

Metallothermic synthesis and consolidation of ultrafine TiCN particles

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Ultrafine titanium carbonitride particles ($\text{TiC}_{0.5}\text{N}_{0.5}$) 100 nm in mean size were successfully synthesized by a nitridation treatment at ordinary temperatures, 1273-1373 K of nanostructured half-stoichiometric titanium carbide ($\text{TiC}_{0.5}$) particles, which were produced by the magnesium reduction of gaseous $\text{TiCl}_4 + 1/4\text{C}_2\text{Cl}_4$. We prepared in the next step two sintered cermets with a basic composition of $\text{TiC}_{0.5}\text{N}_{0.5} + \text{Mo}_2\text{C} + \text{Ni}$ using developed and commercialized TiCN powders (1-2 μm). The ball-milled powders were sintered at different temperatures using a vacuum sintering method as well and the mechanical properties were compared.

Key words: Nano, Titanium carbonitride, Sintering, Hardness, Microstructure.

Introduction

It is well-known that composites made from transition metal carbides with metallic binders are widely used nowadays in the field of cutting tools. There are various families of such types of composites, however two types of materials are mainly used in cutting tool applications [1]. The first group is based on WC-Co carbides, which have high toughness and good hardness. However, they have some weak points including relatively poor oxidation resistance and an ability to undergo plastic deformation at high temperatures [2]. The second group is Ti (C, N) based cermets, which have excellent hardness, oxidation resistance as well as wear resistance, therefore their applications have increased in the tool industry in spite of a slightly higher cost of the raw powders.

On the other hand, as finer raw powders can give the higher mechanical properties required in a tool part, many researchers have concentrated on developing new techniques for the production of raw TiCN powders. The carbothermal reduction of titanium dioxide is one popular commercial process for this [3-5]. The direct reaction of titanium carbide powders with TiN or the reaction of pure titanium powders with C and N, gas-phase reaction, and the synthesis of TiCN powders by sol-gel process have been also researched [6-9]. However, they have some drawbacks such as 1) the formation of a coarse sintered structure, 2) a difficulty in controlling the stoichiometry of the composition, 3) the appearance of undesired compositions such as TiC_xO_y , 4) the requirement of using initial titanium powders with a high purity, and 5) the requirement of post-milling in

order to get finer particles.

Recently, the Mg-thermal reduction has been developed as a good candidate for the production of fine TiCN powders and the process control to obtain the maximized stoichiometry and minimized particle size has been discussed in detail [10].

The main aim of this paper as the next step is to investigate the sintering behavior of the ultrafine $\text{TiC}_{0.5}\text{N}_{0.5}$ developed. The prepared green specimens from the TiCN-Ni-Mo₂C [11-12] system were sintered at various temperatures in a vacuum and the density, hardness and the microstructures were studied and compared with those of the sintered bodies obtained from commercial micrometre-sized TiCN powders.

Experimental Procedure

Commercial Ni, Mo₂C, $\text{TiC}_{0.5}\text{N}_{0.5}$ powders and the ultrafine $\text{TiC}_{0.5}\text{N}_{0.5}$ powder developed were used as raw materials and the mean particle sizes of these powders are listed in Table 1. The microstructure of the ultra fine $\text{TiC}_{0.5}\text{N}_{0.5}$ powder obtained by the Mg-thermal reduction method is demonstrated in Fig. 1. The developed and commercial TiCN powders have been mixed with a common nickel content of 20 wt.% and with a Mo₂C content of 15 wt.% for further investigation.

The starting raw powders dampened in hexane were first mixed by a conventional rotation ball milling technique for 48 hours at 200 rpm using WC-Co balls. After adding 0.15 wt.% of paraffin against the total powder weight, the milling was continued for further 12 hours and then

Table 1. Mean particle sizes of starting powders

	TiCN		Mo ₂ C	Ni
	Developed	Commercial		
Mean particle size	0.05-0.3 μm	3-15 μm	2-6 μm	10-50 μm

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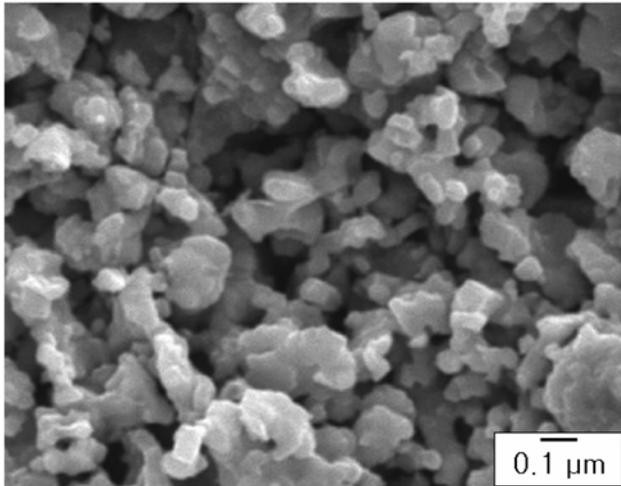


Fig. 1. Microstructural image of the TiCN powder developed.

sample was dried at 373 K in air for 12 hours.

Rectangular shaped specimens were pressed at a uni-axial hydraulic pressure of 200 MPa. The paraffin component in the compacted sample was burnt-out fully at 723 K for 2 hours and the prepared specimens were vacuum-sintered in the temperature ranges from 1583 K to 1753 K.

The sintered densities were measured by the Archimedes method. Also the microstructures were observed by FESEM (JEOL JSM- 6500F, JAPAN) and the Vickers's Hardness of both the coarse and developed ultrafine $TiC_{0.5}N_{0.5}$ based specimens were measured.

Results and Discussions

The densities according to the different sintering temperatures in the cermets made of the micro- and nano-sized $TiC_{0.5}N_{0.5}$ powders are compared in Fig. 2. In case of the micrometre system, the sintered densities gradually increased with an increase of the sintering temperature and then rapidly dropped, showing a peak

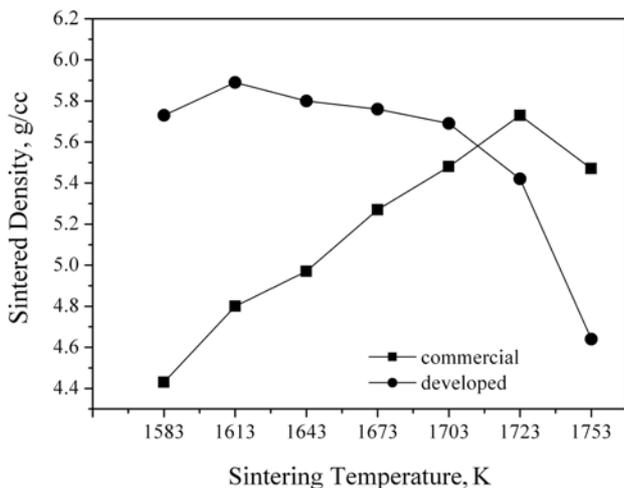


Fig. 2. The density of specimens: micro-sized $TiC_{0.5}N_{0.5}$ and developed ultrafine sized $TiC_{0.5}N_{0.5}$ based cermets.

value of about 6.7 g/cc at 1723 K. It is thus evident that 1723 K is the most suitable temperature to get the highest density in the commercial system. Also the profile of the nano-system developed has a similar tendency but the maximum density occurred at the significantly lower temperature of 1613 K showing a higher density, 6.9 g/cc than that obtained in the micro-powders. Moreover, it should be here noted that densities in the nano-system were almost constant up to 1703 K. This is probably due to the effect of the size refinement of the initial powder, that is, nano-particles contribute good sinter-ability at a relatively low and over a wide range of temperatures. Therefore, for the developed powders, we know that it is possible to obtain a high density in the wide range from 1613 K to 1703 K. The reason why the sintered density was slightly decreased at 1583 K is due to insufficient sintering.

It is well known that the mechanical properties of the cermets depend not only on the chemical composition, but also microstructural features such as density, grain size and distribution, and porosity morphology, etc. As the experimental parameters in this study are the initial particle sizes and sintering temperatures, the effects on hardness can be explained in terms of the density and internal microstructure of the sintered bodies. Fig. 3. shows the micro Vickers hardness values obtained from both the commercial and developed $TiC_{0.5}N_{0.5}$ based cermets. It is clear that the overall tendency of the hardness change with sintering temperature has a similar behavior to the density changes.

For the micro-system, the hardness increases gradually with an increase in the sintering temperature. We found there that a large drop of hardness occurred at 1753 K, in spite of the sufficiently high density. This can be explained by the effect of grain growth during sintering resulting in liquid phase sintering. Also the highest hardness was shown at 1723 K, which corresponded with the maximum density. The cermets sintered at 1703 K and 1673 K also demonstrated fairly good hardness, but sintering

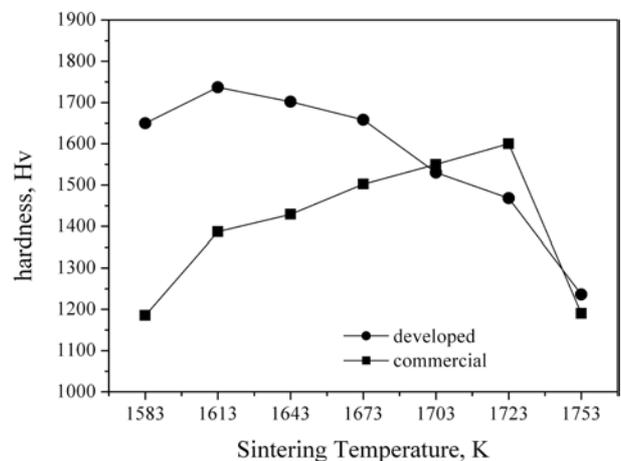


Fig. 3. Vickers's Microhardness of the cermets: micro-sized and developed ultra-fine sized $TiC_{0.5}N_{0.5}$ based cermets sintered at different temperatures.

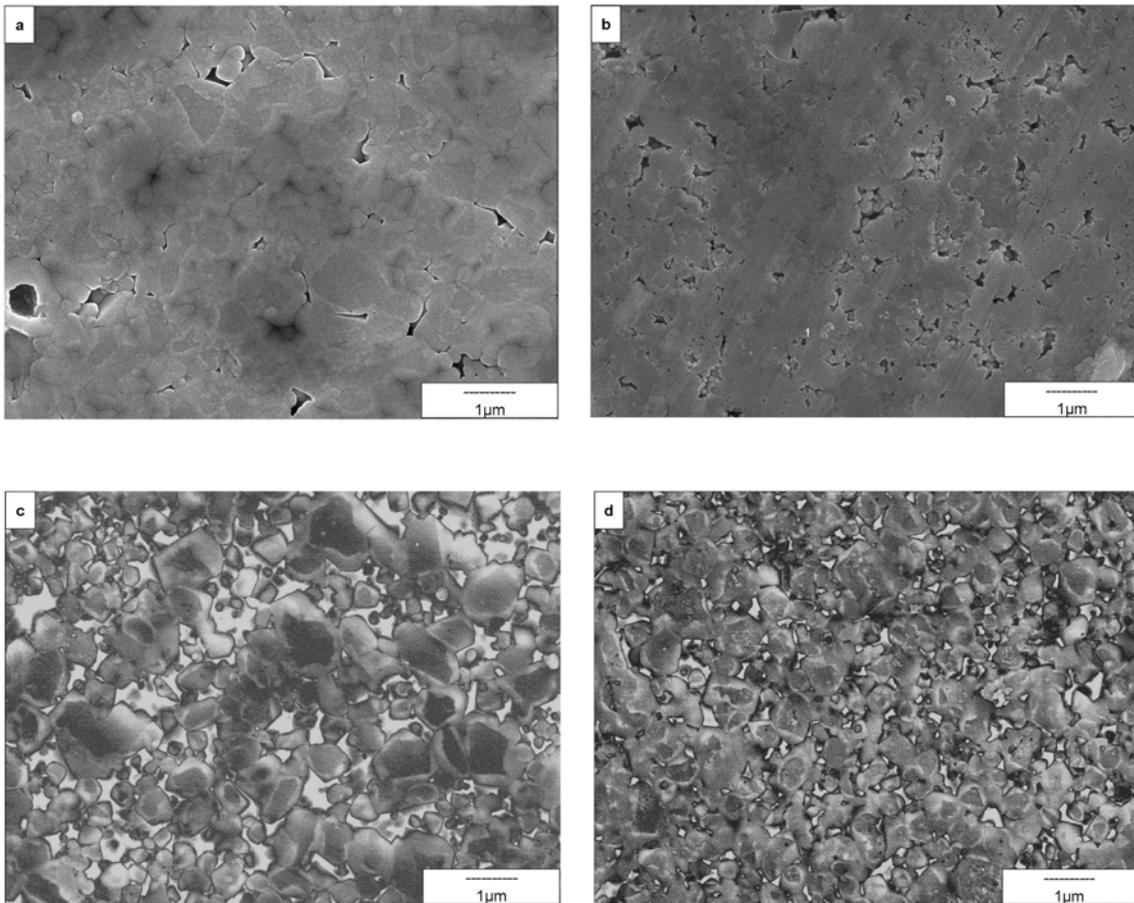


Fig. 4. FESEM images of the specimens: (a) commercial $\text{TiC}_{0.5}\text{N}_{0.5}$ system sintered at 1723 K (normal mode), (b) developed $\text{TiC}_{0.5}\text{N}_{0.5}$ system sintered at 1613 K (normal mode), (c) back scattered electron (BSE) mode for (a), (d) back scattered electron (BSE) mode for (b).

below 1673 K was not enough to obtain a good hardness.

In turning to the developed nano-system, the maximum hardness occurred at 1613 K and further gradually decreased. The effect of hardness decrease with increase of sintering temperature may be caused by the effect of the decrease of melting point by the use of ultra-fine powders and thus an acceleration of liquid phase sintering resulting in the grain growth. Also microstructural evaluation showed that the rapid drop of hardness shown at 1753 K was caused by the effects of large grain growth and the locally distributed large porosities formed by Ostwald ripening. We suggest however that such a hardness decrease can be effectively prevented by means of adding grain growth inhibitors such as WC, VC etc [13].

From the results of Fig. 2 and Fig. 3, we can realize a critical sintering temperature of about 1613 K in the nano-system, which gives us the maximum density and hardness and in particular it was significantly lower than that in use for micro-sized powders. It was necessary therefore to evaluate the microstructures in two samples sintered at the respective optimal temperatures in micro- and nano-systems (Fig. 4(a)-(b), SEM/normal mode). In both structures, the total volume fraction of porosity seems to be almost the same but relatively many small pores are distributed in the developed sample. We suggest

that the developed sintered body might have finer internal grains, which could result in higher hardness. To test such an assumption, the microstructures in the back scattered electron mode (Fig.4(c)-(d)) were observed. Here we found that the developed sample had a more uniform and a finer structure. EDX analysis showed that the black core mainly consists of titanium together with a little molybdenum (~1 at %), because some molybdenum can diffuse into the Ti(CN) cores by the means of dislocations and other crystal defects [14]. Moreover, the metallic composition of the grey rims was mainly molybdenum, and the inner rim located at the interface of the core and outer rim was even more molybdenum rich than the outer rim. Further observation of the images reveals that the cermet based on coarse TiCN powder have thicker outer rims than the ultra fine TiCN based cermets, which means that coarser TiCN powders have a larger solubility in the liquid binder phase [15, 16].

We have tried to compare the results obtained with those reported by other researchers previously even though there are some differences in the chemical compositions and sintering techniques. It was reported, when sintered at 1783 K, a cermet of the (Ti, W) CN system obtained from micro-sized TiCN powders demonstrated a hardness of 1400-1500 H_v [17], and this could be more enhanced

up to 1700 H_v by applying hot isostatic pressing (HIP) as a post process to get nearly full densification [18]. It can be seen that our results obtained without a HIP process can be competed with those of a commercial HIP'ed sample. Moreover, there have also been some attempts to use ultrafine TiCN (0.3 μm), which resulted in increasing the hardness up to 1500 H_v at 1783 K in the (Ti, W) CN system [19]. Also, cermets with finer TiCN, 0.1-0.2 μm in particle size were fabricated and demonstrated 1532 H_v at 1713 K [20].

Finally summarizing, the cermet with a developed ultrafine TiCN had a hardness of 1750 H_v when sintered at 1613 K, which is slightly higher than those of other researches, even in nano-systems. We conclude that the sintered bodies obtained from the developed nano-sized TiCN powders show a good potential to be applied in industries because the mass-production of these powders is possible [21]. Moreover, it is predicted that the mechanical properties can be further increased by applying hot isostatic pressing assisted sintering, which will be used in future studies.

Conclusion

The sintering behavior of ultra-fine sized TiC_{0.5}N_{0.5} powders obtained by Mg-thermal reduction of TiCl₄ was investigated in the present paper. The cermets with the TiCN-20Ni-15Mo₂C composition based on both micro-sized and developed ultra-fine sized TiC_{0.5}N_{0.5} were sintered at various sintering temperatures in vacuum.

Considerably high hardness, 1750 H_v was obtained in developed nano-cermet system with the moderate composition of TiCN-20Mo₂C-15Ni and without inhibitor such as WC and VC. Moreover, such high hardness in developed sample occurred at 1613 K significantly lower than 1723 K shown in use of commercial micron-sized powders. We understood that the satisfied hardness obtained in developed sample is due to the effects of the refinement of initial particle size with the excellent uniformity and the good sinter-ability.

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