

Research Article

Combustion Synthesis of TiC-TiB₂-Based Cermets from Elemental Powders

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TiC-TiB₂-based cermets with Ni binder were fabricated using combustion synthesis assisted by pseudohot isostatic pressing by heating the compacted powder mixture to approximately 700°C. The effects of composition on microstructure and hardness of the synthesized samples were investigated. The samples exhibited finer microstructure and higher hardness as TiC/TiB₂ volume ratio increased and as Ni increased up to 30 vol%. A relatively high hardness value of 1950 HV was obtained for TiC-TiB₂-Ni(52.5/17.5/30 vol%). However, the transverse rupture strength and the modulus of elasticity values were not very high. This may be due to weak bonding strength of the interface between hard phases and Ni binder and/or insufficient densification of the samples.

1. Introduction

Hard materials attract wide interest for their application as mechanical processing equipment. Conventional hard materials, especially cermets based on WC, are widely used for cutting tools because of their excellent hardness, high wear resistance, and good toughness [1]. TiC-TiB₂-based cermets are considered as valid candidates for the usage under extreme conditions in the light of their higher hardness, good chemical stability, and excellent wear resistance at high temperatures compared with the conventional cermets [2]. Furthermore, from the view point of resource reserve, attentions have also been directed to these tungsten-free hard materials as one of alternate materials of WC-Co [3, 4].

In early studies, reaction sintering and hot pressing techniques were employed for the fabrication of TiC-TiB₂-based cermets [5]. Ogwu and Davies [6] attempted to produce dense TiC-TiB₂-based cermets by pressureless sintering at 1550°C for 1.5 h, by using a Ni-based binder. Singh et al. [7] reported the fabrication of porous TiC-TiB₂ based cermets by liquid phase sintering in a hydrogen atmosphere at 1300–1350°C for 1 h with a binder system based on Ni-Mn alloys. Since high sintering temperatures and long sintering times or even liquid-forming additives are required to achieve full

densification, these methods involve expensive techniques and high energy consumption. To overcome the problem of high temperatures, a number of new densification techniques have been investigated. For instance, reactive hot pressing (RHP) by using displacement reactions [8] and high-pressure self-combustion synthesis (HPCS) [9] have been used in a number of studies. A dense TiC-TiB₂-Ni cermet has been fabricated by HPCS from molten titanium with B₄C and nickel of various weight percentages [10].

It is remarkable to note that the fabrication of TiC-TiB₂-based cermets from elemental powders has not been attempted yet. According to previous studies of our group [11, 12], cermets like TiC-Fe, TiB₂-FeAl can successfully be fabricated from elemental powders. Importantly, in these processes, relatively low temperatures below 1000°C were required for the highly exothermic reactions to be ignited between elemental powders. In the present study, we investigate the feasibility of fabrication of TiC-TiB₂-based cermets with Ni binder from elemental powders, by using combustion synthesis assisted by pseudohot isostatic pressure (pseudo-HIP). Furthermore, we examine the correlation between the composition, the synthesis process, and the properties.

2. Experimental Procedure

Elemental powders of titanium ($45\ \mu\text{m}$ in diameter and 99.4 wt% in purity), carbon ($1\ \mu\text{m}$ and 99.0 wt%), boron ($2\ \mu\text{m}$ and 99.9 wt%), and nickel ($45\ \mu\text{m}$ and 99.8 wt%) were thoroughly mixed with a small amount of ethanol added in order to prevent segregation due to difference in the specific gravities of different kinds of powders. When preparing powder mixtures, molar ratios of Ti, C, and B were chosen to obtain the final product with predetermined volume fractions of TiC and/or TiB_2 . The volume fractions of TiC, TiB_2 , and Ni binder were varied in order to investigate the effect of composition on the microstructure and mechanical properties of products. The volume fraction of Ni binder was varied from 20 to 40 vol%, and the volume ratio of TiC/ TiB_2 was varied as 3/1, 1/1, and 1/3. For comparison, the samples comprising only TiC or TiB_2 and Ni binder were also prepared. The powder mixtures were pressed in a metal mold under uniaxial pressure of 640 MPa. The compacts had a cylindrical shape of a 30 mm diameter and an approximately 20 mm height.

The compacts were heated by resistance wire of an Fe-Cr-Al alloy in a pseudo-HIP equipment inside a vacuum chamber shown in Figure 1. Casting sand ($\sim 300\ \mu\text{m}$ in diameter) was used as a pressing medium and as a thermal and electrical insulation material as well. The heating rate was controlled at approximately $15^\circ\text{C}/\text{min}$ under an initial pseudo-HIP pressure of about 30 MPa. The pseudo-HIP pressure was immediately raised to approximately 160 MPa when a sudden temperature rise was monitored indicating the ignition of the combustion reactions, and the electricity for the heating wire was turned off. After keeping the high pressure for 3 minutes, the pressure was removed, and the sample was cooled naturally inside the vacuum chamber.

It has been reported that preheating of the compacts before reactions has effects on reduction of porosity and hard particle size and on increase in Vickers hardness [11]. In this study, therefore, some of the compacts were preheated inside another small vacuum chamber at a temperature of 400°C for 24 h before the combustion synthesis.

An X-ray diffraction (XRD) analysis was performed for the combustion-synthesized samples to identify the reaction products. Metallographic observations of cross sections of the samples were performed using an optical microscope (OM) and a scanning electron microscope (SEM). TiC and TiB_2 particle sizes were measured on the SEM images. The densities of the samples were measured by the Archimedes method using pure water. The porosities were then calculated from the measured densities and the theoretical densities which were evaluated assuming that the samples consist of predetermined volume fraction of each phase (TiC, TiB_2 , and Ni).

Hardness was measured by a Vickers hardness tester with an applied load of 50 kg and a loading time of 30 s. The transverse rupture strength (TRS) at room temperature was measured in a three-point bending test. The test specimens ($20\ \text{mm} \times 3\ \text{mm} \times 3\ \text{mm}$) cut out of the sample were ground with a diamond-grinding plate and polished using diamond spay. The span width was 15 mm with a crosshead speed

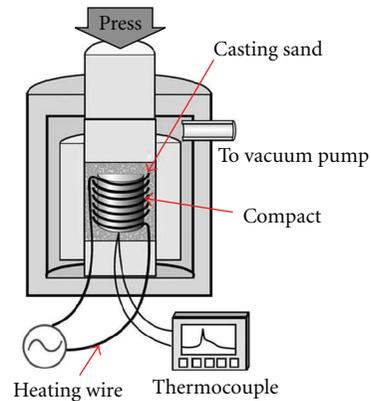


FIGURE 1: Schematic illustration of the pseudo-HIP equipment.

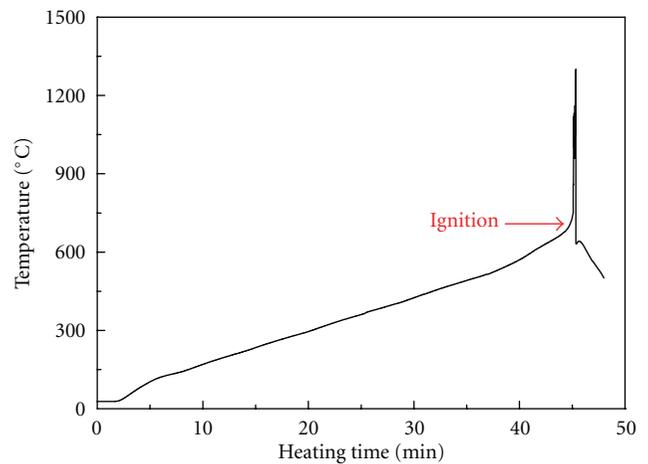


FIGURE 2: Temperature-time curve during heating of TiC-TiB₂-Ni(60/20/20) compact.

of 0.2 mm/min. Three bending experiments were performed for each combustion-synthesized sample, and the results were averaged.

3. Results and Discussion

In order to investigate the effect of TiB_2 volume fraction on the microstructure and mechanical properties of products, the samples with 20 vol% Ni binder were synthesized with different TiB_2 volume fractions of 0, 20, 40, 60, and 80 vol%. Figure 2 shows a heating curve of the sample with 60 vol% TiC and 20 vol% TiB_2 . This sample composition is hereafter referred to as TiC-TiB₂-Ni(60/20/20) and so are the other samples. When the compact was heated to approximately 700°C , a sudden temperature rise indicating the ignition of combustion reactions was monitored. Figure 3 shows the result of XRD analysis of TiC-TiB₂-Ni(60/20/20) after the reaction. On the basis of XRD analysis, no peak of pure element Ti, C, and B was detected, and the sample consists of only TiC, TiB_2 , and the Ni binder phase. This is also the case for the TiC-Ni(80/20) and TiC-TiB₂-Ni(40/40/20) samples

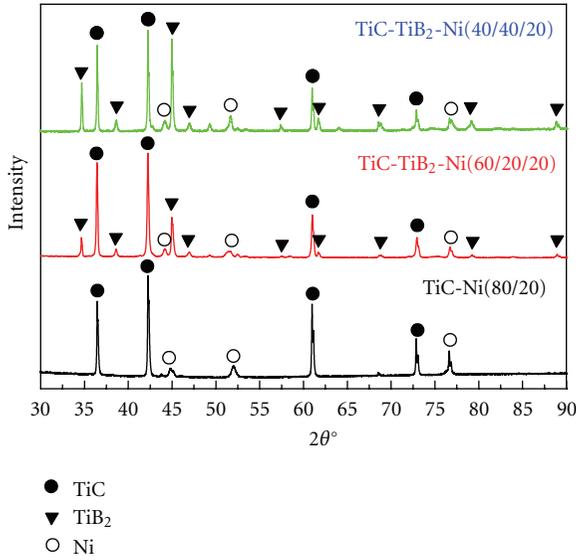


FIGURE 3: XRD patterns of samples with 20 vol% Ni and different volume fraction of TiC and/or TiB₂.

as shown in Figure 3. Thus, the TiC-TiB₂-Ni cermets were successfully synthesized from the elemental powders via the reaction of



It should be pointed out that the samples with higher volume fraction of TiB₂, that is, TiC-TiB₂-Ni(20/60/20) and TiB₂-Ni(80/20) were not successfully synthesized. Instead, explosions occurred after the ignition of combustion reactions and the samples could not maintain the cylindrical shape, and they were broken into some pieces, or even part of the exploded samples went through the casting sand around them. As a result, the investigation of microstructure and mechanical properties could not be carried out for these samples. One may speculate that moisture was absorbed to the surfaces of the elemental powders, and it could be vaporized at the extremely high temperature due to the exothermic combustion reactions. However, considering that all the compacts were prepared by the same procedure and some of them were successfully synthesized, this factor of moisture could not be the main reason for the explosions. To find the reason for the explosions, thermodynamic calculation was carried out to estimate the adiabatic combustion temperature (T_{ad}) of each selected composition. Based on (2) shown below and the related thermodynamic data [14], T_{ad} was calculated assuming that the ignition temperature for each selected composition is 700°C according to the heating curve shown in Figure 2:

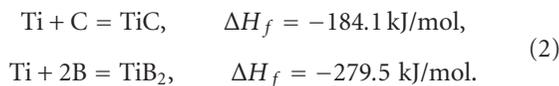


Figure 4 shows the relationship between the calculated T_{ad} and TiB₂ volume fraction of samples with 20 vol% Ni binder. T_{ad} increases as TiB₂ volume fraction increases,

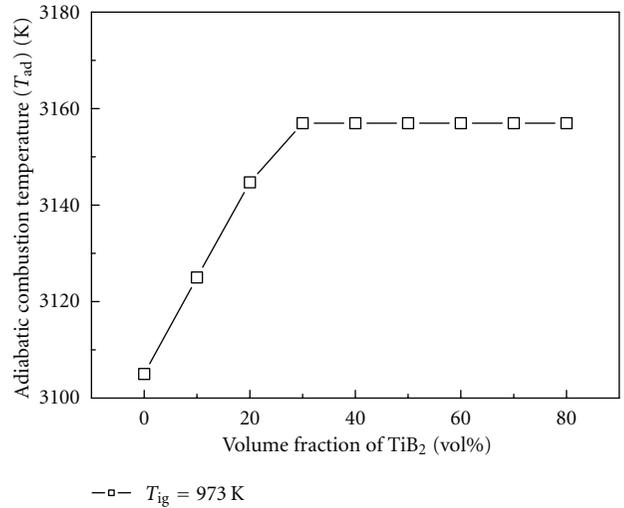


FIGURE 4: Relationship between T_{ad} and TiB₂ volume fraction of samples with 20 vol% Ni.

because the formation enthalpy of TiB₂ is about 50% higher than that of TiC as specified in (2). Furthermore, when TiB₂ is more than 50 vol%, T_{ad} reaches the vaporizing point of Ni (3157K), and gaseous phase could exist. Then, T_{ad} takes the constant value of the vaporizing point because of the absorption of heat during the evaporation of Ni, as shown in Figure 4. The pressure difference between the internal part of sample and the vacuum chamber should be quite large, which leads to a leakage of part of the molten sample through the casting sand around it. Although change of T_{ad} is not significant in Figure 4, this could be the reason for the explosions.

The SEM photographs of samples with 20 vol% Ni binder and different TiB₂ volume fractions are shown in Figure 5. Hard particles can be seen clearly. These were identified as TiC and TiB₂ by EPMA analysis. TiC particles appear to be nearspherical shape, while TiB₂ particles have faceted shapes, which is in good agreement with the previous results of other researchers [15]. The average size of these hard particles in each sample was measured and the results are shown in Figure 6. Both the TiB₂ size and TiC size increase as TiB₂ volume fraction increases. According to Figure 4, the sample with higher TiB₂ volume fraction has higher T_{ad} after the combustion reactions. Hence, as TiB₂ volume fraction increases from 0 to 40 vol%, the sample has a higher and wider temperature range for growth during cooling process, which leads to the larger hard particle sizes. The same trend was also reported for the TiB₂-FeAl system by one of the present authors, in which the TiB₂ size decreased as FeAl volume fraction increased [11].

The relative densities were measured, and the results are shown in Figure 7. The density decreases as TiB₂ increases from 20 to 40 vol%. As mentioned above, the increase of TiB₂ volume fraction results in high T_{ad} which causes a high pressure inside the sample, and hence, the densification of the sample becomes difficult under a fixed pseudo-HIP

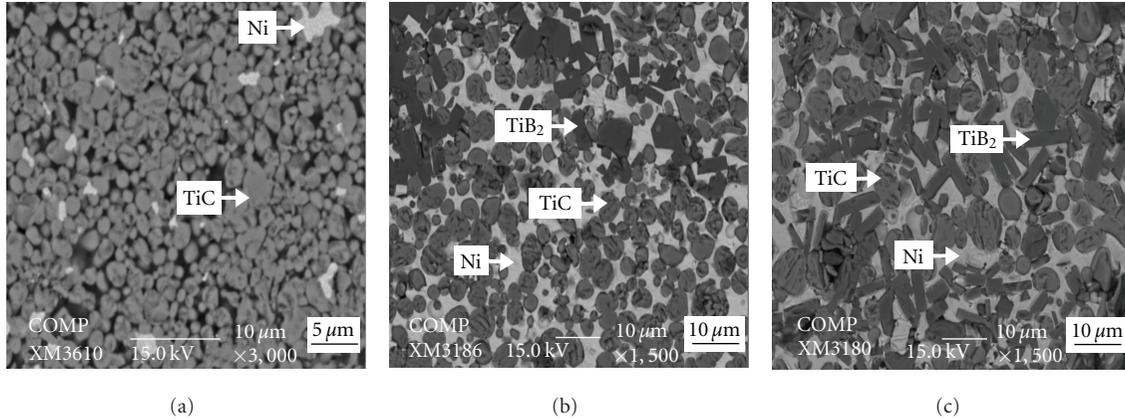


FIGURE 5: SEM photographs of samples with 20 vol% Ni and different volume fraction of TiC and/or TiB₂. (a) TiC-Ni(80/20), (b) TiC-TiB₂-Ni(60/20/20), and (c) TiC-TiB₂-Ni(40/40/20).

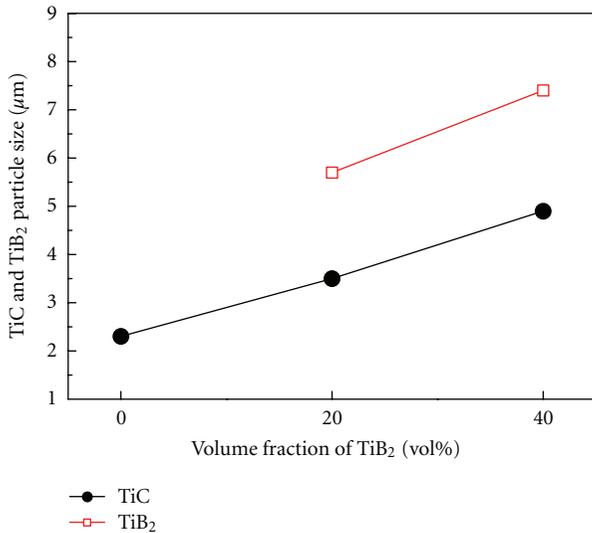


FIGURE 6: Effect of TiB₂ volume fraction on average particle size of samples with 20 vol% Ni.

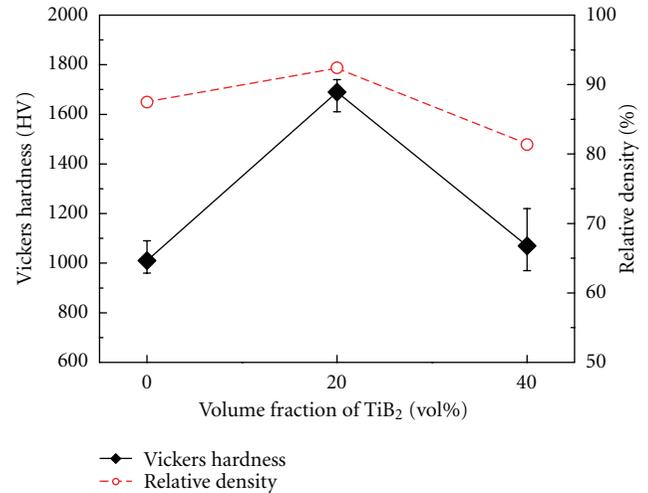


FIGURE 7: Effect of TiB₂ volume fraction on relative density and Vickers hardness of samples with 20 vol% Ni.

load. However, as shown in Figure 7, the sample with no TiB₂ has a lower relative density than the TiC-TiB₂-Ni(60/20/20), though it has a lower T_{ad} . The reason for the lower relative density or higher porosity should be a larger amount of moisture absorbed on surfaces of carbon powders. The carbon powder used in the present study has smaller size and larger specific surface area than boron powder, and hence, the usage of large amount of the carbon powders incurs the problem with the moistures in the present experiments. The Vickers hardness of samples is also shown in Figure 7. The hardness has the same variation tendency as the relative density. Generally, it is considered that the TiC-TiB₂-Ni(40/40/20) should exhibit higher hardness than the TiC-TiB₂-Ni(60/20/20) based on the rule of mixtures, because the former sample has higher fraction of the harder phase TiB₂. However, the former sample exhibits lower hardness than the latter one which is due to the high porosity in the

former sample. Therefore, the densification is quite essential to obtain good hardness.

In order to investigate the effect of Ni volume fraction on the microstructure and mechanical properties of products, the samples with different Ni volume fractions of 20, 30, and 40 vol% were synthesized with the fixed TiC/TiB₂ volume ratio of 3/1. Figure 8 shows the SEM photographs of this series of samples. Figure 9 shows the relationship between T_{ad} and Ni volume fraction. Furthermore, the dependence of the particle size on the Ni volume fraction is demonstrated in Figure 10. The same variation tendency of hard particle size versus T_{ad} is observed as is consistent with the above-mentioned explanation. The increase in Ni binder reduces T_{ad} (Figure 9) and narrows the solidification temperature range, which leads to smaller particle sizes (Figure 10). The relative densities of samples are shown in Figure 11 with the result of the Vickers hardness. The relative density was improved as the volume fraction of Ni binder was

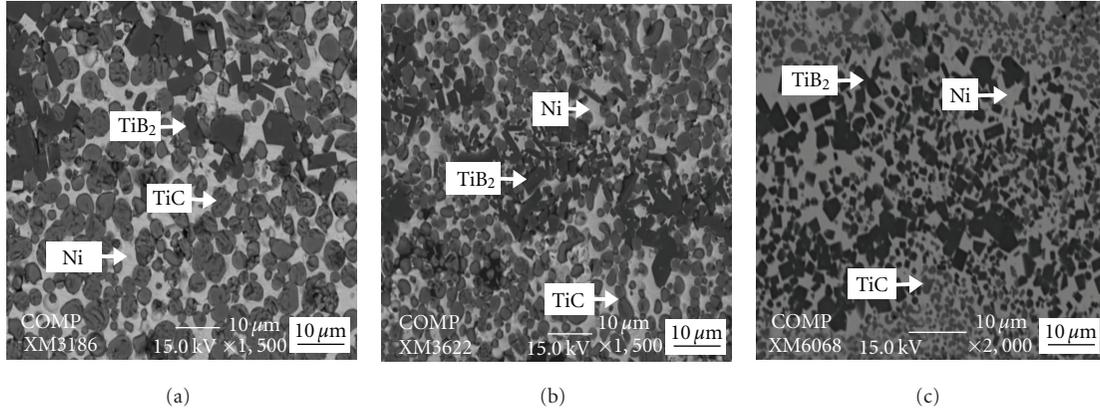


FIGURE 8: SEM photographs of samples with TiC/TiB₂ ratio of 3/1 and 20, 30, 40 vol% Ni, respectively. (a) TiC-TiB₂-Ni(60/20/20), (b) TiC-TiB₂-Ni(52.5/17.5/30), and (c) TiC-TiB₂-Ni(45/15/40).

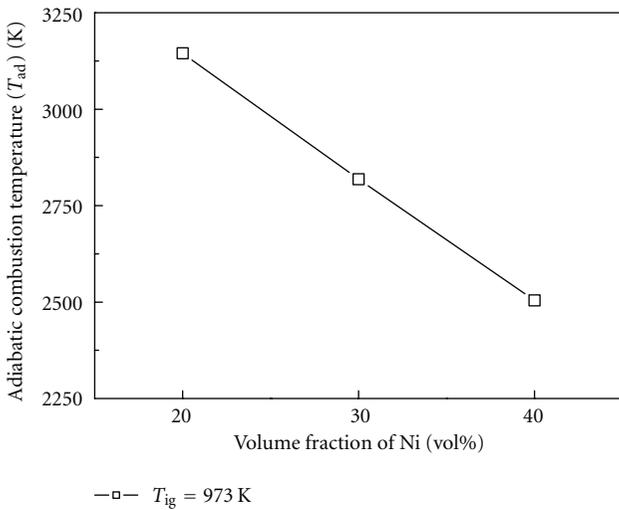


FIGURE 9: Relationship between T_{ad} and Ni volume fraction of samples with a TiC/TiB₂ volume ratio of 3/1.

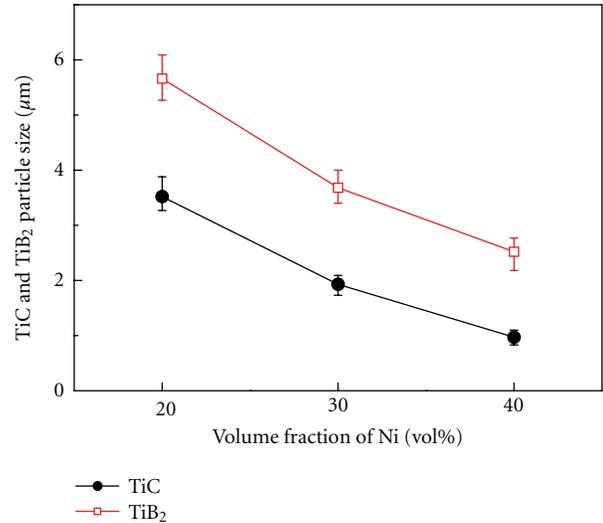


FIGURE 10: Effect of Ni volume fraction on average particle size of samples with a TiC/TiB₂ ratio of 3/1.

increased, which further confirms our explanation that an extremely high thermal energy generated from combustion reactions is not preferable for complete densification because it causes a huge pressure difference between the internal and external parts of the sample. As a result of the increase in relative density, Vickers hardness values increased from 1700 HV to 1850 HV as Ni binder increased from 20 to 30 vol%. However, the hardness decreased significantly as Ni binder increased to 40 vol%, although it was relatively dense. This fact indicates that in order to obtain hard cermets, the amount of hard particles is an important factor, which is also well known as the rule of mixtures. It is important to take a balance of the relative density and the hardness into account in determining the composition of samples.

According to our previous work on the TiB₂-FeAl system [11], preheating of the compact at a temperature below the ignition temperature of combustion synthesis reactions

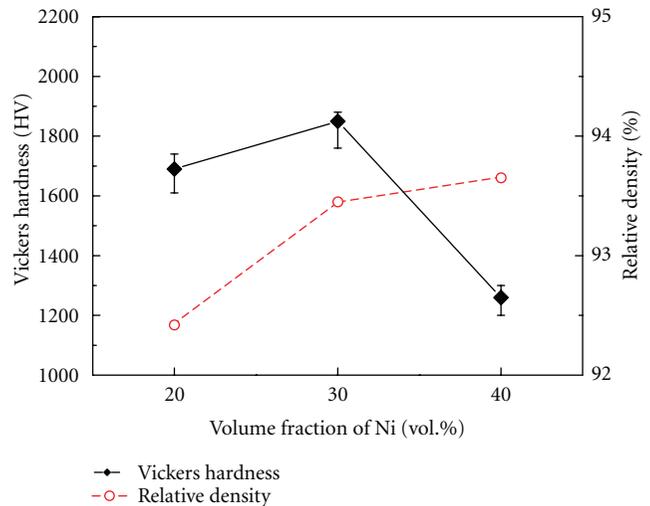


FIGURE 11: Effect of Ni volume fraction on relative density and Vickers hardness of samples with a TiC/TiB₂ ratio of 3/1.

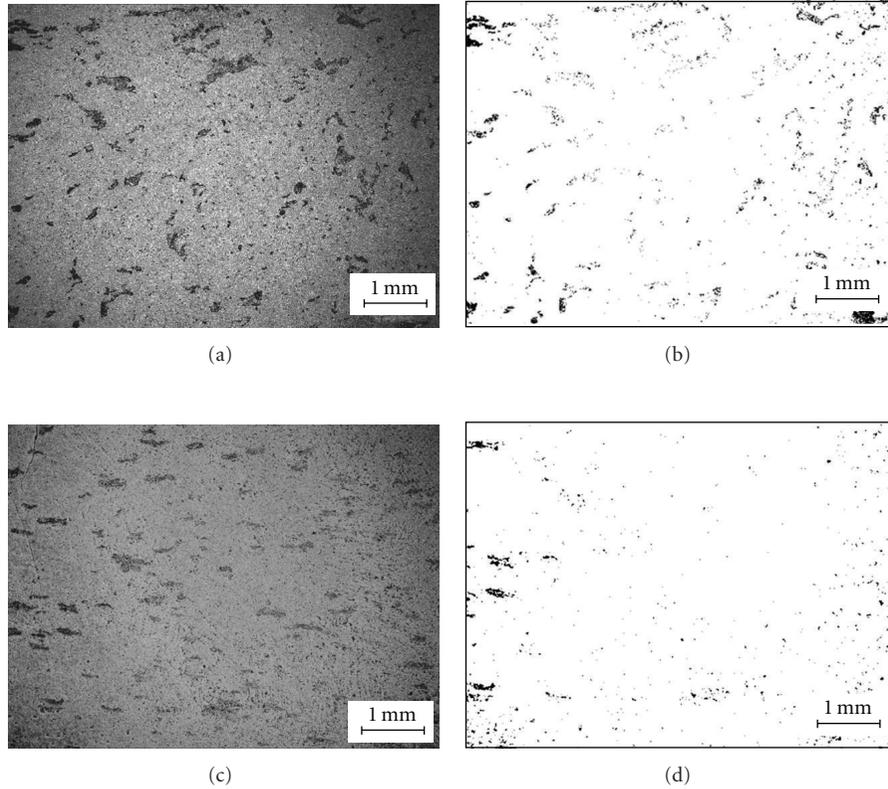


FIGURE 12: OM photographs of samples of TiC-TiB₂-Ni(52.5/17.5/30), (a) without preheating and (c) with preheating at 400°C for 24 h, respectively. The monochrome images of (a) and (c) are shown in (b) and (d), respectively, in which the black area approximately reflects the pores by image process using Canvas software.

can bring about the reduction in hard particle size and porosity and increase in Vickers hardness of the sample. In the present work, to obtain a sample with both high hardness and high relative density, the preheating of the compact of TiC-TiB₂-Ni(52.5/17.5/30) was carried out at 400°C for 24 h before the combustion synthesis. The effect of preheating on the densification is shown in the optical microscopy (OM) photographs in Figure 12. The sample with preheating shows less porosity. Moreover, the density increased from 93.45 to 96.95%, and the hardness increased from 1850 HV to 1950 HV by the preheating treatment. The reason for the decrease in porosity due to the preheating can be explained as follows. Some intermetallic compounds were formed by solid-state reactions during preheating between different elemental powders. This formation of the compounds reduces total amount of heat generation by the subsequent combustion reactions. Hence, the combustion temperature is relatively lowered. This is effective for a better densification. However, unlike the previous work, the decrease in the hard particle size due to preheating cannot be found in the present work. This may be because we chose a relatively lower preheating temperature that limited the solid-state reactions during preheating.

The bending test was carried out only for the sample TiC-TiB₂-Ni(52.5/17.5/30) with preheating, which has the highest relative density of 96.95% among all the samples that

TABLE 1: Comparison of mechanical properties between the sample in the present work (A) and that in literature (B) [13].

Sample	Composition	Relative density (%)	HV (kg/mm ²)	TRS (MPa)
A	TiC-TiB ₂ -Ni (52.5/17.5/30) vol.%	96.95	1950	330
B	TiC-TiN-WC-Mo-Ni-C (40/10/15/14/20/1) wt.%	99.98	1750	1521

were synthesized. The transverse rupture strength (TRS) and the modulus of elasticity (E) were calculated according to,

$$\text{TRS} = \frac{3}{2} \cdot \frac{LF}{WT^2}, \quad (3)$$

$$E = \frac{L^3}{4WT^3} \cdot \frac{F}{\Delta l},$$

where L is the span width in the bending test, F the load, W the length of the specimen, T the thickness of the specimen, and Δl the crosshead distance until fracture. The calculated results of TRS and E were approximately 330 MPa and 74 GPa, respectively. Table 1 shows the comparison between

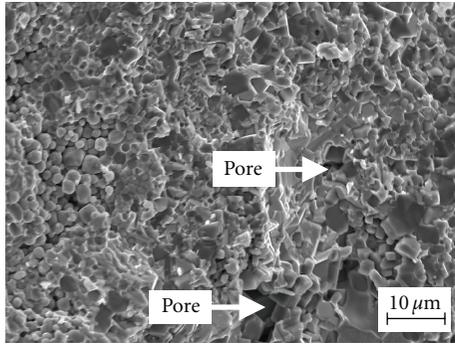


FIGURE 13: SEM photograph of fractured surface after three-point bending test of the specimen of TiC-TiB₂-Ni(52.5/17.5/30) with preheating.

the mechanical properties of the present sample and the conventional cermet used for cutting tools. The value of TRS in the present sample is much lower than the one in the conventional cermet. There are several possible reasons for the low values of TRS obtained in the present work. Figure 13 shows the SEM photograph of fracture surface after the bending test. It can be clearly seen that the fracture of specimen was almost caused by intergranular rupture. The hard particle sizes in the present sample are in the range of 2–4 μm which are relatively coarse. The fracture of cermets with coarse grains generally tends to occur by transcrystalline rupture [16]. That is to say, the bonding strength of the phase interface should be significantly weak in the present sample. It can also be seen that a large-sized pore exists on the fractured surface in Figure 13, although the relative density of 96.95% is the highest in the present study. The existence of the large pores could be one of the reasons for low strength. Furthermore, although the surface of specimens was well ground and polished before the bending test, it could be inferred that there were pores on the surfaces of the specimens and they would weaken the TRS due to stress concentration. It is also possible that the contamination on the surfaces of starting powders decreased the wettability between Ni binder and hard particles. In recent studies on combustion synthesis [16, 17], some elements are added to the starting powders in order to increase the wettability between hard phase and binder. For instance, Molybdenum is often added to the starting powders in order to obtain a good wetting of TiC, TiN, with Ni. Therefore, it is expected that the addition of some elements for improving the wettability yields better mechanical properties of the present sample. This attempt remains as a future work.

4. Conclusions

TiC-TiB₂-based cermets with Ni binder can be successfully fabricated by combustion synthesis assisted by pseudo-HIP from elemental starting powders. As a result of the exothermic reactions between elemental starting powders, the process of combustion synthesis can be self-propagated after heating the compacted powder mixture to approximately 700°C, which is much lower than the synthesis temperature in conventional processes.

As the composition of powder mixture influences the combustion temperature as well as the densification, it has considerable effects on microstructure and mechanical properties of synthesized samples. When the volume fraction of Ni binder is 20 vol%, the finer microstructure and higher hardness were observed for the higher TiC/TiB₂ ratio. In the samples with the TiC/TiB₂ volume ratio of 3:1, the relative density increases with the volume fraction of Ni. The hardness increases as Ni increased from 20 to 30 vol%, but it decreases as Ni increases to 40 vol%. TiC-TiB₂-Ni(52.5/17.5/30) exhibited high relative density of 93.45% and high hardness of 1850 HV.

The preheating treatment of the compacted powder mixture was quite effective for the densification of TiC-TiB₂-Ni(52.5/17.5/30). The relative density increased from 93.45 to 96.95% by preheating at 400°C for 24 h in vacuum. As a result, the hardness increased from 1850 HV to 1950 HV. However, the refinement of hard particle size due to the preheating was not observed in the present work.

The transverse rupture strength of the present sample was not very high, which is considered attributable to weak bonding strength of the interface between hard phase and Ni binder and insufficient densification.

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