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Pseudo-HIP Combustion Synthesis of FeAl-TiB₂ Composites*

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FeAl-TiB₂ composites have been produced from iron, aluminum, titanium and boron powders using the pseudo-HIP combustion synthesis process. The effects of TiB₂ volume fraction and preheating conditions such as time, temperature and pressure on the TiB₂ particle size and porosity in the synthesized composites were investigated. When the mixtures of the elemental powders were heated, sudden and rapid temperature rise was always observed at temperatures near the melting point of aluminum, and the powder mixtures were melted. X-ray diffraction analyses revealed that the reaction products consisted of only FeAl and TiB₂. Based on metallographic investigations and electron probe microanalyses, it was found that fine TiB₂ particle dispersed FeAl-based composites were synthesized by the above-mentioned exothermic reaction, although the composites included a lot of pores. The use of pseudo-isostatic pressure during the exothermic reaction brought about dramatic reduction in porosity. When the volume fraction of the TiB₂ particles increased, their average diameter also increased. The increase in volume fraction of the TiB₂ particles brought about the increase in the Vickers hardness and the volume fraction of pores. The volume fraction of pores was markedly reduced by preheating the powder mixture in vacuum. The preheating also reduced the TiB₂ size. The application of pressure during the preheating brought about most significant reduction in TiB₂ size and the effect of preheating temperature was more significant than that of preheating time. [doi:10.2320/matertrans.F-MRA2008804]

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1. Introduction

An iron aluminide FeAl has a low density and an excellent corrosion and oxidation resistances, and it consists of inexpensive raw materials of iron and aluminum.¹⁾ Therefore, FeAl can be a candidate material for engine components. It can be expected that the dispersion of hard ceramic particles such as TiB₂ in FeAl improves the mechanical properties such as hardness, wear resistance, compressive strength and so on. Schneibel *et al.*²⁾ produced FeAl-ceramic composites using the liquid phase sintering method based on infiltrating of molten FeAl in a sintered TiB₂ powder compact, and they found that the hardness of the composite increased, as the volume fraction of ceramic phase increased. Kransowski³⁾ produced an FeAl-30 mol%TiC composite using a mechanical alloying method based on ball-milling of a powder mixture of iron, aluminum, titanium, and carbon for 35 hours and hot-pressing of the mechanically-alloyed powder mixture, and they found that the composite has a high hardness of 1287 in Vickers hardness number.

However, it seems that there is still great room for improvement in the former methods from viewpoints of processing time and cost. Therefore, in this study, we propose a more simple and inexpensive production method for the production of hard ceramic particle dispersed FeAl alloys based on the combustion synthesis or the Self-propagating High-temperature Synthesis (SHS)⁴⁾ from elementary powders, using FeAl-TiB₂ composites as a demonstration material. Because SHS products usually include a lot of pores,⁵⁾ we will focus on the densification of the reaction product by performing the SHS under pseudo isostatic pressure and using preheated powder mixture compacts as the reactants.

In the SHS reaction of the FeAl-TiB₂ pseudo binary system, the amount of heat generation varies depending on

the composition because the formation enthalpy of TiB₂ is much larger than that of FeAl. Therefore, it is predicted that the temperature after the SHS reaction increases as the concentration of TiB₂ increases, and this will affect the microstructure of the TiB₂ particles, particularly their size. We consider that the preheating of the powder mixture will reduce the temperature after the SHS reaction because some slow solid-solid reactions will proceed at the contact surfaces between the elemental powders during the preheating. Due to the preheating, the reactants of the SHS reaction decreases and the pre-products will absorb the heat generated from the SHS reaction, and hence the temperature after the SHS reaction will decrease as the pre-products increase during the preheating. Thus, the microstructure may be controlled by controlling the temperature after the SHS reaction via the control of the preheating condition. Moreover, the adsorption gas on the powder surface will be removed by the preheating, which will contribute the reduction in porosity in the SHS reaction product. Therefore, in this study, we investigate the effects of preheating on the porosity and the TiB₂ particle size of the SHS reaction produced FeAl-TiB₂ composites.

2. Procedure

Elemental powders of iron (100 μm in diameter), aluminum (150 μm), titanium (45 μm), and boron (20 μm) were mixed by hand in a glass beaker using a stainless steel spoon with the addition of a small amount of C₂H₅OH. The powder mixture was pressed in a cylindrical metal mold of a 25-mm inner diameter, an 80-mm outer diameter and a 125-mm height under uniaxial pressure of 600 MPa. The compact had a cylindrical shape of a 25-mm diameter and a 20-mm height. The molar ratios of the elemental metals in the mixed powder were Fe : Al = 1 : 1 and Ti : B = 1 : 2, and the estimated volume fraction of TiB₂ was varied from 0 to 0.8 by changing the composition of powder mixture.

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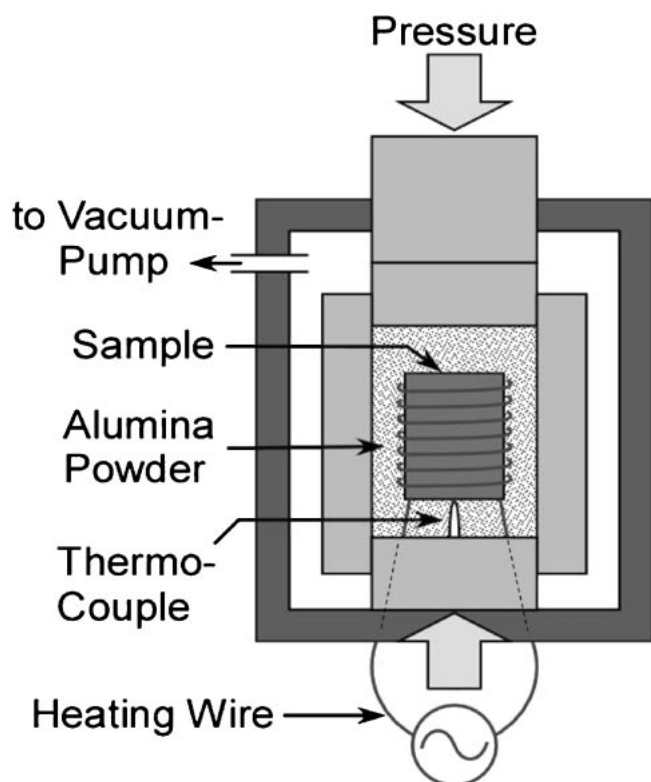


Fig. 1 Schematic illustration of the pseudo-HIP equipment.

The compact was heated in a pseudo hot isostatic pressure (pseudo-HIP) equipment shown in Fig. 1. Al₂O₃ powder (100–500 μ m in diameter) was used as a pressing medium and also as a thermal and electrical insulation material. The sample was heated at a rate of approximately 20°C/min using a resistance wire of an Fe-Cr-Al alloy under a reduced atmospheric pressure of about 6 Pa with an initial pseudo-HIP pressure of about 100 MPa. The pseudo-HIP pressure was immediately raised to about 600 MPa when the SHS reaction was detected via sudden temperature rise. After keeping the pressure for 1 minute, the pressure was removed and the electricity for the heating wire was turned off to cool the sample naturally in the equipment.

Some compacts were preheated in the pseudo-HIP equipment before the SHS reaction. In the preheating experiments, the volume fraction of TiB₂ was fixed at 0.6. The preheating temperature and time were 450 to 550°C and 0.5 to 3 hours. The preheating was performed under the normal pressure or a pseudo-HIP pressure of 50 MPa. An X-ray diffraction (XRD) analysis and an electron probe microanalysis (EPMA) were performed for the SHS-ed samples to identify the reaction products. Metallographic observations of cross sections of the SHS-ed samples were performed using a scanning electron microscope (SEM), and TiB₂ particle size was measured on the SEM images. The density and hardness of the SHS-ed sample were measured using the Archimedes method with pure water and Vickers hardness tester with an applied load of 300 g. The porosity of the sample was calculated from the measured density and the theoretical density that was evaluated assuming that the composite sample was consisted of pure TiB₂ and FeAl.

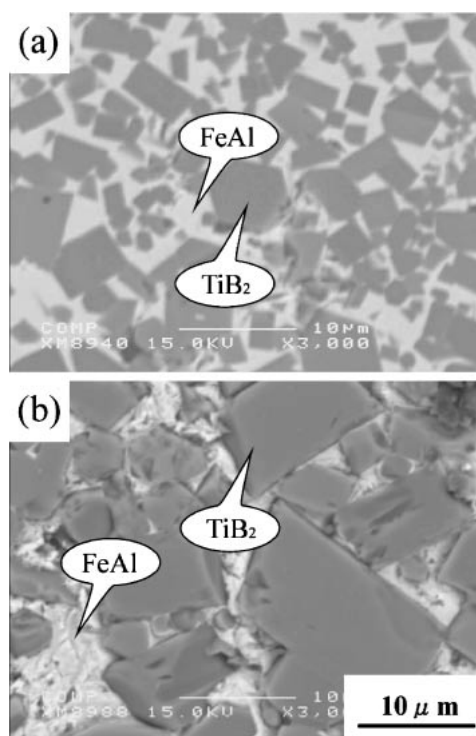


Fig. 2 SEM images of samples. (a) $f_v = 0.6$, (b) 0.8.

3. Results and Discussion

3.1 SHS under pressure

A sudden rise in temperature was observed when the sample temperature reached near the melting point of aluminum, which indicated that an SHS reaction occurred between the elemental powders. The XRD analysis revealed that all the heated samples consisted of only FeAl and TiB₂. It has been already reported that FeAl-TiB₂ mixtures can be obtained by heating powder mixtures of iron, aluminum, titanium and boron.⁶⁾ Figure 2 shows micrographs of an SHS-ed sample having TiB₂ volume fractions of (a) 0.6 and (b) 0.8. In both samples, dark particles were dispersed in the bright matrix phase. The EPMA examination revealed that the dark gray particles were TiB₂ and the matrix was FeAl and that the matrix FeAl contained low concentrations of titanium and boron of 3 to 4 mol%, while the TiB₂ contained a trace of iron and aluminum.

The TiB₂ particle size increased with the increase in the volume fraction of TiB₂, as shown in Fig. 3. The diameter increased from 1 to 7 μ m as the volume fraction increased from 0.3 to 0.8. Although a detailed Al-Fe-Ti-B quaternary equilibrium phase diagram has not been published yet, a TiB₂-FeAl pseudo-binary eutectic or peritectic phase diagram may be assumed based on a TiC-Fe₃Al pseudo-binary eutectic phase diagram proposed by Ko and Hanada.⁷⁾ The assumed TiB₂-FeAl pseudo-binary peritectic phase diagram is shown in Fig. 4. According to this phase diagram, during cooling of the quaternary liquid produced by the SHS reaction, TiB₂ appears in the liquid as the primary crystal, and then FeAl appears the secondary crystal due to the peritectic reaction. As the concentration of TiB₂ increases, the crystallizing temperature of TiB₂ increases and the

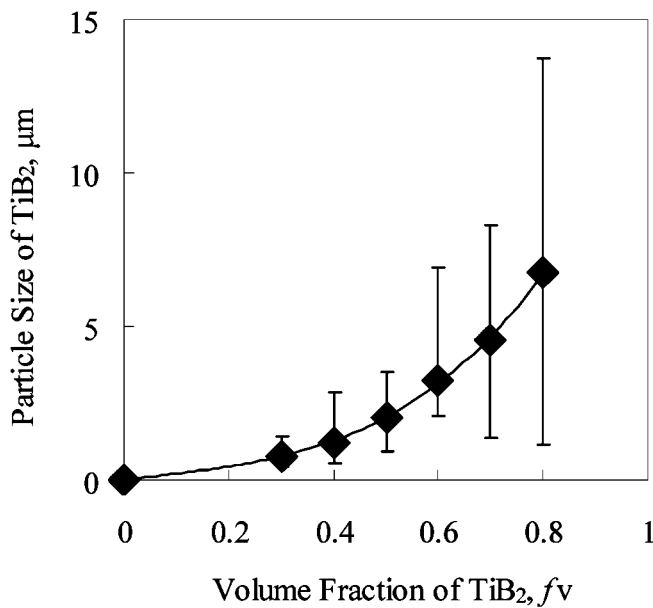


Fig. 3 Relationship between the volume fraction and average size of TiB₂ particles.

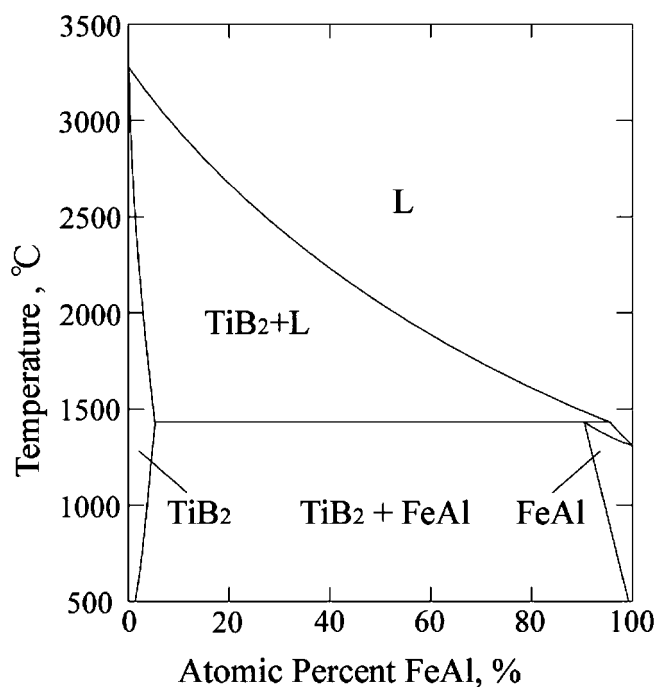


Fig. 4 Hypothetical TiB₂-FeAl pseudo-binary phase diagram.

solidification temperature range increases. Therefore, as the concentration of TiB₂ increases, both the temperature and period of time TiB₂ crystal coexists with the residual liquid increase. This leads to the increase in TiB₂ size with the increase in TiB₂ concentration. Moreover, it is likely that the increase in TiB₂ concentration reduces the cooling rate of the quaternary liquid after reaching the maximum temperature, and this also leads to the increase in TiB₂ size with the increase in TiB₂ concentration. The reduction in cooling rate can be explained as follows. The formation enthalpy of TiB₂ is 320 kJ/mol and this is very large compared with 36 kJ/mol for FeAl. Therefore, the max-

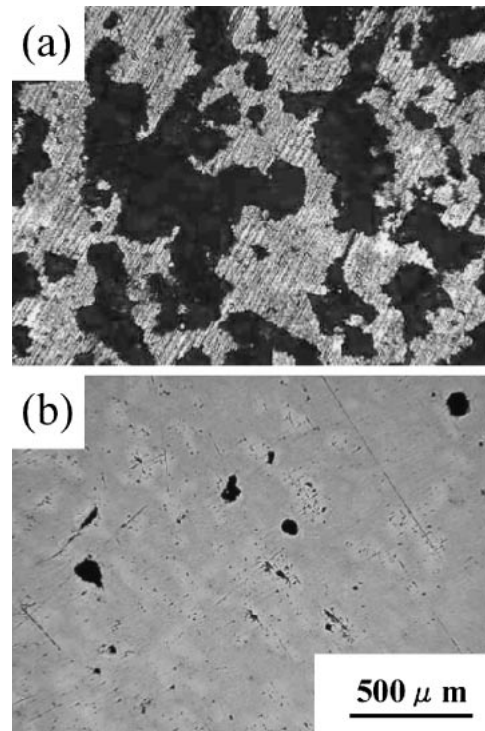


Fig. 5 Reduction in porosity due to SHS with pressure for $f_v = 0$. (a) without pressure, (b) with pressure.

imum temperature after the SHS reaction is high when TiB₂ concentration is high. The temperature of the alumina powder surrounding the sample as the pressing media of the pseudo-HIP equipment is higher when the TiB₂ concentration is higher. This hot alumina powder will reduce the cooling rate of the sample. Therefore, when the TiB₂ concentration is high, the cooling rate becomes lower and TiB₂ particle size becomes larger.

The application of pressure during the SHS reaction was very effective for the reduction in porosity remaining in the reaction products. The reaction product contained quite a lot of pores for the sample produced without pressure, as shown in Fig. 5(a). The formation of the pores was thought to be mainly due to the evaporation of absorbed gaseous materials such as water on the raw powder particle surface during the exothermic SHS reaction. The difference in average density between the reactant elements and the reaction product may be another factor of the pore formation: the former is smaller than the latter, which causes the shrinkage in volume and hence may lead to the formation of pores. The porosity was dramatically reduced when the SHS was performed under the pseudo-HIP condition, as shown in Fig. 5(b).

Figure 6 shows the effect of the TiB₂ volume fraction on the porosity of the SHS reaction product. As the TiB₂ volume fraction increased, the porosity increased for both the conditions with and without the pressure. However, the application of the pressure dramatically reduced the porosity. Because the boron powder used for the reactant material was very fine and the surface area of the powder is extremely large compared with other elemental powders, the increase in boron concentration increases the amount of the surface-

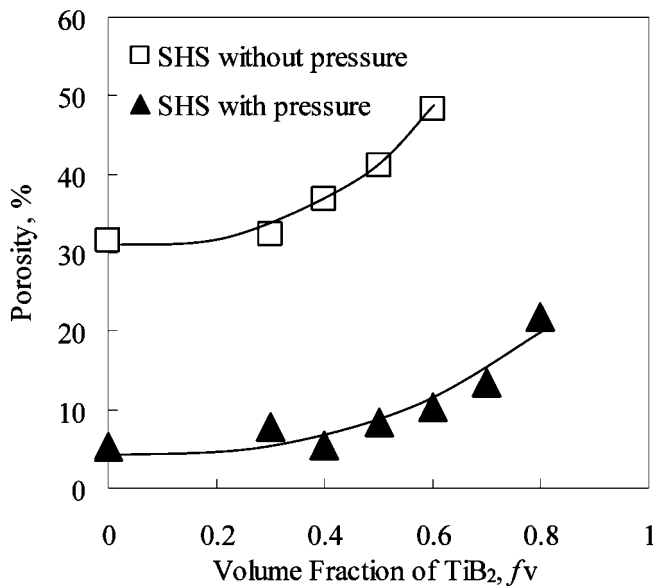


Fig. 6 Effect of pseudo-HIP on the porosity.

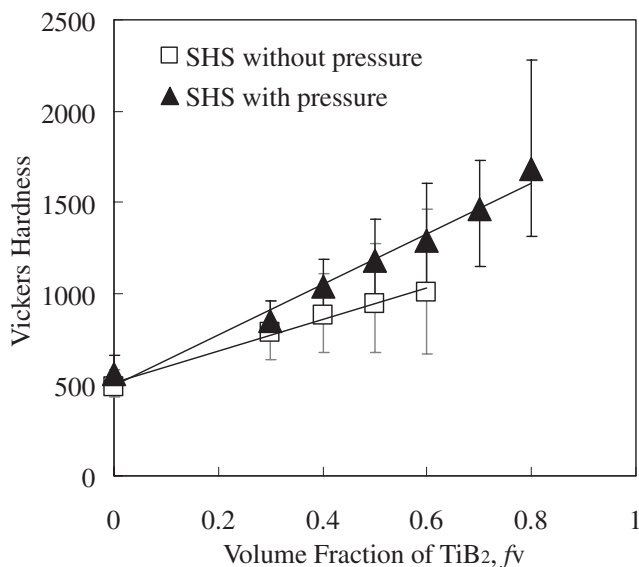


Fig. 7 Effect of pseudo-HIP on the Vickers hardness.

absorbed materials and hence the amount of pores in the reaction product. Thus, markedly dense reaction products were obtained by using the pseudo-HIP method. However, the porosity is still high when the volume fraction of TiB₂ is high: the porosity was about 20% when the volume fraction was 0.8. The porosity should be significantly reduced if the composites are used as working tools, for example.

Figure 7 shows the Vickers hardness of the composites. Vickers hardness increased with the increase in volume fraction of TiB₂. This increase is thought to be due to the rule of mixture for the TiB₂ particles and FeAl phase. Moreover, the hardness of the sample produced by pseudo-HIP method is higher than that of the non HIP-ed samples. This increase is thought to be due to the decrease in porosity by pseudo-HIP method.

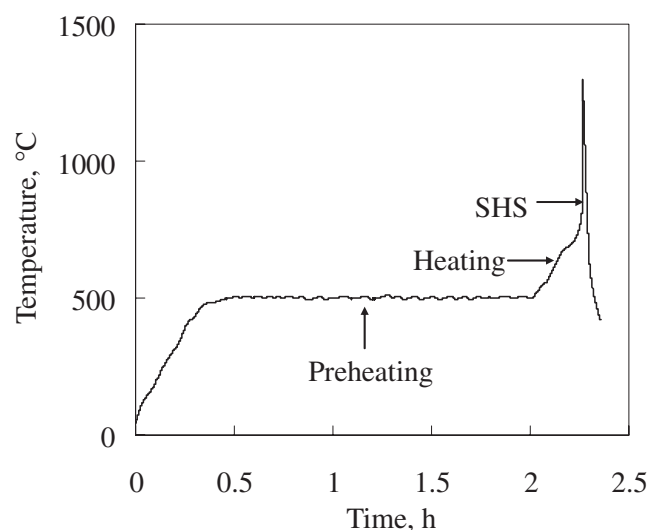
As mentioned above, FeAl-TiB₂ composites were obtained by very simple method based on heating of elementary

powder mixture. However, when the TiB₂ volume fraction was high, the TiB₂ particle diameter was large and the porosity was high. From the view point of mechanical properties of the composite, TiB₂ particle diameter should be fine and the porosity should be low. So, in this study, the effect of preheating on the TiB₂ size and porosity has been investigated.

3.2 Preheating of powder mixture

The reason why the TiB₂ particle size increased with the increase in TiB₂ volume fraction was considered that TiB₂ particles coexisted with liquid at high temperatures for long periods of time when TiB₂ concentration was high, as described in the former section. Therefore, it was predicted that the growth of TiB₂ particles could be controlled by decreasing the maximum temperature after the SHS reaction. If the compact of the elementary powders is preheated at a temperature below the ignition temperature of the SHS reaction, reactive sintering will proceed based on the diffusion between the elemental powders and some inter-metallic alloys and solid solutions will be produced at the interface between the elemental powders. These reactive sintering products will consume the heat from the subsequent SHS reaction and will reduce the maximum temperature after the SHS reaction. Thus, preheating of the compact will reduce the TiB₂ particle size in the SHS reaction products. The preheating is also considered to be effective for reducing the porosity in the reaction products, because it will remove the gaseous materials from the surface of the powders. Therefore, it is expected that preheating of the compact should reduce the TiB₂ particle size and porosity.

Figure 8 shows the temperature change when preheating was performed before the SHS reaction for a sample of $f_v = 0.6$. After preheated at 500°C for 1.5 hours under a pressure of 50 MPa, the temperature of the sample was raised. At about 700°C, sudden temperature increase was observed, as shown in Fig. 8, which implies the exothermic SHS reaction occurred even after the reactive sintering. The

Fig. 8 Temperature change during and after preheating of the compact. $f_v = 0.6$.

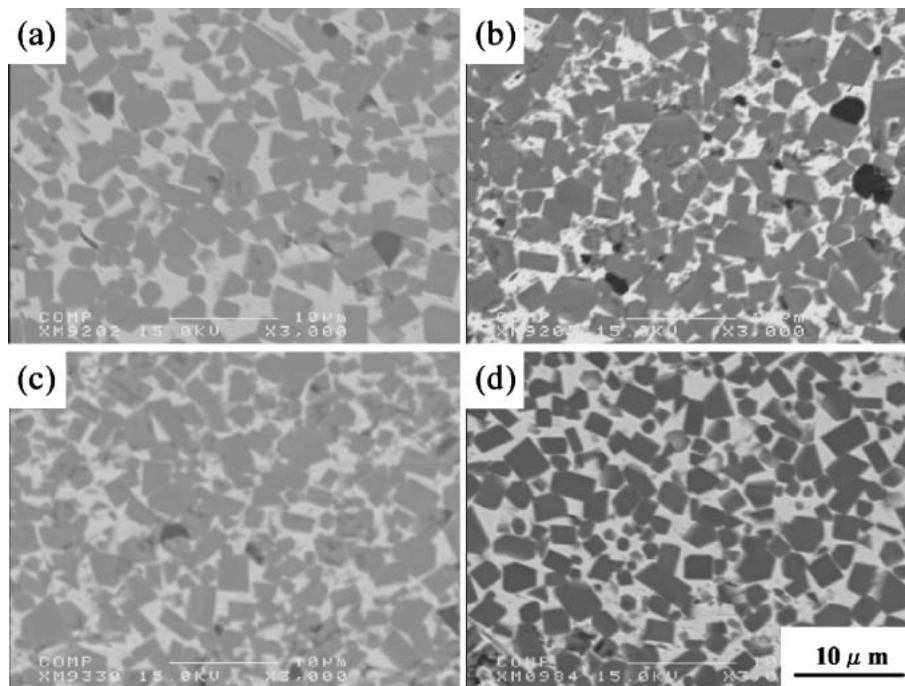


Fig. 9 Effect of preheating time on the TiB_2 particle size, $f_V = 0.6$, at 500°C without pressure. (a) 0.5 h, (b) 1.0 h, (c) 1.5 h, (d) 3.0 h.

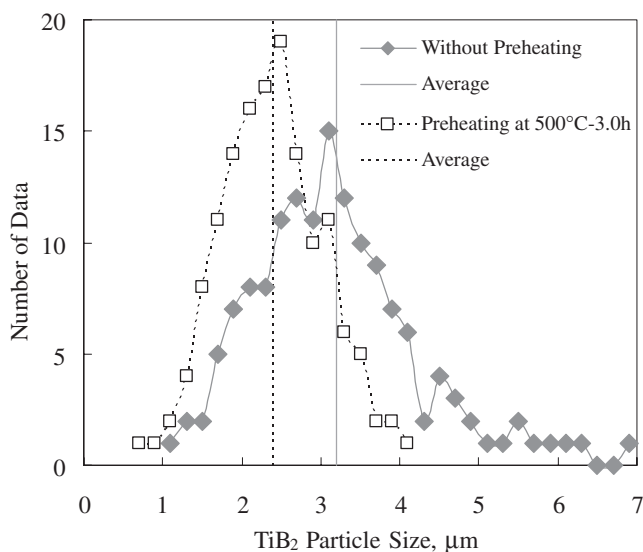


Fig. 10 Distribution of TiB_2 particle size.

XRD and EPMA examinations revealed that the sample consisted of only FeAl and TiB_2 .

Figure 9 shows the microstructures of the samples produced by the pseudo-HIP SHS after preheating at 500°C for (a) 0.5, (b) 1.0, (c) 1.5, (d) 3.0 hours under normal pressure for $f_V = 0.6$. The TiB_2 particle size decreased as the preheating time increased. The average TiB_2 diameter decreased from 3.2 to $2.4\mu\text{m}$ due to the preheating for 3 hours. The particle size distributions are shown in Fig. 10. It is clearly shown in the figure that TiB_2 diameter became smaller due to the preheating.

Figure 11 shows the microstructures of the samples produced by the pseudo-HIP SHS after preheating under pressure. The preheating conditions were 500°C for (a) 0.5, (b) 1.5, (c) 3.0 hours, (d) 450°C for 1.5 hours, and (e) 550°C

for 1.5 hours. Figures 11(a), (b) and (c) show that the increase in preheating time reduces the TiB_2 particle diameter: the diameter was reduced to $1\mu\text{m}$ by preheating at 500°C for 3.0 hours. Moreover, the increase in preheating temperature also reduces the TiB_2 particle diameter (see Figs. 11(b), (d) and (e)). These results will be explained by the fact that reactive sintering and alloying of the elemental powders progress faster and to a long distance at higher temperatures and for longer periods of time because they are based on the diffusion of atoms. By comparison between Figs. 9 and 11, one can find that the application of pressure during preheating reduces the TiB_2 particle size. This may be due to the increase in contact area between the elemental powders, which promotes the reactive sintering and alloying during preheating and hence reduces the maximum temperature after the SHS reaction and retards the growth of TiB_2 particles.

Figure 12 summarizes the effects of the preheating on the TiB_2 particle size. It can be said that the effect of pressure is crucial compared with those of temperature and time, and that the effect of temperature seems to be more significant than that of time. Thus, preheating under pressure and at high temperatures is very effective to reduce TiB_2 particle size.

The reduction in TiB_2 particle size is considered to be due to the reactive sintering and alloying of the elemental powders, as mentioned above. To confirm this, the XRD examination was performed for samples produced with and without the preheating. Samples were taken out from the pseudo HIP equipment after the preheating before the subsequent heating for the SHS reaction. The results are presented in Fig. 13. In the case of the sample without preheating (Fig. 13(a)), clear peaks of iron, aluminum, and titanium were detected, which means that no reaction occurred in this case. The peak of boron was not detected

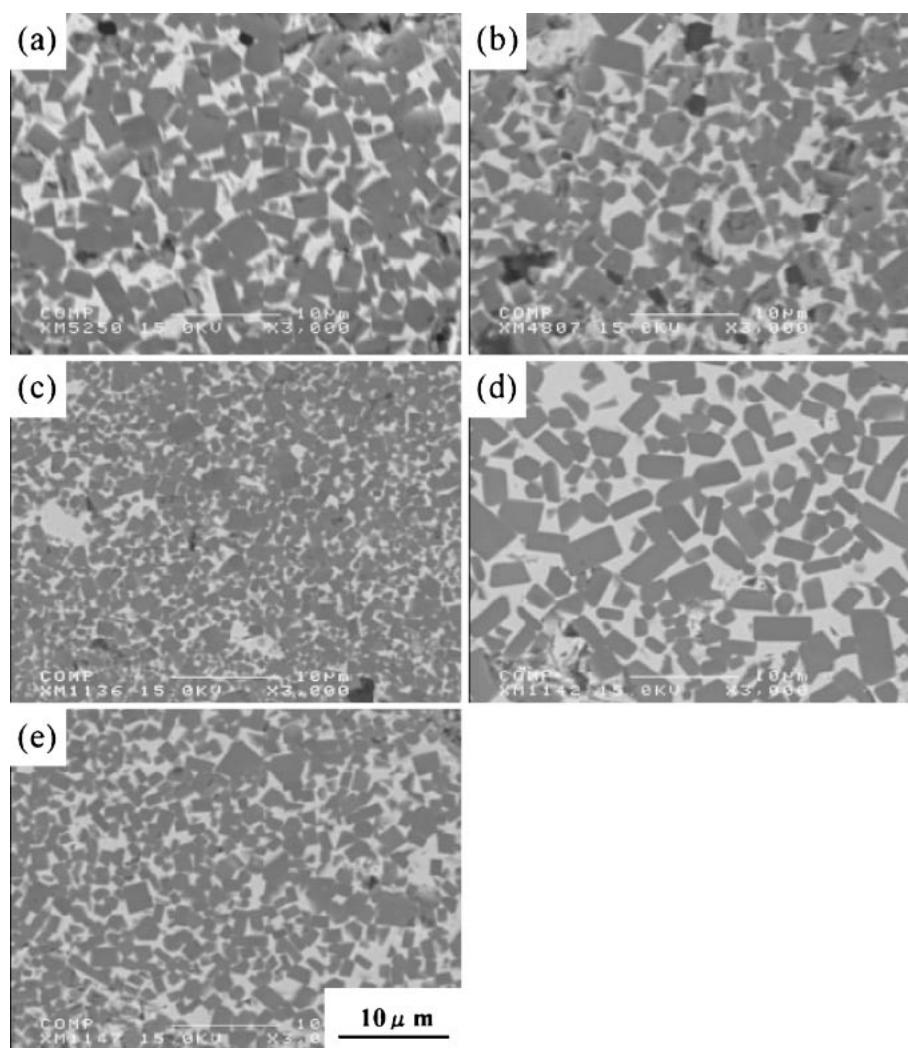


Fig. 11 Effect of preheating temperature and time on the TiB₂ particle size, $f_V = 0.6$ with pressure, (a) 500°C-0.5 h, (b) 500°C-1.5 h, (c) 500°C-3.0 h, (d) 450°C-1.5 h, (e) 550°C-1.5 h.

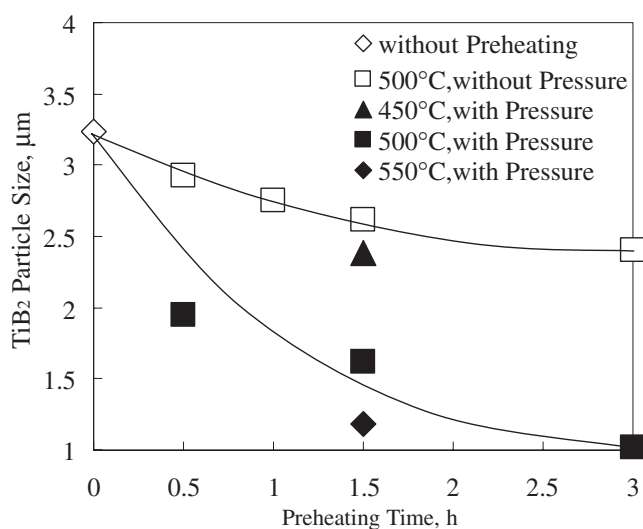


Fig. 12 Effect of preheating temperature, time and pressure on the TiB₂ particle size.

because amorphous boron powder was used. On the other hand, in the case of the preheated sample, the intensities of the peaks of elementary metals decreased, and the new peaks appeared, as shown in Fig. 13(b). It was difficult to identify the newly produced compound because quite a lot of small peaks were detected, and there was a possibility that ternary and quaternary complex compounds may be produced in the preheated sample. However, from the difference between the two XRD spectra, it can be said that reactive sintering or alloying of the elemental powders occurred to a certain extent.

The effect of preheating on the porosity is shown in Fig. 14. The pores became small and the volume fraction decreased due to the preheating. Porosity in each preheating condition is shown in Table 1. These samples were preheated under pressure. Porosity decreased from 10.3% to 7.3% due to preheating at 550°C for 1.5 hours. Thus, preheating before SHS is effective for densification of the SHS products. Moreover, an increase in preheating temperature reduced the porosity. It was suggested that preheating at higher temperatures was effective for the removal of the gaseous materials on the powder surface. However, longer preheating time at a constant temperature was not effective.

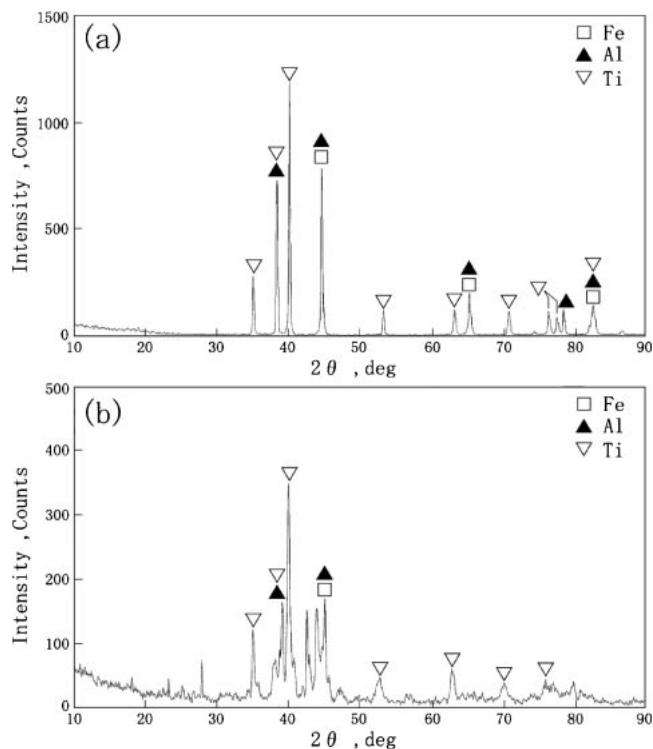


Fig. 13 Change in XRD spectrum due to preheating at 500°C for 0.5 h for $f_v = 0.6$. (a) without and (b) with preheating.

Table 1 Effect of preheating temperature and time on the porosity and hardness for $f_v = 0.6$.

Preheating Condition	TiB ₂ Particle Size (μm)	Porosity (%)	Hardness (HV)
Without Preheating	3.2	10.3	1290
450°C for 1.5 h	2.4	9.2	1300
500°C for 0.5 h	2.0	8.5	1350
500°C for 1.5 h	1.6	8.4	1420
500°C for 3.0 h	1.0	8.2	1470
550°C for 1.5 h	1.2	7.3	1520

Table 1 also shows Vickers hardness of the SHS products. Although the hardness was about 1300 HV for the sample without preheating, it increased to about 1500 HV due to preheating at 550°C for 1.5 hours. This increase in hardness is considered to be related to the decreases in porosity and TiB₂ particle size due to the preheating.

4. Summary

FeAl-TiB₂ composites were successfully produced from elementary powders of iron, aluminum, titanium and boron using the pseudo-HIP combustion synthesis or the Self-propagating High-temperature Synthesis (SHS). When the elemental powder mixtures having molar ratios of Fe : Al = 1 : 1 and Ti : B = 1 : 2 were heated to a temperature near the

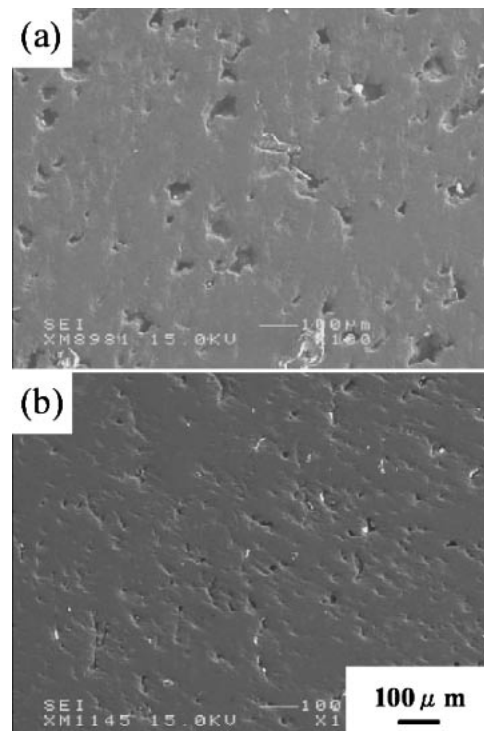


Fig. 14 Reduction in porosity due to preheating at 550°C for 1.5 h for $f_v = 0.6$. (a) without and (b) with preheating.

melting point of aluminum, the SHS reaction occurred and TiB₂ dispersed FeAl-based composites were produced. The application of a pseudo HIP pressure during the SHS reaction led to a dramatic decrease in porosity of the SHS products. As the volume fraction of TiB₂ increased, the TiB₂ particle size, Vickers hardness and porosity increased. Preheating of the powder mixture before the SHS reaction at temperatures below the ignition temperature of the SHS reaction brought about decreases in TiB₂ particle size and porosity and it increased the Vickers hardness of the SHS products. The Vickers hardness was about 1600 HV when the volume fraction of TiB₂ was 0.8. The average TiB₂ particle diameter ranged from 1 to 7 μm depending on the chemical composition of the powder mixture and the preheating and SHS conditions. Application of pressure during the preheating exhibited considerable effect on reducing the TiB₂ particle size in the SHS products.

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