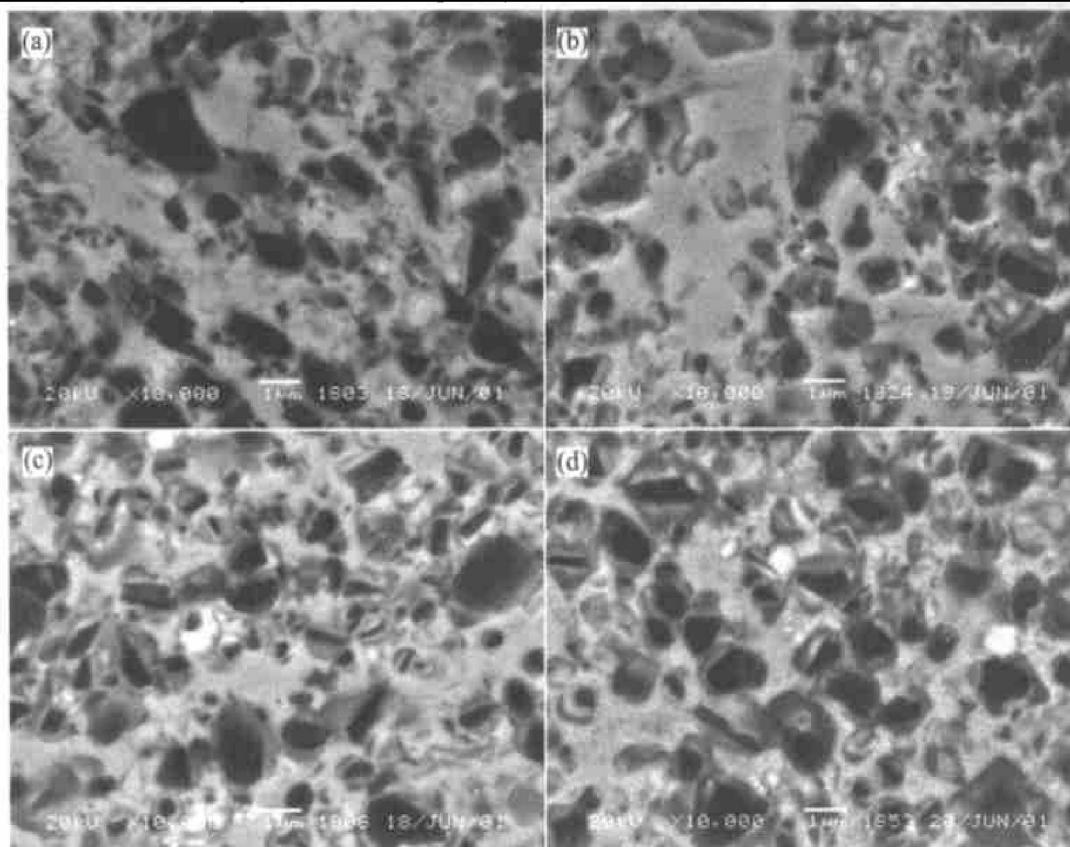
Fig. 1 SEM micrographs of cermets sintered under different sintering conditions
(a) −1 370 ℃, 20 min; (b) −1 370 ℃, 120 min; (c) −1 410 ℃, 60 min; (d) −1 450 ℃, 60 min

as shown in Fig. 1. The diffusion of Mo into TiC from the liquid should be almost identical all along the solid-liquid interface, and consequently uniform thickness of the surrounding structure would be resulted in, which isn't the case.

To elucidate the characteristics and the evolution of the rim phase, TEM observation on the materials sintered at 1 450 ℃ for 60 min was performed, as shown in Fig. 2. The inner rim and outer rim can be distinguished. The inner rim is very thin and incomplete, and isn't evenly distributed around the cores.

The results of EDX microanalysis on the inner rim(spot 1) and the outer rim(spot 2) are presented in Fig. 3. The quantitive results are summarized in Table 2.

Fig. 2 Bright field TEM image of
cermet sintered at 1 450 ℃ for 60 min

The inner rim has a substantially higher Mo and W content compared with that of the outer rim. It has been reported that $(Mo, Ti)C_{1-x}$ $(0 \leqslant x \leqslant 1)$ is stable when Ti content exceeds 1.8% (mole fraction)[9]. On the other hand, the bonding strength in diatomic molecules has been measured spectroscopically for Ti—C and Ti—N bonds and the room temperature strengths are reported to be 423 and 476 kJ/mol, respectively[10]. In addition, The lattice parameters of TiC and TiN are known to be 4.328 Å and 4.240 Å respectively[10]. All this evidences indicate a stronger Ti—N bond than Ti—C bond in B1-NaCl structure. So when a part of C atoms are replaced by N atoms, the higher affinity of N with the neighbouring elements results in the increase of the stability of carbonitride . Fu-
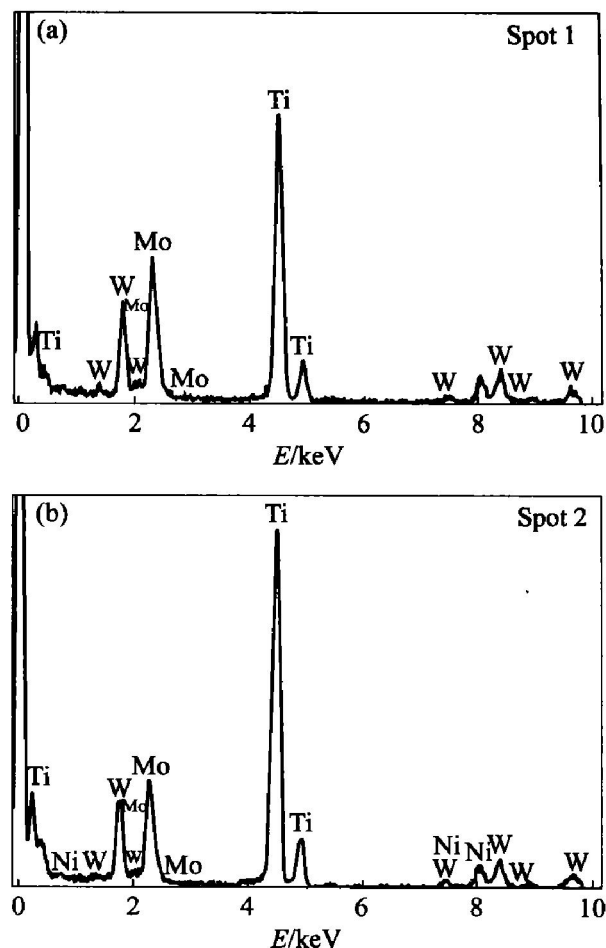
Fig. 3 EDX results of rim phase marked in Fig. 2

Table 2 Element content of rim phase
in cermet sintered at 1450 ℃ for 60 min
(mass fraction, %)

Phase	Ti	W	Mo	Ni
Inner rim	40.15	6.30	53.55	0
Outer rim	52.61	4.51	42.38	0.50

rthermore, there are also calculated results indicating that the dissolution of N in carbide can increase its stability at temperatures below 1 800 ℃, when the ratio of N/C is less than 3/7[11]. It can be concluded that it is impossible for the inner rim and the outer rim to form by the decomposition of carbonitride solid solution. On the other hand, some thermodynamic calculations also indicate that the composition of the rim can be determined by N activity. Lower N activity can result in a higher Mo and W content of the rim and vice versa[12]. It is believed that the inner rim and the outer rim are formed at different sintering stages. During solid state sintering there is an open porosity and the dissolved N may be lost in the atmosphere and give a lower N activity, so the inner rim with a higher Mo and W content is formed. On the contrary, the outer rim with a lower Mo and W content is formed during the liquid sintering at which there is a higher activity due to enclosed porosity.
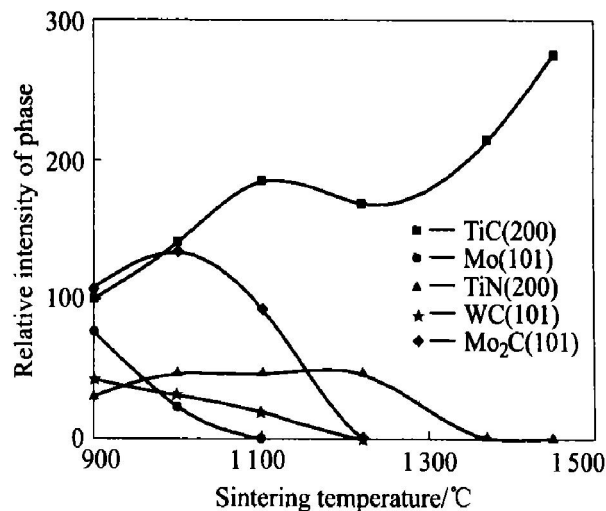
In the case of submicron Ti(C, N)-base cermet, it is expected that as temperature rises, counter diffusion of carbides and TiC occurs and then the dissolution and precipitation in the liquid phase take place. During solid state sintering, the large TiC grains don't dissolve the carbides completely, and the inner rim, which is just the solid-dissolved (Ti, Mo, W) C, is formed around the remaining TiC core. After the binder has melted, the outer rim starts to form on the inner rim due to the dissolution of small grains and reprecipitation on large ones (Ostwald ripening mechanism). At high temperatures, part of C atoms are replaced by N atoms, and the rim changes to carbonitrides.

To explain the microstructure evolution of Ti(C, N)-based cermet further, the phase transition during sintering was investigated. Fig. 4 shows the results of X-ray diffraction analysis on the specimens sintered at different temperatures. The relative intensities of TiC(200), $Mo_2C(200)$, Mo(111), TiN(200), WC(101) were calculated from the ratio of the X-ray peak height for any of the constituent phases in the specimens sintered at different temperature (I) to that of the standard materials (I_0). The height of TiC(200) diffraction peak was used as unification standard. Fig. 5 shows the calculated results according to the above method.

The relative intensities are proportional to the content of each phase. The amount of Mo decreases with increasing temperature until it disappears completely at about 1 100 ℃. Mo_2C has formed be-
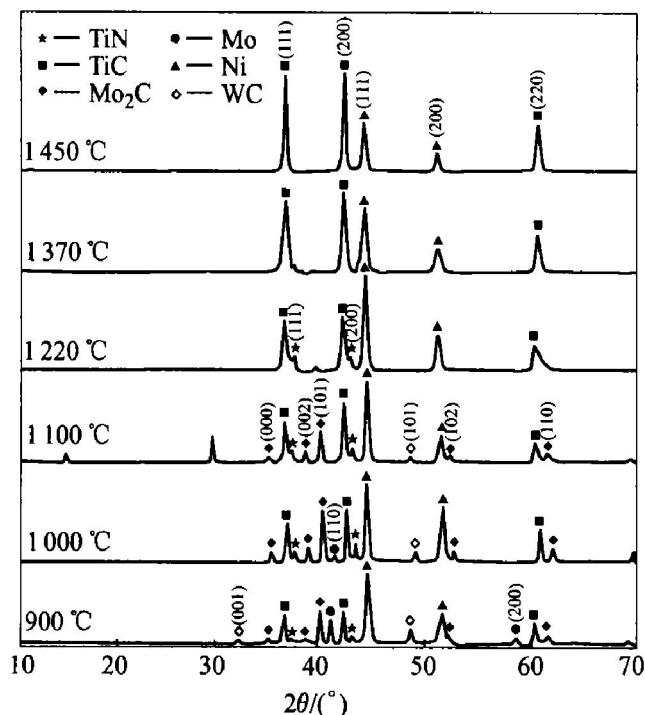
Fig. 5   XRD relative intensities of main phases of cermets vs sintering temperature

fore 900 ℃, and the amount of Mo_2C increases with increasing temperature below 1 000 ℃, remarkably in the range of 900 ﹣1 000 ℃. Then it decreases with increasing temperature above 1 000 ℃ and disappears at 1 200 ℃. Mo_2C is supposed to have been formed below 1 000 ℃ by the reaction between Mo and C. The amount of TiN remains unchanged below 1 220 ℃ and decreases above 1 220 ℃ with increasing temperature, and completely disappears at 1 370 ℃. The amount of WC decreases with increasing temperature and disappears at 1 220 ℃. The amount of TiC increases between 900 ℃ and 1 100 ℃, and slightly drops between 1 100 ℃ and 1220 ℃. However, it again increases with a rapid rate above 1 220 ℃.

To further investigate the phase transformation during sintering, the lattice parameters of TiC and Ni phases in the cermets sintered at various temperatures were calculated by standard procedure, as shown in Fig. 6. The lattice parameter of TiC decreases with increasing temperature. On the other hand, the lattice parameter of Ni phase increases from 900 ℃ upwards; at 1 100﹣1 220 ℃ it slightly decreases and above 1 220 ℃ it again increases rapidly.

Both TiC and TiN have a NaCl structure. In addition, they are isomorphous, and the C atoms in the TiC superlattice can be replaced by N atoms in any proportion (and vice versa), therefore a continuous series of solid solutions can be formed. The lattice parameter of Ti(C_x, N_{1-x}) can be expressed as[13]

$$a = x \cdot a(TiC) + (1 - x) \cdot a(TiN) \qquad (1)$$

where x represents the ratio of C to N in mole fraction.

Taking into account of the atomic radii of the main elements contained in the cermets, which are Ti 1. 4318 Å, W 1. 3705 Å, Mo 1. 3626 Å, Ni

Fig. 4   XRD patterns of Ti(C, N) cermets sintered at different temperatures
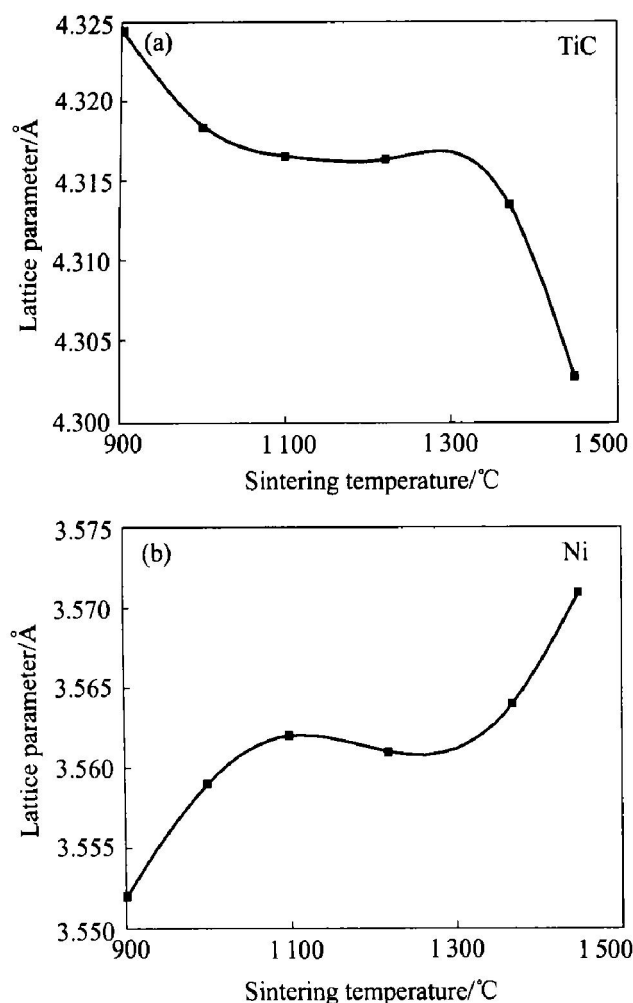
Fig. 6　Lattice parameters of TiC and Ni phases of Ti(C, N)-based cermet vs sintering temperature

1. 245 8 Å, C 0. 77 Å, N 0. 75 Å[14], it can be deduced that the lattice parameter of (Ti, Mo, W)-(C, N) decreases with increasing Mo, W (Mo and W atoms occupy some of Ti sites in the lattice) and N content (N atoms occupy some of C sites in the lattice), and that of Ni phase increases with increasing Ti, Mo and W content.

Summarizing the above deduction and Fig. 5 and Fig. 6, we can interpret the phase transition and microstructure evolution during sintering. At temperature below 1 100 ℃, a part of WC, Mo₂C and Mo dissolve in the Ni binder and expand the lattice parameter, whereas others diffuse to TiC and form the complex carbides, which reduces its lattice parameter. Between 1 100 ℃ and 1 220 ℃, the lattice parameter of TiC nearly keeps constant and that of Ni binder slight drops. It is interpreted that the dissolved WC, Mo₂C, etc in the binder may be diffuse to TiC to form the complex carbide. It is evident that the inner rim has formed at the temperature below 1 220 ℃. The lattice parameter of TiC continues to decrease and that of Ni binder increases between 1 220 ℃ and 1 370 ℃, and the relative XRD intensity of

TiN markedly decreases, which indicates that the inner rim forms at a higher rate, and part of C atoms are replaced by N atoms. The liquid phase appears above 1 370 ℃(The melting point of the studied cermet is 1 365 ℃[15]). The increase of lattice parameter of Ni phase is due to the marked increase of solubility of Ti, Mo and W in the binder(Table 3[16]). During the liquid sintering, the forming rate of the rim on the remaining TiC cores increases greatly[17], which leads to a great increase of content of Mo and W, and consequently reduction of lattice parameter of TiC. In the mean time, the N enriched in the inner rim diffuses to the core and the outer rim, and a part of C atoms in the cores and the outer rim are replaced by N atoms. It is evident that the outer rim is formed by Ostwald ripening mechanism during the liquid sintering.

Table 3　Solubility of hard phases in Ni phase(mass fraction, %)[16]

Temperature/ ℃	TiC	TiN	Mo₂C	WC
1 250(Solid)	1	< 0. 1	13	22
1 400(Liquid)	11	< 0. 5	36	27

4　CONCLUSIONS

1) Ti(C, N)-based cermets consist mainly of hard cores, inner and outer rim and metal phase. The inner rim is enriched in Mo and W comparing with the outer rim.

2) The inner rim is formed during the solid sintering by counter diffusion of TiC, Mo₂C and WC, and the outer rim by Ostwald ripening mechanism during the liquid sintering.

REFERENCES

[1]　Humenik M Jr, Parikh N M. Cermets: I , Fundamental concepts related to microstructure and physical properties of cermet systems[J]. J Am Ceram Soc, 1956, 39(2): 60 - 63.

[2]　XIONG Wei-hao. Research on the Microstructure and Interfaces of Particle Reinforced Hard Composite[D]. Wuhan: Huazhong University of Science and Technology, 1994. (in Chinese)

[3]　Laoui T, Zou H, van der Biest O. Analytical electron microscopy of the core/rim structure in titanium carbonitride cermets[J]. RM & HM, 1992, 11: 207 - 212.

[4]　Moskowitz D, Humenik M Jr. Cemented Titanium Carbide Cutting Tools, Modern Development in Powder Metallurgy[M]. Hausener H H ed. New York: Plenum Press, 1966. 83 - 84.

[5]　Moskowitz D, Humenik M Jr. Binder-Carbide Phase Interactions in TiC Base System, Science of Hard Materials [M]. Viswanadham R K, Rowcliffe D J, Gurland J, ed. New York: Plenum Press, 1983. 299 - 309.

[6]　Rudy E. Boundary phase stability and critical phenomena

in higher order solid solution systems[J]. J Less-Common Met, 1973, 3: 343 - 370.

[7]   Chun D Ⅱ, Kim D Y. Microstructure evalution during the sintering of TiC-Mo-Ni cermets[J]. J Am Ceramic Soc, 1993, 76(8): 2049 - 2052.

[8]   Ahn S Y, Kang S. Formation of core/rim structure in Ti (C, N)-WC-Ni cermets via a dissolution and precipitation process[J]. J Am Ceramic Soc, 2000, 83(6): 1489 - 1494.

[9]   Eromenko V N, Veikanva T Y, Shabanova S V. Equilibrium diagram of the titanium-molybdenum-carbon system (Ti-Mo-C ternary system phase diagram)[J]. Inorg Mater, 1970, 6: 4 - 9.

[10]   Kang S. Stability of N in Ti(CN) solid solutions for cermet applications[J]. Powder Metallurgy, 1997, 40(2): 139 - 142.

[11]   Jung I J, Kang S. A study of the characteristics of Ti(CN) solid solutions[J]. Journal of Materials Science, 2000, 35(1): 87 - 90.

[12]   Lindahl P, Gustafson P, Rolander U, et al. Microstructure of model cermets with high Mo or W content[J]. RM & HM, 1999, 17: 411 - 421.

[13]   Jonsson S. Calculation of Ti-C-N system[J]. Z Metallkd, 1996, 87(9): 713 - 720.

[14]   Weast R C. CRC Handbook of Chemistry and Physics [M]. 70th Edition. Boca Raton, Florida: CRC Press, 1989. F188 - 190.

[15]   ZHENG Yong. Research on a Composite of Fine Grained Ti (C, N)-based Cermet [D]. Wuhan: Huazhong University of Science and Technology, 2002. (in Chinese)

[16]   Chen L, Lengauer W, Ettmayer P, et al. Fundamentals of liquid phase sintering for modern cermets and functionally graded cemented carbonitrides(FGCC) [J]. RM & HM, 2000, 18: 307 - 322.

[17]   Zackrisson J, Rolander U, Andren H O. Development of cermet microstructures during sintering[J]. Metallurgical and Materials Transactions A, 2001, 32A(1): 85 - 94.

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