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Influence of molybdenum addition on the microstructure and mechanical properties of TiC-based cermets with nano-TiN modification

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Abstract

Effect of Mo addition on the microstructure and mechanical properties of TiC–TiN(nm)–WC–Co–Ni–C system cermets was studied in the work. Specimens were fabricated by conventional powder metallurgy techniques. The microstructure was investigated using transmission electron microscope (TEM) and the scanning electron microscope (SEM). Chemical compositions of different phases such as ceramic phase with core/rim structure [the core being TiC and rim being (Ti,W,Mo)(C,N)] and metallic phase were analyzed quantitatively by EDX. Mechanical properties such as flexural strength, fracture toughness and hardness were also measured. Results show that flexural strength and fracture toughness have a trend to decline with increasing Mo addition, but the change of hardness is not apparent with the increase of Mo addition. Results also reveal that finer microstructure and thicker rim phase will be obtained with the increase of Mo addition. The optimal addition of Mo can be estimated to be 4 wt.% with respect to TiC–10TiN(nm)–15WC–5Co–Mo–5Ni–1C system cermets. Fracture micrographs show that main failure mode of the cermets is a mixed one, i.e., trans-granular and inter-granular fractures both exist.

Keywords: B. Microstructure-final; C. Mechanical properties; D. Carbides; D. Nitrides

1. Introduction

Titanium carbonitride-based cermets have been widely used as cutting tool materials in mechanic processing owing to their excellent wear resistance and toughness which are superior to those of TiC–Mo (or Mo_2C)–Ni cermets [1–4]. Molybdenum-free titanium carbonitride based cermets can be obtained through a pre-sintering solid solution (PRSSS) treatment of titanium carbonitride [5]. Earlier researches have indicated that addition of molybdenum or molybdenum carbide into titanium carbonitride cermets can improve the wettability between ceramic phase [TiC or Ti(C,N)] and metallic phase (Ni) [6,7] and cermets with finer microstructure and better mechanical properties can be obtained. Researches have also revealed that microstructure in cermets consists of ceramic phase and metal phase and the coarse ceramic phase in the microstructure exhibits a core/rim structure, i.e. the coarse ceramic phase generally consists of a Ti(C,N) or a TiC core surrounded by a rim [8,9]. Subsequent investigations found that too much addition of molybdenum into titanium carbonitride cermets will make rim phase in cermets too thick. It is well known that thicker rim phase means coarser ceramic phase grains. Consequently, too much addition of molybdenum is not beneficial to the improvement of mechanical properties. Therefore, how to determine an appropriate addition amount of molybdenum has become a subject worth of discussion. In addition, as wettability of Co on the ceramic phase is higher than that of Ni, so less Mo addition can be realized in cermets with Ni and Co addition. In summary, how to optimize the amount of Mo addition has become a key job in studying titanium carbonitride-based cermets with Co/Ni addition [10].

Nano-technology appeared at the end of the past century. Now it is developing quickly and a 'nano-era' is

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coming near [11]. Nanoparticulate composites are very important in the research and production of nanoparticulate materials. Some researchers found that properties such as hardness, fracture toughness and flexural strength could be improved by adding nanoparticulate powder into conventional materials [12–14]. Though there are many investigations about the microstructure, mechanical properties and mechanic application of conventional titanium carbonitride based cermets and the production of nano powder recently, unfortunately, there are only several studies on the microstructure, mechanical properties and application of titanium carbide based cermets with nano TiN addition [1,15]. Simultaneously, researchers also found that TiC based cermets cutter with nano-TiN modification (TiC–WC–Mo–20Ni–C system) readily failed in the form of gross wear under high speed cutting in processing normalized medium carbon steel [10]. In order to realize such application, it is necessary to improve the wear resistance of such cermets cutter by decreasing metallic phase content. Additionally, the effect of molybdenum addition on the microstructure and mechanical properties of titanium carbide based cermets with nano TiN modification has not been reported so far. The aim of the investigations presented here is to investigate the influence of the molybdenum addition on the microstructure and mechanical properties of TiC–WC–Mo–5Ni–5Co-C system cermets with nano-TiN addition for their high-speed cutting application. An optimal addition amount of Mo is determined in accordance with the experimental results. Quantitative analysis of chemical compositions of ceramic phase and metallic phase in the cermets was also conducted. In general, the experimental results will benefit a better understanding and the practical application of such cermets.

2. Experimental

The chemical composition (wt.%) of the cermets was chosen as $(65-x)$TiC–10TiN–xMo–15WC–5Co–5Ni–1C [the value of x ranges from 4 to 12 (wt.%)]. Nano TiN powder (purchased from Institute of Chengdu Organic Chemistry of Academia Sinica) was dispersed by using ultrasonic device and then dispersion effect was observed on a Hitachi-800 transmission electron microscope (Appropriate amounts (5–10 vol.%) of nano-sized TiN powder were dispersed ultrasonically in water/ammonia solution at pH$\sim$10 for 1.5 h). Commercially-obtained powders of TiC (2.5 μm), nano TiN (30–50 nm), WC (1.5 μm), Mo (2.6 μm), Ni (1.8 μm), Co (1.6 μm) and C (2.7 μm) were mixed thoroughly in a planetary ball mill, at a ball-to-powder weight ratio of 10:1 for 24 h, and then dried and sieved. 5 wt.% of polyvinyl alcohol was added to the powder-mix before making the green compacts, the latter being produced in a cold steel die at a uniaxial pressure of 170MPa. Then the compacts were treated for binder burn-out at 400 °C for 2 h in vacuum. Finally, the green compacts were sintered at 1400 °C for 1 h in vacuum. The technique parameters for raw powders are shown in Table 1.

Specimens for scanning electron microscopy (SEM) were prepared by conventional method and etched by compound acid (HCl:HF = 1:1). Microstructure examination was conducted on a Hitachi X650 scanning electron microscope (SEM). Quantitative analysis of chemical composition of ceramic phase and metallic phase was conducted by using EDX attached to the SEM. Thin foils for transmission electron microscopy were prepared by ion milling using 5 kV argon ions in a Gatan dual-ion mill model 600. Conventional TEM analysis was performed on a Hitachi H-800 transmission electron microscopy operated at 200 kV.

Flexural strength (σ_{bb}) test was conducted on a Shimadzu electron testing machine model DCS-3000 by three-point flexural method (span 25 mm; crosshead speed, 1 mm·min^{-1}). Fracture toughness (K_{IC}) was estimated on a Shimadzu electron universal material testing machine model DCS-3000 by the introduction of a sharp pre-made crack, the length of which is 2.5 mm. Each data in the paper are the average of the twelve tested specimens. Rockwell hardness was conducted on a common Rockwell hardometer. Relative density measurement was conducted by using Archimedes method. Fracture morphology was examined by SEM on a Hitachi X650.

3. Results and discussion

3.1. Mo addition on the microstructure

Morphology of nano-TiN powder after dispersion is shown in Fig. 1. From the figure it can be seen that no obvious aggregation phenomenon is observed. The average diameter of a nano TiN particle is estimated to be 30–50 nm. In fact, the well-dispersed nano TiN powders will play a significant role in the successful preparation of TiC based cermets with nano TiN modification. That is, whether the dispersion effect is good or

Table 1
Chemical composition of raw powder

Powder	Composition (wt.%)						Size (μm)
	C	S	N	Fe	O	Rest	
TiC	18.8	0.027			0.00172	Ti	3.87
Ni	0.178	0.0033		0.003	0.00106	Ni	2.95
Mo	0.0094	0.0032			0.00122	Mo	3.28
C			0.00015		0.30	C	3.25
TiN(μm)	0.089	0.0012	19.9		0.0014	Ti	2.3
TiN(nm)	1		19.3		2	Ti	<0.1

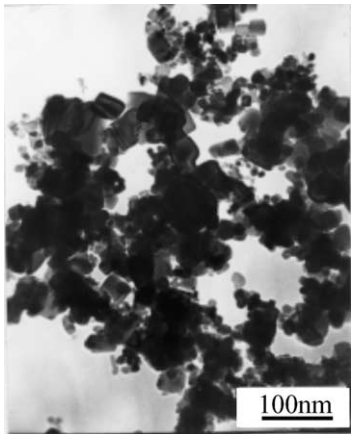

Fig. 1. TEM micrograph of nano TiN powder after dispersion.

Fig. 2. TEM micrograph showing the location of nano TiN particles.

not will directly determine the microstructure and mechanical properties of such cermets, which can be confirmed by literature [1,15]. Fig. 2 shows the locations of nano TiN particles in TiC based cermets. It can be found that nano TiN particle is distributed at the interface of TiC/TiC. In fact, most nano TiN particles can also be located among three TiC particles. The impedance of nano TiN particles on the growth of TiC matrix makes microstructure in such TiC-based cermets finer than that of the conventional TiC based cermets [1,15].

Fig. 3 shows SEM photographs of microstructure of TiC–TiN–WC–5Ni–5Co–C system cermets containing different Mo (magnification, 3000). It can be found that the microstructure has a trend to become finer with the decrease of Mo addition. It must be emphasized that the fining effect is not obvious. SEM micrographs of the microstructure of the above cermets system under different Mo additions are shown in Fig. 4 (magnification, 10000). It is worth noting that apparent core/rim structure exists in the coarser ceramic phases. There are many researches on the formation mechanism and chemical composition of the core/rim structures [8,9]. Now the concerted view is that the core is TiC and the rim consists of (Ti,W,Mo)(C,N) solid solution. Regarding the core/rim structure in the Ti(C,N) based cermets there will be more detailed description in the following discussions. In addition, the reason why no obvious metallic phases are found in Figs. 3 and 4 can be related to the gross etching and relatively less content of metallic phase. At the same time, some pores located among three ceramic phase particles can be observed in the above two figures.

The reasons why the microstructure, especially the ceramic phase of TiC–TiN–WC–5Ni–5Co–C system, becomes finer with the decrease of Mo addition can be

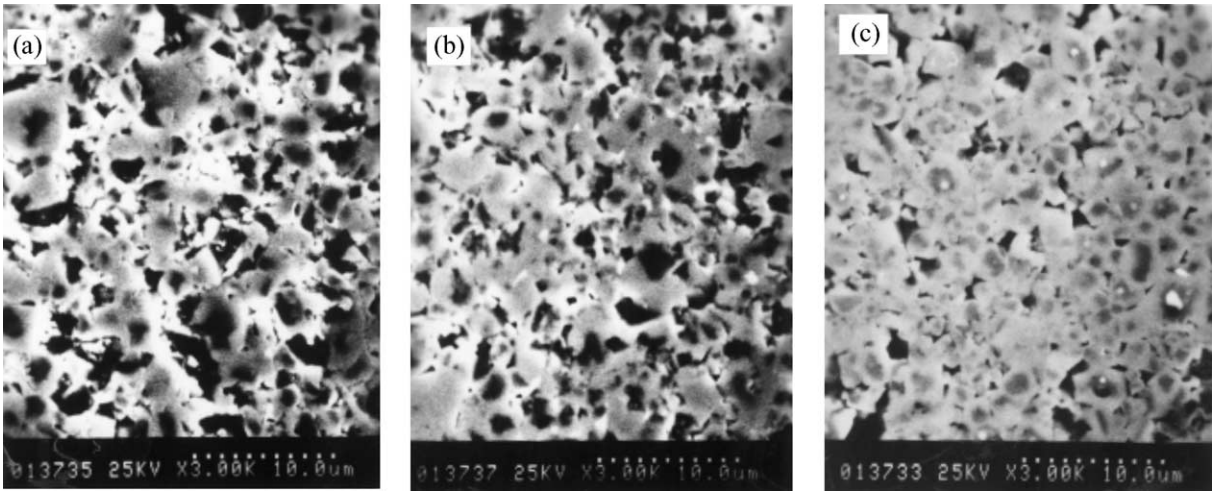

Fig. 3. SEM micrographs showing the microstructure of cermets (SEI,×3000). Mo, 12 wt.%, (b) Mo, 8 wt.%, (c) Mo, 4 wt.%.

described as follows. On the one hand, according to the earlier reports, some Mo are distributed in the ceramic phase [rim phase, i.e. (Ti,W,Mo)(C,N)]. Therefore, the ceramic phase particles will become coarser with increasing Mo addition (in fact, it is the thickness of the rim phase that becomes coarser with the increase of Mo addition). On the other hand, it is well-known that the addition of molybdenum or molybdenum carbide into titanium carbonitride cermets improves the wettability between ceramic phase [TiC or Ti(C,N)] and metallic phase (Ni) and fining effect of TiC matrix [6,7]. However, more Mo addition means that more Mo is dissolved in metallic phases, and metallic phase will become non-uniform and discontinuous in some regions [shown in Fig. 5 (b)]. Consequently, more spaces in materials will be occupied by ceramic phases particles, and coarser ceramic particles will appear in some areas in the materials.

Back scattered electron images (BSE image) of TiC–TiN–WC–5Ni–5Co–C system with different Mo additions can be seen in Fig. 5. Ceramic phases [TiC and Ti(C,N)] are dark in the microstructure owing to the

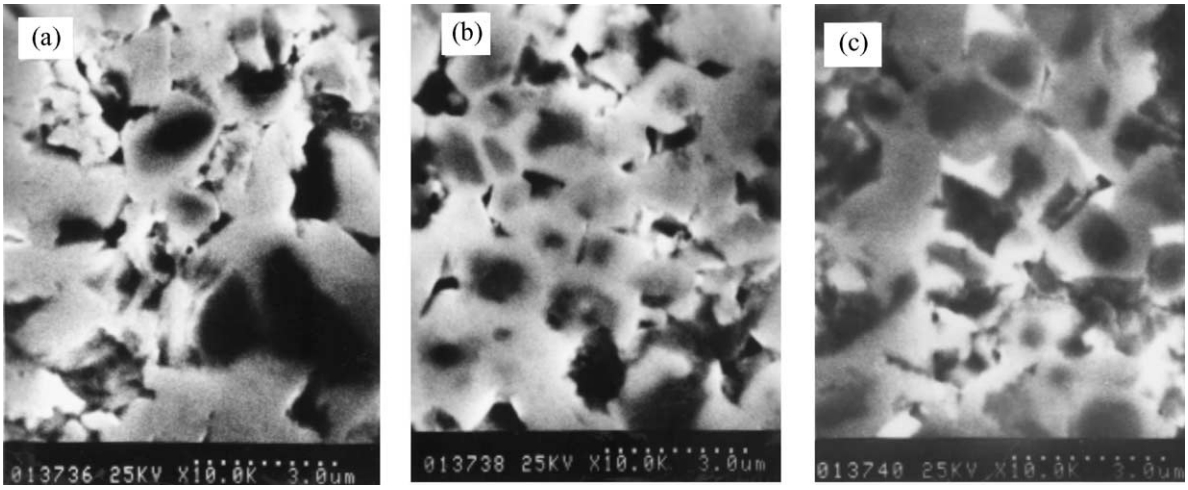

Fig. 4. SEM micrographs showing the microstructure of cermets (SEI,×10000). Mo, 12 wt.%, (b) Mo, 8 wt.%, (c) Mo, 4 wt.%.

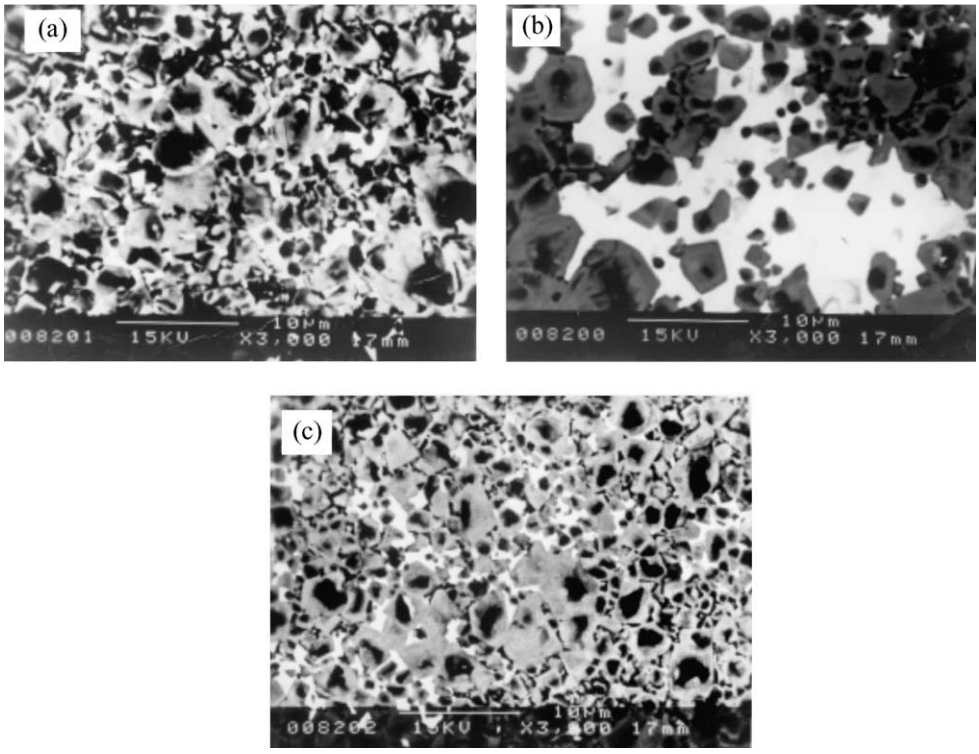

Fig. 5. SEM micrographs showing the microstructure of cermets (BSI, ×3000). (a) Mo, 12 wt.%, (b) Mo, 8 wt.%, (c) Mo, 4 wt.%.

Table 2
EDX analytic results (wt.%)

Zone	Ti	Co	Ni	Mo	W
A	43.24	0.32	0.37	12.18	43.89
B	45.44	0.00	0.00	7.47	47.09
C	3.31	13.88	7.77	20.62	54.43
D	50.25	0.38	0.00	3.92	45.46
E	3.21	13.74	6.67	9.73	66.64

lower average atomic number. Similarly, larger atomic number makes metallic phases appear to be white and gray. It can be seen form Fig. 5 that the fining effect is not remarkable with the decrease of Mo addition. The probable reason is related to etching, sample difference and choice of the field of view, etc. Subsequent EDX analysis shows that the white phase is metallic phase containing Co,Ni,Mo,W and Ti (Co and Ni account for 20 wt.%), as shown in Table 2 (zone C and zone E). The gray phase is rim phase, i.e. (Ti,Mo,W)(C,N) solid solution (zone A, zone B and zone D). The formation of the rim phase has some relation to the dissolving of Mo_2C and TiC into the liquid phase and then re-precipitation on the coarse TiC or Ti(C,N) grains. In fact, Mo_2C phase exists below 900 °C and then disappears above 1200 °C. Apparently, there are such phenomena as the dissolving and precipitation of Mo_2C, the diffusion of Mo_2C or Mo into the Ti(C,N) solid solution in the sintering process. However, the formation mechanism of the rim phase is an exceptionally sophisticated process, which is worth discussing in detail and systematically.

It is well known that microstructure in cermets is usually composed of ceramic phases (hard phases) bonded together with metallic phases (binder). However, from Fig. 5 it can be found that some metallic phase blocks are aggregated (zone B) in cermets with 8 wt.% Mo additions. The reason why the aggregation exists is to be investigated in the later examinations.

Fracture morphologies of cermets with different Mo additions are shown in Fig. 6. A SEM high-magnification image of the surface fracture at room temperature revealed that mainly a typical trans-granular fracture [especially the coarser ceramic particles, i.e. Ti(C,N), TiC or (Ti,W,Mo)(C,N) particles]: the crack passing through the grains [5]. In fact, fracture mode of cermets with different Mo additions and nano TiN modification is a mixed one, i.e. inter-granular fracture (the crack propagates along the boundaries of two ceramic phase particles or passes through the interface between ceramic phase particles and metallic phase particles) also exists, as shown in Fig. 6. Additionally, a small amount of cleavage fracture can be observed in some coarser ceramics phase particles. In fact, the phenomena such as the abscission of hard phase and tear edge of metal phase also exist (the tearing is not very apparent because of the lower metallic contents).

3.2. Mo addition on the mechanical properties

Effects of addition of Mo on flexural strength, fracture toughness and hardness are shown in Figs. 7–9. From Fig. 7 it can be found that flexural strength has a trend to decline with the increase of Mo addition, but the change is not obvious. As discussed earlier, the ceramic phase (especially rim phase) will be coarser with increasing Mo addition. Furthermore, microstructure in the cermets will become finer with the decrease of Mo addition. Consequently, flexural strength of the cermets declines with the increase of Mo addition.

On the other hand, it can be seen from Fig. 8 that fracture toughness also decreases with the increase of Mo addition, and the variation is relatively apparent. The reasons can be described as follows. Firstly, coarser

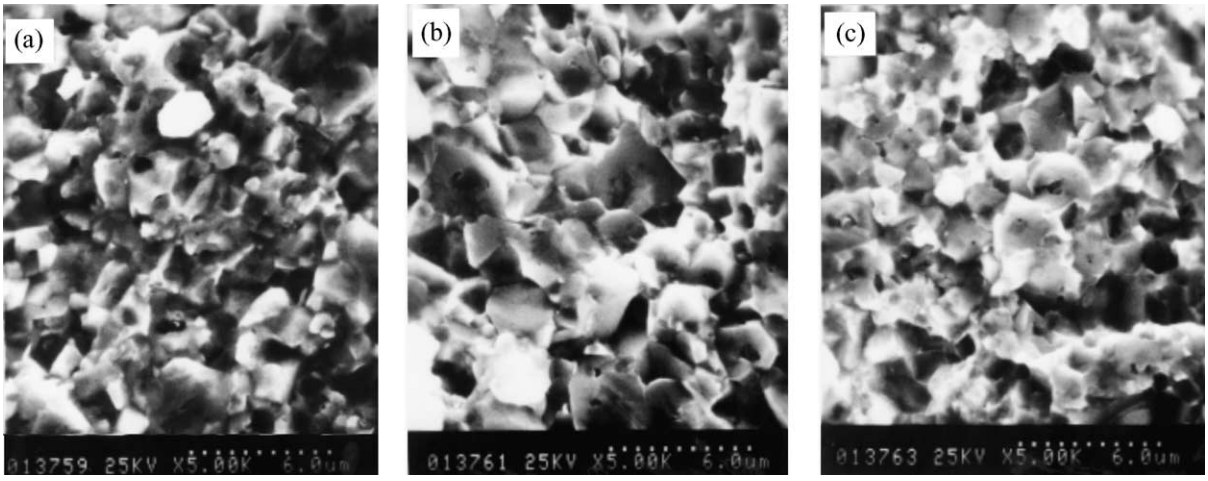

Fig. 6. Fracture images of fracture toughness samples with different Mo additions (×5000). Mo, 12 wt.%, (b) Mo, 8 wt.%, (c) Mo, 4 wt.%.

microstructure in cermets will be obtained with the increase of Mo addition. In fact, micro-cracks are apt to appear at the interface of the two coarser ceramic phase grains and readily propagate through the coarser grains (i.e., trans-granular fracture or cleavage fracture) or along the interface of the two ceramic phase grains. Therefore, fracture toughness of the cermets does not benefit from the increased Mo addition. Secondly, as described earlier, obvious aggregation of the metallic phase in the microstructure can be found in Fig. 5(b) (Mo addition is 8 wt.%). In contrast, uniform distribution of metallic phases can be seen in Fig. 5(c) (Mo addition is 4 wt.%). Therefore, there is an obvious decline when Mo addition ranges from 4 to 8 wt.%. In addition, it can be found from Fig. 8 that the decrease is not obvious when Mo addition goes from 8 to 12 wt.%. Thirdly, more additions will make it difficult for the pores to disappear in the liquid phase sintering process, i.e. lower relative density will be obtained. In general, the decline of fracture toughness is related to the grain size of microstructure, the distribution of metallic phases and relative density of testing samples.

In addition, Fig. 9 reveals that there is an obvious decline of hardness when Mo addition is from 4 to 8 wt.%. On the one hand, the result is relevant to the aggregation of metallic phases in cermets containing 8 wt.%. On the other hand, there will be more ceramic phases (TiC) while Mo addition is decreased. However, it must be also noted that the change of hardness of the cermets is not apparent.

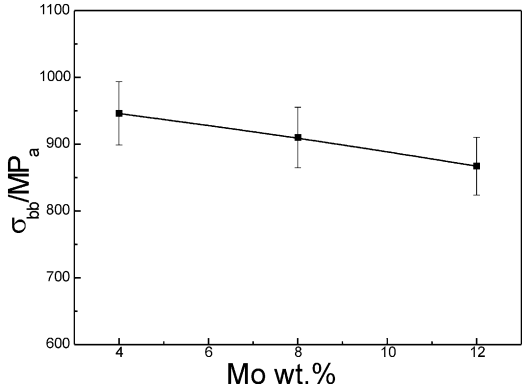

Fig. 7. Addition of Mo on flexural strength.

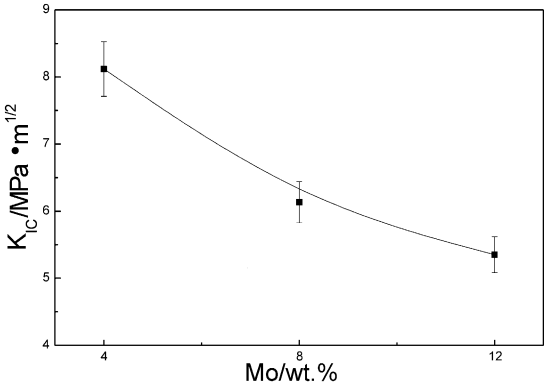

Fig. 8. Addition of Mo on fracture toughness.

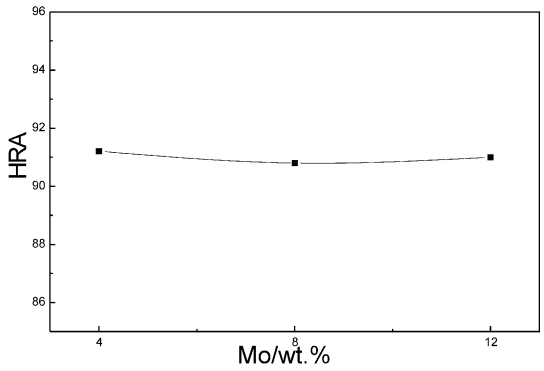

Fig. 9. Addition of Mo on hardness.

3.3. EDX analysis of ceramic phase

Figs. 10 and 11 are SEM micrographs showing core/rim structure in the coarser ceramic phase grains and line-scan result of the coarser ceramic grains, respectively. It can be found from Figs. 10 and 11 that little metallic phase exists in the core and the main elements

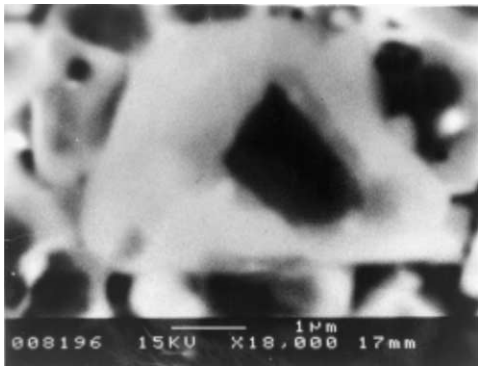

Fig. 10. Core/rim structure of ceramic phase.

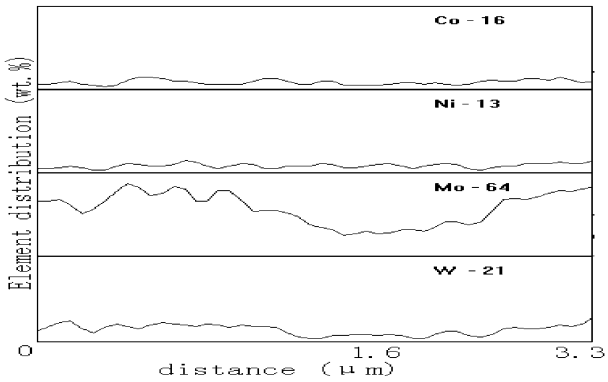

Fig. 11. Element distribution of a ceramic grain with core/rim structure.

of the core are Ti (>90 wt.%) and C. The result shows that the core is actually the TiC grain un-dissolved in the sintering process. In addition, The main elements appearing in the rim are Mo,W and Ti. It must be declared that elements such as N and C were not examined in the experiment considering the error of EDX. Actually, there is some amount of N and C in the rim. Therefore, it can be concluded that the rim is a (Ti,W, Mo)(C,N) solid solution.

4. Conclusions

This study discussed the influence of nano TiN addition on the microstructures and properties. Flexural strength and fracture toughness have a trend to decline with the increase of Mo addition, but the change is not apparent. Similarly, the variation of hardness is also not apparent with the increase of Mo addition. Results of the study also reveal that finer microstructure and thicker rim phase will be obtained as the Mo addition is increased. According to the experimental results, the optimal addition of Mo can be estimated to be 4 wt.% regarding TiC–10TiN(nm)–15WC–Mo–5Co–5Ni–1C cermets system. Fracture micrographs show that main failure mode of the cermets is a mixed one, i.e. trans-granular and inter-granular fractures both exist.

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