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Effect of nano-micro TiN addition on the microstructure and mechanical properties of TiC based cermets

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Abstract

In this paper the titanium carbide based cermets with addition of nano-micro titanium nitride were fabricated by conventional powder metallurgy techniques. The microstructure of TiC based cermets with nano-micro TiN addition has been investigated by transmission electron microscope (TEM) and a scanning electron microscope (SEM). Bending strength, fracture toughness and hardness were also measured. Results reveal that mechanical properties do not change monotonously with increasing nano TiN addition. Results also show that nano titanium nitride addition can prevent the coalescence of TiC grains. It is also found that nano TiN is distributed at the interface of TiC/TiC grains and that the growth of TiC grains is impeded by the presence of nano TiN particles and that the result is an increase in mechanical properties. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: TiC; Cermets; TiN; Mechanical properties; Microstructure-final

1. Introduction

Recently, TiC–TiN based cermets attract much attention as cutting tool materials because of their excellent wear resistance and toughness which are superior to those of TiC–Mo(or Mo_2C)–Ni cermets.[1–4] Mechanical properties such as hardness and transverse rupture strength (TRS) of TiC–TiN based cermets were studied by several researchers.[5,6] Scientists also investigated the effect of TiN addition to TiC–Mo_2C–Ni cermets on room temperature TRS and discussed the results in relation to the size of the defects such as residual voids and coarse carbide particles.[4,5] In addition, the concentration of Mo was quantitatively measured and it was found that the concentration of Mo in the binder phase greatly increases with TiN addition and consequently, the wear resistance of the cermets is considerably improved.[7,8]

At the end of the 1980s nano science and technology (Nano-ST) appeared, as a high and new science and technology, it is developing very quickly now.[9,10] As nano material possesses high strength, high hardness and excellent ductility and toughness, undoubtedly, more attention has been paid for the application of nano material. Scientists found that the properties of materials (especially ceramics) can be improved by adding nano powder into the conventional materials.[11–13] Though there are many reports about the production of nano TiN powder recently,[14–16] unfortunately, the application of nano TiN powder in TiC based cermets has not been reported so far. In this case, the effect of nano-micro TiN addition on the microstructure and mechanical properties of TiC based cermets have been conducted and the modification mechanism has also been investigated in this paper to provide a theoretical basis for practical application of such cermets.

2. Experimental

Nano TiN powder was dispersed by using an ultrasonic device and the then dispersion effect was observed

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on H-800 TEM. Powder mixtures consisting of TiC, nano TiN, micro TiN, Mo, Ni and C were mixed in a ball mill in ethanol together with cemented carbides balls for 24 h, and then dried and sieved. The sieved powders were pressed into specimens in a die under 170 MPa. The green compacts were sintered at 1400 °C for 1 h in vacuum. The technique parameters for raw powder and the chemical composition of the cermets are shown in Tables 1 and 2 respectively.

Specimens for scanning electron microscopy (SEM) were prepared by the conventional method and etched by compound acid (HCl:HF = 1:1). The microstructure was characterized on a Hitachi X650. Thin foils for transmission electron microscopy (TEM) 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.

The bending strength (σ_{bb}) and fracture toughness (K_{IC}) were measured on a Shimadzu electron testing machine model DCS-3000 by the three-point bend method. The fracture toughness was conducted by the introduction of a sharp pre-made crack the length of which is 2.5 mm. All data in the paper are the average of 12 tested specimens. Rockwell hardness was conducted on the common Rockwell hardometer. Density measurement was carried out by using Archimedes method.The fracture morphology was examined by SEM on a Hitachi X650.

Table 1
Technique parameters for 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

Table 2
Chemical composition of testing specimens

Sample series	Composition (wt.%)					
	TiN (nm)	TiN (μm)	TiC	Mo	Ni	C
1	10	0				
2	0	10				
3	2	8	Rest	15	20	1.5
4	4	6				
5	6	4				
6	8	2				

3. Results

The morphology of nano TiN powder used as starting materials is shown in Fig. 1. From the figure it can be seen that the average diameter of a nano TiN particle is 30–50 nm. Fig. 2 gives the effect of nano-micro TiN addition on the microstructure of TiC based cermets. Fig. 2 shows that nano TiN addition can prevent the coalescence of TiC grains. From Fig. 2(e) and (f) it can be found that there is obvious difference between conventional micro TiN addition and nano-micro addition, the nano TiN can obviously prevent the coalescence of the TiC grains. Fig. 2 also gives a microstructure consisting of ceramic phase and metal phase. The coarse ceramic phase grains [carbonitride Ti(C,N)] have a core/shell structure. That is to say, the carbonitride grains generally consist of a Ti(C,N) core surrounded by a rim/shell that in addition to the Ti(C,N) contains heavier elements, such as W, Mo.

Fig. 3 shows the morphology of nano TiN distributed at the interface of the TiC grain. It can be seen that some nano TiN particles are distributed in the interface of two or three TiC grains.

The retained nano TiN particles could be from the growth and aggregation of a single particle, several or more nano TiN particles, but most of the TiN particles still belong to the nano level. In addition, such nano TiN particles can exist in the grain boundary of two or more hard phases when most TiN particles do not dissolve in the sintering process and they do not diffuse into the hard phase. A lot of TEM observations have shown that less retained nano TiN is distributed at the interface of TiC grains when nano TiN addition is below 6 wt.%, this can be confirmed by literature.[17] However, there will be more nano TiN particles which are widely

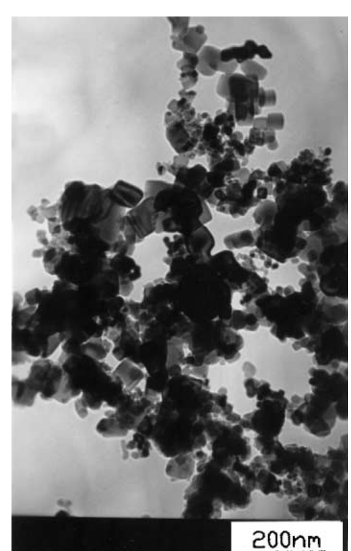


Fig. 1. TEM image of nano TiN powder.

distributed at the boundaries between two TiC grains or among three TiC grains when nano TiN addition is above 6 wt.%. These TiN particles can prevent the TiC grain boundaries from moving and avoid the growth of TiC grains, hence the coalescence of the TiC grains can be prevented when increasing nano TiN addition.

Figs. 4, 5 and 6 give the influence of nano TiN addition on the bending strength, fracture toughness and hardness, respectively. The effect of nano TiN addition on density was shown in Fig. 7. The relative sizes of the TiC and nano TiN particles can be expected to lead to a much more compact packing than the TiC + micro TiN since the intergrain pores would be occupied, so the density of the composite decreases at high nano TiN content. Results reveal that the mechanical properties do not increase monotonously with increasing nano TiN addition. The properties increase with increasing nano TiN addition, reach the maximum values and then decrease with increasing nano TiN addition. As to bending strength, the decrease is slight when nano TiN addition is above 6 wt.%, whereas, hardness and fracture toughness decrease obviously when nano TiN addition is above 6 wt.%. The above results correspond with the microstructure shown in Fig. 2.

It is also seen from Fig. 2 that the coalescence of the TiC grains is not observed when increasing nano TiN addition. It is seen from Fig. 3 that more nano TiN particles are widely distributed at the boundaries of TiC

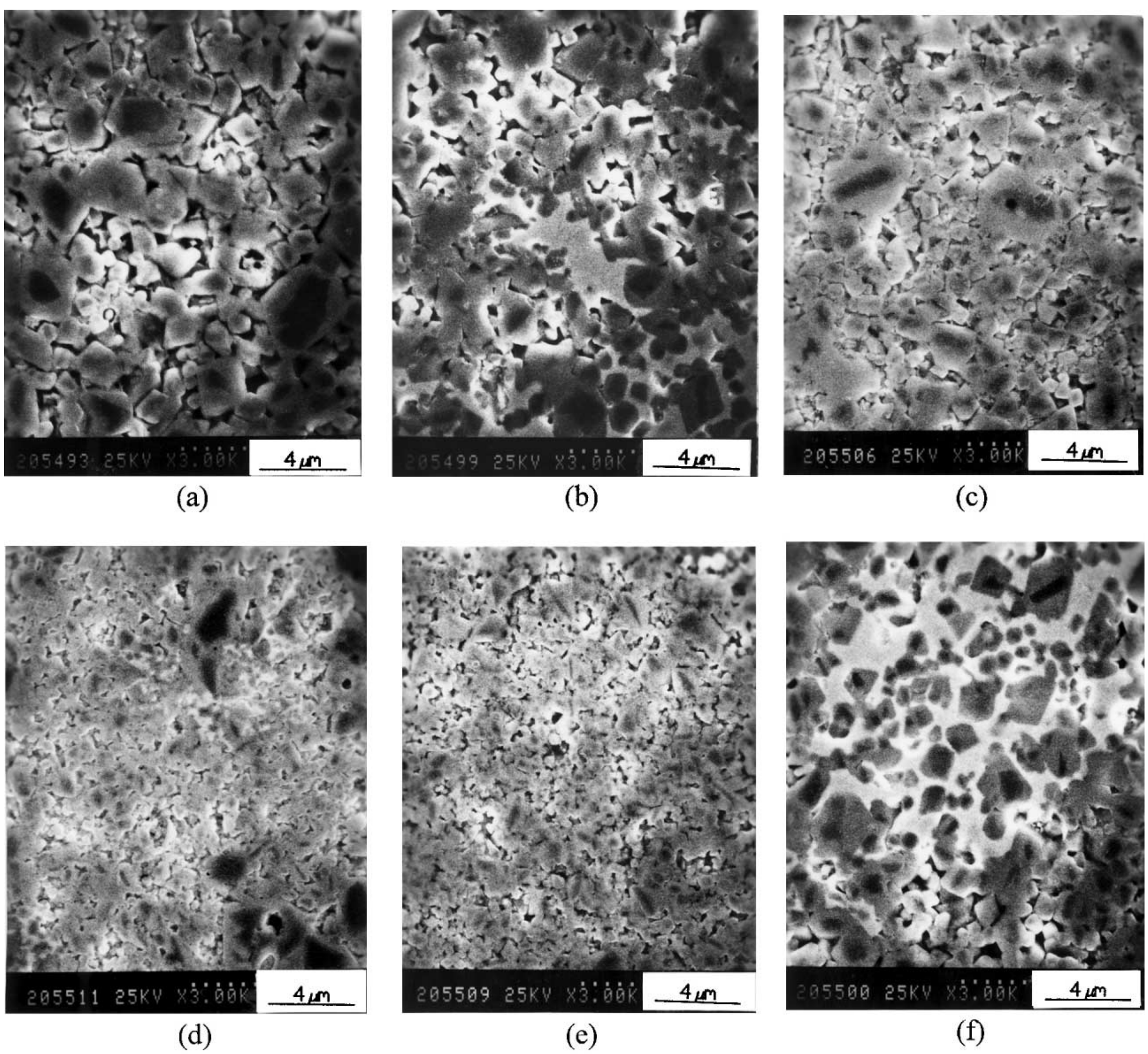


Fig. 2. SEM micrographs showing the microstructure of cermets (a) TiN_{nm}, 2 wt.% , (b) TiN_{nm}, 4 wt.% , (c) TiN_{nm}, 6 wt.%, (d) TiN_{nm}, 8 wt.%, (e) TiN_{nm}, 10 wt.%, (f) $TiN_{\mu m}$, 10 wt.%.

grains. As mentioned above, these TiN particles can prevent the coalescence of TiC grains and prevent the crack from propagating further. According to the Hall–Petch formula, the yielding strength will increase with the fining of TiC grains, so bending strength and hardness are improved.

Fracture morphology of bending strength test specimens is shown in Fig. 8. The fracture mechanism can be intergranular (ceramic phase/ceramic phase or ceramic phase/binder phase) and transgranular (ceramic phase). But there is a small amount of cleavage fracture (ceramics phase). In fact, the abscission of hard phase and tear edge of metal phase also exist. Under the condition of the same chemical composition, the fracture surface of nano TiN addition shows the remarkable fining effect compared with conventional TiN addition, as shown in Fig. 8(a) and (b), respectively.

4. Discussion

In earlier studies, it has been found that micro TiN can fine TiC grains and the properties of TiC–TiN cermets can be improved.[4,17]Among nitrides TiN and TaC

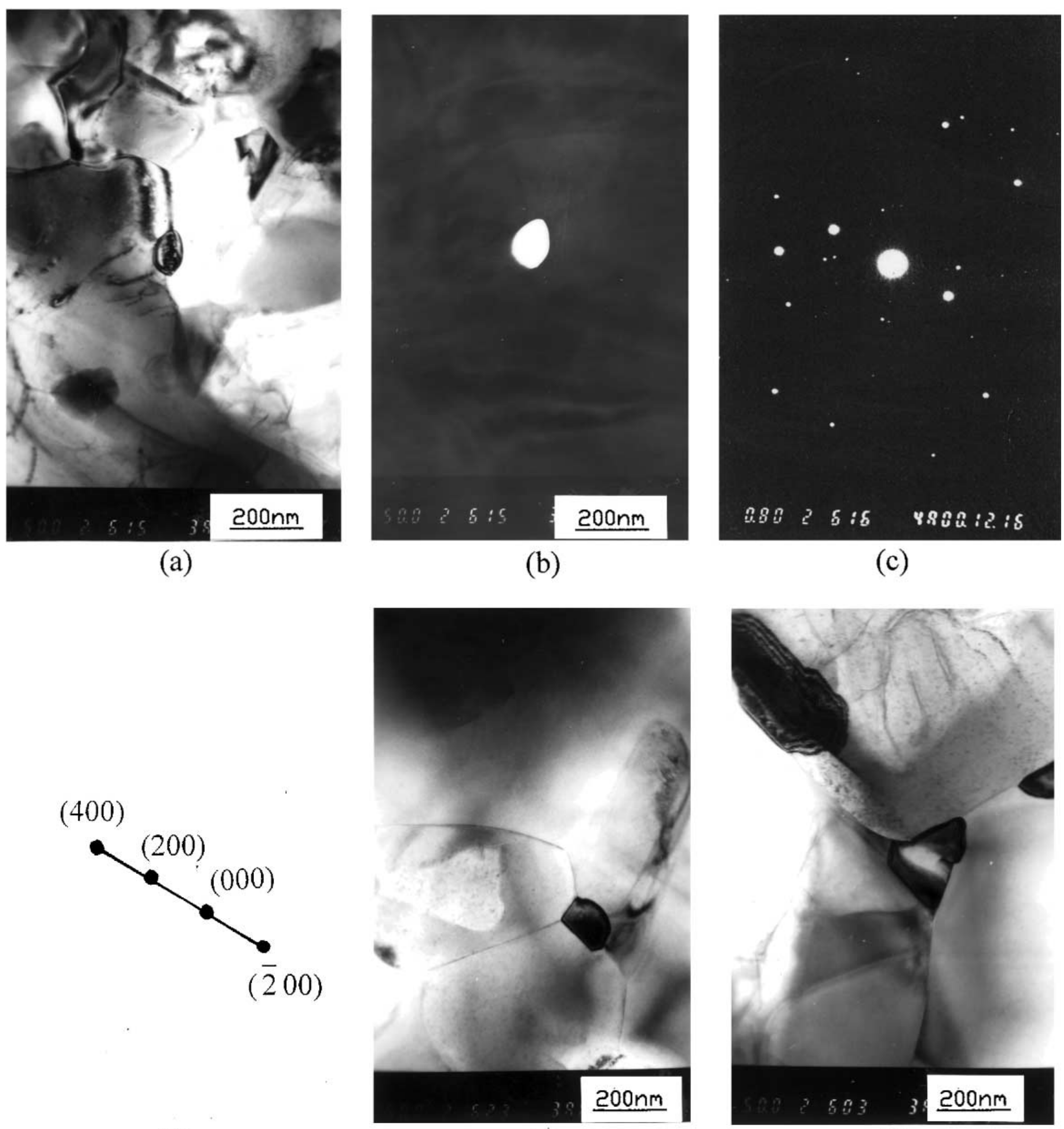


Fig. 3. TEM micrographs showing the morphology of nano TiN distributed at the interface of TiC/TiC grains. (a) Bright image, (b) dark image, (c) diffraction pattern, (d) index, 4 wt.% TiN_{nm}, (e) bright image, 6 wt.% TiN_{nm}, (f) bright image, 8 wt.% TiN_{nm}.

have gained special attention, small additions of TiN increase the hardness, principally due to grain refinement; by further substitution of TiN for TiC a continuous decrease of hardness occurred, the reason being the lower hardness of TiN.[18] Literature[19] found that the improvement in transverse rupture strength was caused by a solid solution strengthening effect of the binder phase through the dissolution of a large amount of refractory metals such as Mo and W.

As mentioned above, there will be more TiN particles which are widely distributed at the interface of TiC/TiC grains when nano TiN addition is above 6 wt.%, these particles prevent the TiC grains from moving and hence the coalescence of TiC grains is prevented. This, we believe, is the most important reason why the microstructure does not become coarser with increasing nano TiN addition and the properties are improved.

A large amount of SEM examinations have shown that intergranular fracture is usually the main failure mode.[17] Therefore, when the crack propagates forward and reaches the nano TiN particles distributed at the boundaries of TiC grains, it is difficult for the crack to cross through the TiN particles and the crack will deflect and propagate along the TiC/TiN interface. In that case, more propagating energies are needed for the further propagation of the crack. Though the nano TiN addition benefits the obtaining of a fine microstructure, more defects such as pores will exist in the microstructure when nano TiN addition is above 6 wt.%, this can be confirmed by Fig. 7. Consequently, mechanical properties will decrease when nano TiN addition is above 6 wt.%.

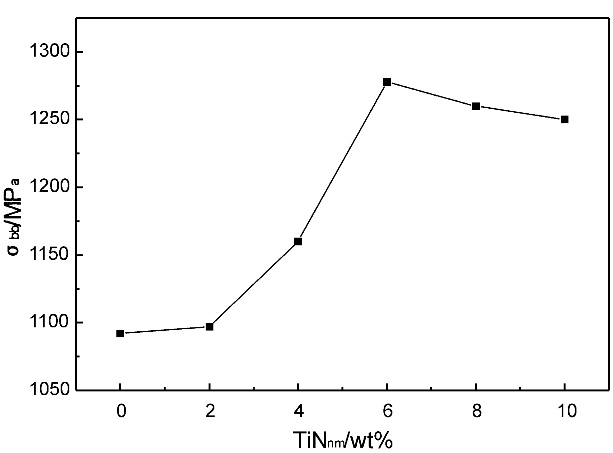


Fig. 4. The effect of nano TiN addition on bending strength.

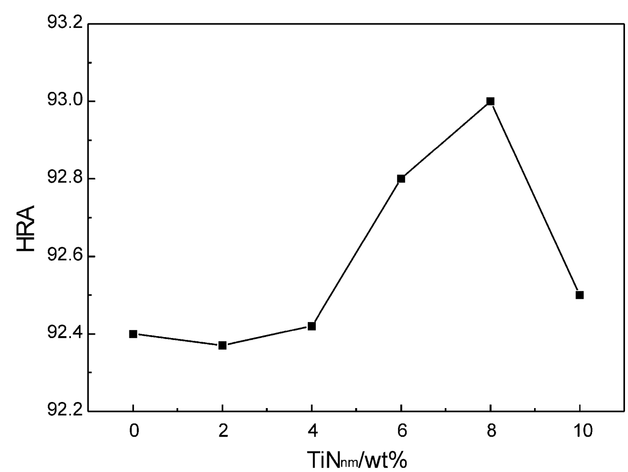


Fig. 6. Effect of nano TiN addition on hardness.

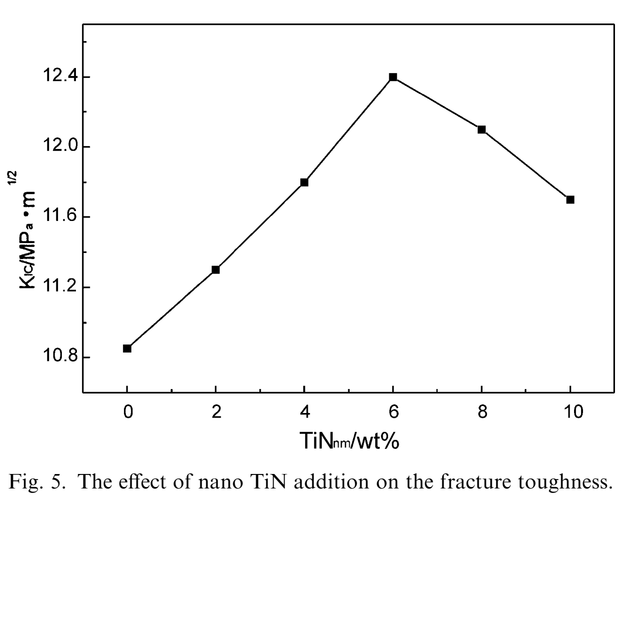


Fig. 5. The effect of nano TiN addition on the fracture toughness.

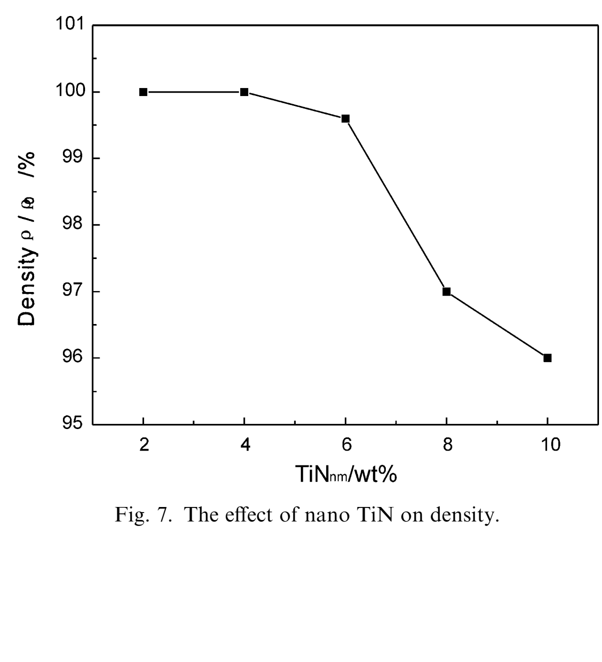
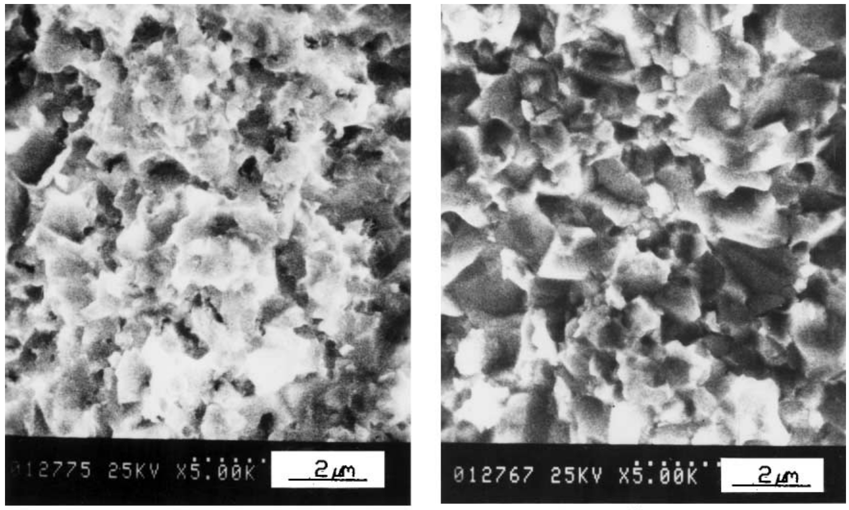


Fig. 7. The effect of nano TiN on density.



(a) (b)

Fig. 8. SEM micrographs showing the fracture morphology of bending test specimens (a) TiN_{nm}, 10 wt.%; (b) $TiN_{\mu m}$, 10 wt.%.

5. Conclusions

In this study, the influence of nano TiN addition on the microstructures and properties has been discussed. Results reveal that nano TiN addition can prevent the coalescence of TiC grains. Results also show that the wide distribution of nano TiN at the interface of TiC/TiC grains leads to the fine TiC grains. The mechanical properties of TiC based cermets with nano-micro TiN addition do not increase monotonously with increasing nano TiN addition. The decrease of mechanical properties is caused by the defects in cermets when nano TiN addition is above 6 wt.%.

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