PAS Fabrication and Densification Mechanism of B-Al-Ti-C System Ceramics

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Abstract. In this paper, B-Al-Ti-C system ceramics were fabricated by plasma activated sintering (PAS) technique. The final sintered products consisted mainly of AlB₁₂C₂ and TiB₂. The specimens could be densified at the temperature of 1460 °C~1600 °C, which is near 400 °C lower than the dense pure AlB₁₂C₂ and TiB₂ ceramics. The sintered samples are nearly fully dense, and there are substantially no pores observed by observing the SEM photograph. The mechanism of low temperature densification and the phenomenon of varied specimens during sintering were explained in details in this study.

1. Introduction

AlB₁₂ has the B₁₂ icosahedrons containing in their cells, the special structure similar to B₄C endows AlB₁₂ with superior mechanical properties.[1] Lightweight high strength AlB₁₂-based ceramics are expected to be widely used as protective armor or constructional ceramics for nuclear power plants, interest in higher aluminum borides and AlB₁₂ in particular exists for a long time. [2-7] TiB₂ is widely used as the second phase to reinforce the matrix because of the outstanding mechanical properties such as high modulus and hardness.[8-11]

Both AlB₁₂ and TiB₂ contain superior mechanical properties and are promising structure material. It is expected that TiB₂ toughened AlB₁₂ multiphase ceramics will have excellent mechanical properties. But AlB₁₂ and TiB₂ are difficult to be densified and require extremely high sintering temperature more than 1900 °C because of their covalent bonding. To promote the densification, numerous studies have been carried out. The addition of metals and alloys with low melting point can provide proper liquid phase and significantly accelerate the densification of ceramics. Mizrahi et al [12] have found that the addition of 3.5-5.5 vol.% of Fe enhanced the densification of B₄C thanks to the liquid phase during sintering. Rehman et al [13] have fabricated dense B₄C by spark plasma sintering at 1700 °C for 5 min with the addition of FeAl₃. Other than this, the reactive liquid-phase sintering can improve the densification also. Matjaz Valant et al [14] have fabricated the dense BaTiO₃ at 820°C with more than 95% relative density and applied reactive liquid-phase sintering to a number of different compounds with very different crystal-chemistry characteristics.

Metal is especially critical for reducing sintering temperature and promoting sintering. In our study to fabricated TiB₂-toughened AlB₁₂ multiphase ceramics, AlB₁₂ and TiB₂ can be formed via the in situ
reaction from Al-B and Ti-B respectively, and C is introduced into the reaction system to eliminate the oxide film on the surface of the raw material powder. Therefore, the B-Al-Ti-C system has been finally established by us.

The purpose of this study is to obtain fully dense AlB12-TiB2 multiphase ceramics at a relatively low temperature via reactive PAS technique from B-Al-Ti-C. And then, investigate the mechanism of low temperature densification.

2. Experimental details

As shown in Figure 1, the starting materials are commercial available B powder (0.25 μm, purity 98.0%; Macklin, Shanghai, China), Al powder (1 μm, purity 99.0%; Aladdin, Shanghai, China), Ti powder (3-5 μm, purity 99.0%; Aladdin, Shanghai, China) and organic carbon source. The raw powders were weighted and mixed in anhydrous ethanol using ZrO2 balls in a low energy ball milling apparatus (QM-A, Xianyang, China) for 24 h with a nominal composition of T05, T10, T15, T20 on behalf of (5 vol.% TiB2, 10 vol.% TiB2, 15 vol.% TiB2, 20 vol.% TiB2). After being mixed, the mixture powders were dried in the vacuum freeze drier (FD-1C-80, Shanghai, China) for 12 h. Then the mixture powders were passed through 200 mesh sieve and then pressed into disks (φ20×5 mm) under the pressure of 30 MPa in the steel mold. Finally, the green bodies were put into a graphite mold with an inner diameter of 20 mm and then sintered by plasma activated sintering at the temperature of 1460 °C–1580°C for 3 min with a heating rate of 100°C/min under the pressure of 10 MPa.

![Image](image_url)

**Figure 1.** The schematic of AlB12C2-TiB2 multiphase ceramics prepared by spark plasma sintering; SEM images of (a~c): Raw B, Al and Ti powders, (d): B-Al-Ti-C mixed powders.

The densities and the porosities of the composites were measured by the water displacement method according to Archimedes principle. Phase identification was performed by X ray diffraction (XRD: RINT 2500, Rigaku, Tokyo, Japan) with CuKα radiation. The microstructure of these specimens was observed by the field-emission scanning electron microscope (FESEM) analyzer (FEI Quanta FEG250, America).
3. Mechanism of low temperature sintering

Figure 2 is the XRD pattern of samples T05 to T20, as shown in Figure 2, the raw B, Al, Ti and C mixture powders were in situ converted into AlB$_{12}$C$_2$ and TiB$_2$ during sintering. And the peak appeared at $2\theta=26.6^\circ$ is the characteristic diffraction peak of carbon. During the sintering process, the raw carbon can react with AlB$_{12}$ to form AlB$_{12}$C$_2$, and the residual carbon may be graphitized at such a high sintering temperature. So that the characteristic line of C can be observed in the XRD pattern, and the final specimens consist mainly of AlB$_{12}$C$_2$ and TiB$_2$ rather than AlB$_{12}$ and TiB$_2$. According to the results of XRD, the final products contain some by-products, so the theoretical density and relative density of the final sintered samples cannot be accurately calculated. To investigate the densification of the samples, the opening porosity was calculated and the respective density and porosity of T05-T20 are shown in Figure 3. The opening porosities of all the samples are lower than 0.004, and T20 has the lowest opening porosity of 0.0018. As the content of TiB$_2$ increased, the density of the sample also increased, but the porosity decreased. It seems that it is Ti rather than Al can promote sintering densification.

![Image 1](image1.png)

**Figure 2.** The XRD pattern of specimens T05-T20.

![Image 2](image2.png)

**Figure 3.** The density and porosity values of samples T05-T20.
To investigate the densification mechanism in the sintering procedure, we collected the sintering under the guidance of the real-time shrinkage curve depends on temperature. For a more intuitive comparison of the sintering densification process of different component samples, we got the real-time percentage of shrinkage by processing the data. Figure 4 shows the evolution of shrinkage with the temperature rising during the whole sintering process, the ordinate is obtained by the real-time shrinkage value dividing the total shrinkage during whole sintering period. The positive values represent expansion and negative values represent shrinkage, in the early stage of heating process, all of the powders exhibit a certain degree of regular volume expansion, the Al powder reacted with B powder, forming AlB₂, leading a shrinkage curve rising in the sintering process. Then, the shrinkage happened with the continuous heating which corresponds the process of densification. With the temperature improved to 1460 °C~1580 °C, the shrinkage curve of the specimen stops dropping with the rising of temperature, revealing the finish of sintering procedure. The extremely low porosity shown in Figure 3 corresponds a relative high density. Compared to the sintering temperature of pure densified AlB₁₂ and TiB₂, the almost fully dense AlB₁₂-TiB₂ composites were fabricated at a relative lower temperature.

As shown in Figure 4, the shrinkage plots of the specimens with varied component proportion were recorded, as the content of Al increasing from T20 to T05, the sintering temperature increases as well. The specimen T20 can be densified at the temperature of 1460 °C, but with the content of Al rising, the sintering temperature of T05 is increased to 1580 °C. However, the contribution on promoting sintering provided by Al can be proved by comparing the SEM micrographs between the B-Ti-C and B-Al-Ti-C system shown in Figure 5. The Figure 5(b) shows the polished surface of T20 specimen sintered at the temperature of 1460 °C, the sintered samples are so dense that the hole is hardly observed and the ashen TiB₂ particles distributes in the matrix dark phase AlB₁₂C₂ uniformly.
However, as shown in Figure 5(a), the densification of the specimen sintered at 1650 °C without the addition of Al is poor, the holes can be discovered obviously. It reveals that the liquid phase mass transportation is not the only mechanism to lower the sintering temperature, and Ti plays a vital role in reducing sintering temperature and promoting densification during sintering procedure.

![Figure 5. SEM images of polished surface of (a) no Al specimen sintered at 1650°C; (b) T20 sintered at 1460 °C.](image)

Many reactions happened during sintering process in the B-Al-Ti-C system, and the heat released by in situ reactions happened during the sintering procedure can promote sintering also. To investigated the thermodynamics in the system, the enthalpy changes of these reaction were calculated via the message from thermodynamics database and listed in Figure 6. As shown in Figure 6, with the reactions going on, much quantity of heat will be released. These exothermic reactions can afford the extra heat during sintering period and lower the sintering temperature. The heat released during the sintering process mainly comes from the following two reactions:

\[
\begin{align*}
\text{(a)} & \quad Al + 12B = AlB_{12} \\
\text{(b)} & \quad Ti + 2B = TiB_{2}
\end{align*}
\]

According to the heat releasing data, the difference in calorific value released by the two reactions is not read. But, to release the same heat, 12 moles boron should be consumed by the reaction (a), and 2 moles only for reaction (b). The more boron that participates in reaction b, the more heat is eventually released. Therefore, from T05 to T20, as the TiB$_2$ content increases, the volume fraction of AlB$_{12}$C$_2$ decreases, the total heat released increases. The following formula[15]describes the relation between reagent conversion rate and the matters involved in the reactions:

\[
\frac{dG}{d\tau} = KC_1C_2F
\]

In this equation, G is the degree of reaction going on, τ is the reaction time, C$_1$ and C$_2$ are the concentrations of the reactant, and F is the area of surface contacting. In one reaction system, the thermal conditions and the reaction process are assumed, the value of concentration C$_1$, C$_2$ and the coefficient K of a reaction between a solid phase and a liquid phase or a reaction between two solid phase is almost the same. So, the degree of reaction conversion depends mainly on the surface contact areas F. Figure 1 shows the good distribution of the mixture powder, the flaky B particles adhere to the globular Al powders and larger size Ti powder uniformly, it means a good surface conduct among raw
materials and a high reaction rate. As the temperature increased, the liquid phase appeared in the reaction system, expanding the surfaces contact areas among the reactants, and then accelerating the reaction rate. As mentioned above, the reaction during sintering can release much heat, create lots structural vacancies, accelerate the sintering, the liquid phase appearing in the system can facilitate these effects. Thanks to the liquid phase accelerating effect, the influence of the heat releasing on the sintering promoting may be magnified. In addition, the difference in the exothermic effect between reactions (a) and (b) will also be expanded. This is an explanation for why the sintering temperature is greatly reduced, and as the content of titanium powder in the raw material powder increases, the sintering temperature is gradually lowered.

In such an extremely complicated system, the matrix and secondary phase are both formed by in situ reaction during sintering procedure. And because of the large amount of exothermic reaction, the whole system has been in a high energy state. Then the structural vacancies are created as lots of reaction going on. The coefficient of lattice-diffusion is in direct proportion to the vacancy concentration, so the rate of reaction and mass transportation is higher thanks to the structural vacancies generated during sintering process. [15] Further, according to formula (1), the liquid phase generated during the sintering process can accelerate the progress of the reaction, promote the formation of vacancies, thereby amplifying its promotion effect on sintering.

4. Conclusion
In summary, almost fully dense B-Al-Ti-C system multiphase ceramics can be synthesized at a relative low temperature using B, Al and Ti powders and organic C source as starting materials. In this sintering system, the high rate liquid phase mass transportation via the liquid phase provided by Al can promote the sintering a lot. The reaction Ti reacted with B and forming TiB₂ releases much more heat than Al, and lots structural vacancies appears during sintering. Thanks to the mixed powders with a good surface contact and the liquid phase, the reaction rate is dramatically promoted, the vacancies in the system can greatly accelerate the mass transfer process, and the instantaneous vast heat released by the reaction can sharply accelerate the sintering.

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