Microstructure and properties of B₄Cₚ/Al composite prepared by microwave sintering with low temperature

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Abstract
In this study, B₄Cₚ/Al composites were prepared by microwave sintering using 20 vol% B₄C and Al powder as raw materials. The effects of sintering temperature and time on the microstructure and properties of B₄Cₚ/Al composites were studied. The results show that in the presence of microwave field, the pores amount at the B₄C/Al interface and the densification has been changed. When the sintering temperature is 580 °C and the sintering time is 45 min, the B₄C particles are dispersed. At this time, the B₄C/Al interface is clean and tight together with few transient phase Al₃BC(s) that commonly generated in abnormally hyperthermal areas. When the temperature is enhanced or time prolonged, the liquid aluminum will appear in the composite, the fluidity of the aluminum matrix will increase greatly. A more serious aluminizing phenomenon will occur, resulting in the uneven distribution of B₄C particles in the matrix. As for the properties, the optimized composite material exhibits the best compactness and Vickers hardness as 93.2% and 112.5HV₁. The nanoindentation test reveals that the hardness and elastic modulus of interface are 8.494 GPa and 142.537 GPa.

1. Introduction

With the implementation of the global sustainable development strategy, higher standards have been put forward for the use of materials. In order to comply with the requirements of the new era, new materials have also developed a new trend towards the integration of lightweight and structural functions [1]. Particle Reinforced Metal Matrix Composites (PMMCs) obtained by introducing high performance ceramic reinforcement particles into metal matrix have the characteristics of easy processing and moulding of metals. It shows high modulus, high strength and multi-function due to the reinforcement effect of the reinforcement. The characteristics have been widely used in aerospace, transportation, energy and other high-tech fields [2].

Boron carbide particle-reinforced aluminum-based composites (B₄C/Al) are a new type of particle-reinforced metal-based composites with the dual advantages of lightweight and structural and functional integration [3, 4]. The density of B₄C is only 2.51 g cm⁻³. The density of B₄C is the lowest in commonly used Al matrix composite reinforcements TiB₂, TiC, ZrB₂, Al₂O₃ and so on. The hardness of B₄C is second only to that of diamond and standing BN. B₄C has excellent thermal neutron absorption capacity due to its ultra-high neutron absorption cross section of isotope ¹⁰B and its lattice capacity to accommodate atoms. It is the most important material for nuclear reaction control elements and shielding devices up to now [5]. With the introduction of the reinforcement and the increase of the content, the plastic toughness of the B₄C/Al composite material is greatly reduced, which is unfavorable for its forming and service safety [6]. An important reason for the low plastic toughness of PMMCs is the thermal expansion coefficient mismatch and modulus mismatch between the reinforcement and the matrix. During the cooling process of the composite material prepared at high temperature, the matrix around the reinforcement undergoes extensive plastic deformation to cause work hardening. Further, the plastic deformation ability of the matrix is reduced [7–9]. At the same time, the hardening of the matrix is also the most important reason for the strengthening of PMMCs [10–12]. In order to overcome this ‘contradiction between strength and toughness’, the traditional toughening method produces
large non-strengthened plastic zone in PMMCs through ‘regulation of spatial distribution of reinforcement’. The purpose of improving toughness is to passivate and deflect cracks through deformation of plastic zone. However, this method is not only complex in technology, but also causes local concentration of reinforcement, often at the expense of strength and plasticity [13–15].

In recent years, human beings are facing increasing pressure on energy, environment and resources. Microwave sintering has attracted wide attention in the preparation of new materials because of its energy-saving, high efficiency, clean and environmental protection, and as a new and environmentally friendly heating method [16]. Compared with traditional sintering methods, microwave sintering has many unique advantages [17]:

1. Microwave sintering can achieve rapid sintering of composite materials at low temperatures. This sintering method reduces the sintering conditions between B₄C/Al and reduces the formation of brittle phase Al₃BC. Therefore, the microstructure and mechanical properties of the B₄Cp/Al composites are improved.

2. Microwave sintering has a unique ‘internal heating effect’ to achieve the overall heating of composite materials. It can make the sintering temperature rise faster and more uniformly, eliminating the temperature gradient and hysteresis effect.

3. Microwave sintering can use the absorbing effect of B₄Cp ceramic particles in the microwave field, so that the sintering process has the characteristics of fast heating speed, uniform heating, selective heating, easy control, energy saving and high efficiency. It is obviously superior to the conventional heating method that only relies on heat radiation, heat conduction or heat convection. Its energy conversion efficiency is greatly improved [18].

4. The high-frequency electromagnetic wave in the microwave sintering process can stimulate the residual gas in the pores of the composite material to generate a plasma phenomenon. A specific high-temperature region is generated at the phase interface, which can promote the growth of the sinter neck. It improves the sintering performance of the sample [19].

The comparison of the heating rate of different B₄Cp/Al composite materials preparation methods is shown in figure 1.

In this study, B₄Cp/Al composites were prepared by microwave low temperature sintering. Utilize the coupling effect between particles and microwaves to control the microstructure of the composite material to obtain a new B₄Cp/Al composite material with the dual advantages of light weight and structural and functional integration. The specific preparation method is ‘powder pretreatment–high energy ball milling–ultrasonic dispersion–cold isostatic pressing–microwave sintering’. The influence of sintering time and sintering temperature on the microstructure and mechanical properties of B₄Cp/Al composites was studied by SEM, EDS, x-ray diffraction analysis, nanoindentation, and Vickers hardness.
2. Experimental procedures

The aluminum powder (purity 99.99%, $D_{50} = 10 \, \mu m$) used in this experiment, as shown in figure 2(a). The reinforced granular boron carbide powder (purity 99.9%, $D_{50} = 2 \, \mu m$) used in this experiment, as shown in figure 2(b).

The microwave sintering parameters are given in table 1. With the addition of boron carbide of 20 vol%, the high energy vacuum ball milling mixing powder was carried out by using the star ball mill (MITR-YXQM-4L). The ball milling medium uses ZrO balls (diameter 5 mm, 10 mm, 15 mm respectively, the add ratio is 1:3:2). The ball to material ratio is 5:1. With absolute ethanol as the ball milling process control agent, the added amount is 45 ml. Using anhydrous ethanol as a ball milling aid, the ball milling time is 12 h, and the ball milling speed is 200 r min$^{-1}$. Composite powders with dispersed and homogeneous powders were obtained. The composite powder was dried in a vacuum drying oven (DZF, Shanghai Kuntian Laboratory Instrument Co., Ltd), the

![Figure 2. SEM images of powder topography: (a) un-milled Al powder ($\times1000$); (b) un-milled B$_4$C particles ($\times1000$); (c) milled B$_4$C/Al mixed powder and EDS analysis ($\times3000$); (d) size distribution.](image-url)
drying temperature was 68.4°C, and the time was 36 h, and the ball milling aid anhydrous ethanol was completely removed. The SEM and EDS of the final composite powders were shown in figure 2(c) and the particles size distribution was shown in figure 2(d). The energy output during the high-energy vacuum ball milling is sufficient to plastically deform the Al powder and crush the reinforcement particles at the same time. The composite powder continuously undergoes a cyclic process of crushing and cold welding, so that the two are evenly distributed, providing a basis for the combination of B4C particles and Al matrix. The final composite powder particles are small and uniform in size distribution. Both of the two particulates sizes are in the range of 2∼5 μm. The external morphology of Al powder changed greatly, from a smooth surface to a rough surface. The edges and corners of the flaky matrix particles became blurred. Reinforcement particles are dispersedly distributed between the matrix particles, and the B4C/Al mixed powder has high uniformity.

A cold isostatic press (KJYs-150) was used to press the composite powder into shape. The static pressure is 250 MPa and the holding time is 5 min. A cylindrical sample preform having a size of Φ25 mm × 50 mm was prepared.

Using microwave sintering furnace (WBMW-JS2), put the sample first, and then evacuate to below 10 Pa. After that, argon was passed in, and the preform was sintered under the protection of an argon atmosphere. First, the sintering temperature was 580°C, and the sintering times were 30 min, 45 min, 60 min, and 75 min, respectively. The influence of sintering time on the microstructure and properties of B4Cp/Al composites was studied. Then the sintering time is 45 min and the sintering temperatures are 450°C, 520°C, 580°C and 650°C, respectively. The influence of sintering temperature on the microstructure and properties of B4Cp/Al composites is studied. The schematic diagram of microwave sintering is shown in figure 3. The SiC material composed of the absorbing layer, which exhibit the outstanding microwave absorbing ability. During the post process of microwave sintering, the composite becomes contact with inferior microwave absorbing ability. On this condition, the SiC absorbing layer can act as the heat resource to the sintering.

| Table 1. Microwave sintering parameters. |
|------------------------------------------|
| 1 Composite | Heating rate k (°C min⁻¹) | Sintering temperature T (°C) | Sintering time t (min) | Remarks |
|--------------|-----------------------------|-----------------------------|------------------------|---------|
| 1            | 50                          | 580                         | 30                     | Examine the effect of sintering time and get the optimized value t* |
| 2            | 50                          | 580                         | 45                     |         |
| 3            | 50                          | 580                         | 60                     |         |
| 4            | 50                          | 580                         | 75                     |         |
| 5            | 50                          | 450                         | 45                     | Examine the effect of sintering temperature and get the optimized value T* |
| 6            | 50                          | 520                         | 45                     |         |
| 7            | 50                          | 580                         | 45                     |         |
| 8            | 50                          | 650                         | 45                     |         |

Figure 3. Schematic for microwave sintering apparatus.
In this experiment, laser particle size analyzer (MS 3000) was used to detect powder before and after ball milling. The optical system includes two types of light sources, red and blue. The maximum value (M) of the red light source is 4 mW. The He–Ne system is used and the wavelength is 632 nm. The maximum blue light source (M) is 10 mW. It uses an LED system with a wavelength of 470 nm and an effective focal length of 300 mm. The particle size range is 0.01–3500 μm (diameter). It is tested by dynamic light scattering method. The number of particle size classification is 100 (adjustable). The accuracy/reproducibility is better than 0.5% variable. Archimedes’ principle was used to measure the density of the sample. A Vickers hardness tester (DYDHV-1000, Shanghai Dianying Optical Instrument Co., Ltd) was used to measure the microhardness of the samples. The load was 9.8 N. Each sample was measured five times at least. The average value of the microhardness value was taken. An x-ray diffractometer (Bucker D8 ADVANCE) was used for phase analysis of the sample. The diffraction range was 10°–90° and the speed was 5° min⁻¹. A field emission scanning electron microscope (Nova Nano SEM 450, FEI) was used to observe the microstructure and morphology of the samples. The nanoindentation hardness tester (TTX-NHT3) was used to measure the indentation hardness and elastic modulus of the composite. The loading range was 0.2 mN–500 mN, the maximum indentation depth was 200 nm, the minimum contact force was 1 uN, and the displacement resolution was 0.05 nm, thermal drift ≤0.04 nm s⁻¹.

3. Results and discussion

3.1. Microstructure

3.1.1. Effect of sintering time

Figure 4 shows the effect of sintering time on the microstructure of B₄Cₚ/Al composites when the sintering temperature is 580 °C. It can be seen from figure 4 that as the sintering time increases from 30 min to 45 min, the pores marked by yellow arrow at the interface between the B₄C particles and the Al matrix decrease, and the microstructure of the composite becomes dense. When the sintering time is 45 min, the interface pores are the smallest and the interface bonding strength between the particles and the matrix is the highest that detected by nanoindentation test. At this time, B₄C particles disperse uniformly in the Al matrix, which are beneficial to exhibit the dispersion strengthening.
For the Al matrix and B₄C ceramic particles, these two phases have completely different relative permittivity and permeability, which meet the boundary conditions of microwave field propagation at the interface with two different media [20, 21]. That is, when the microwave magnetic field passes through the B₄C/Al interface with different relative permeability, the two particles will be coupled with the microwave, showing strong microwave absorption capacity, and the particles themselves become microwave absorbers [22]. Microwaves are converted into thermal energy by coupling with the medium inside the molecule. The residual gas adsorbed on the particle surface directly receives thermal radiation, absorbs thermal energy and accelerates the dissipation of residual gas between the pores, further reduces the pores at the B₄C/Al interface and improves the interface bonding strength. Furthermore, it is beneficial to improve the pore shape between B₄C particles and Al matrix, that is, from large and irregular pores to small and narrow, uniform microstructure with even distribution of pores.

When the sintering time is prolonged to 60 min, even 75 min, the thermal energy at the interface of B₄C/Al accumulates too much, part of the composites is overheated and liquefied, and grain growth occurs.

### 3.1.2. Effect of sintering temperature

Figure 5 shows the results of SEM analysis on the microstructure of B₄Cₚ/Al composites with different sintering temperature (450 °C, 520 °C, 580 °C and 650 °C). It can be seen from figure 5 that with the increase of the sintering temperature from 450 °C, 520 °C to 580 °C, the pores marked by yellow arrows at the B₄C/Al interface in the composite gradually shrink or even disappear, hence, the compactness of composites is utmost. Besides, the distribution of particles in the aluminum matrix is dispersed progressively. As for the action mechanism of microwave inside the composites, as shown in figure 6, it can be analyzed from three aspects:

Firstly, it is concerned with the electromagnetic field performance of microwave. When the B₄Cₚ/Al composite is in a microwave field, the molecules inside the material will induce the formation of electric dipoles [23]. Each electric dipole rotates through torque and rearranges. During the directional polarization transition of the dipole, the molecules absorb microwave energy, which intensifies the thermal motion between the molecules. The friction between adjacent molecules exotherms, causing the overall temperature of the particles to rise [24]. This speed up the sintering process and helps eliminate the temperature gradient inside the composite, and then achieves overall heating.

Secondly, as for the effect of microwave behavior, it has a great penetration depth when it imposes on a specific particle especially in the presence of high porosity. The multiple scattering of microwave promotes the energy absorption of particle and then the reflectivity of microwave is limited [25]. When the microwave is...
traveling in the composite, the amplitude is gradually attenuated. Furthermore, because the limited penetration depth is less than the particulate size, the absorbing energy will be gradually lowered down. The ability of different particles to absorb and attenuate microwave energy is different, which depends on the dielectric properties of the material. The attenuation state is determined by the microwave’s ability to penetrate the medium. The penetration depth ($\delta$) of the microwave inside the material is defined as the distance from the particle surface, which can be expressed as [26]:

$$\delta = \frac{1}{\sqrt{(\pi f \sigma \mu)}}$$ (1)

Among them, $\delta$ is the penetration depth of the microwave inside the material, $f$ is the microwave frequency ($2.45$ GHz), $\sigma$ is the electrical conductivity ($S/m$) of certain particle, and $\mu$ is the magnetic permeability ($H/m$) of certain particle. Table 2 is the relevant parameters of the two phases in the composite material at low temperature:

| Particles | Conductivity ($S/m$) | Magnetic permeability ($H/m$) | Penetration depth $\delta$ ($\mu m$) |
|-----------|----------------------|-----------------------------|-----------------------------------|
| B$_4$C    | $6.2 \times 10^7$    | $4\pi \times 10^{-7}$       | 40.83                             |
| Al        | $3.5 \times 10^7$    | $4\pi \times 10^{-7}$       | 1.71                              |

On the condition of higher temperature, the $\sigma$ will be changed. The relationship can be expressed by formula (2) through the introducing of temperature coefficient $K$.

$$\delta = \frac{2K}{\sqrt{f \mu}}$$ (2)

Where $K$ is the temperature coefficient and its expression is:

$$K = 1 + \frac{T - 20}{234.5}$$ (3)

Where $T$ is the thermodynamic temperature (K).

It can be known from formula (3) that when the sintering temperature $T$ is increased, the temperature coefficient $K$ is also increased, which will increase the penetration depth ($\delta$) of the B$_4$Cp/Al composite. This is beneficial for the B$_4$C ceramic particles to absorb microwave and accelerate the conversion efficiency from

![Figure 6. Schematic for the penetration depth of microwave in two particles.](image-url)
microwave energy to internal thermal energy, therefore, improves the microwave sintering efficiency. Namely, on the condition of higher temperature, the microwave sintering exhibits a remarkable efficiency.

Table 3 shows the calculation results of the penetration depth of Al particles at different sintering temperatures.

| Sintering temperature (°C) | Conductivity temperature coefficient $K$ | Microwave frequency $f$(GHz) | Penetration depth of Al particles $\delta$(μm) |
|---------------------------|-----------------------------------------|-----------------------------|---------------------------------------------|
| 450                       | 3.9985                                  | 2.45                        | 2.73                                        |
| 520                       | 4.2970                                  | 2.45                        | 2.82                                        |
| 580                       | 4.5528                                  | 2.45                        | 2.93                                        |
| 650                       | 4.8513                                  | 2.45                        | 3.02                                        |

Figure 6 shows the penetration depth of microwave in Al particles and B$_4$C particles. In the BALL I, the area covered by the arrows means the penetration depth layer where the microwave can be penetrated and absorbed by Al particles. In the core, the microwave cannot reach, hence, the part will be heated through the conduction approach. It is attributed that size (2 ~ 10μm) of certain particle is larger than the $\delta$ value in the range of $1.71 \sim 3.02\mu m$ (room temperature ~650 °C) though they are in the same micrometer level.

It is not the case with the B$_4$C due to its large penetration depth of 40.83 μm at room temperature, and even larger at higher sintering temperature. So, during the whole sintering process, the B$_4$C particles act as the strong sites to absorb microwave and become the hot spots in the composite during the sintering process.

On the basis of the above-mentioned factors, when the sintering time is 580 °C, the conversion efficiency of microwave in the composite is utmost. In general, the temperature gradient has been eliminated, the internal temperature distribution tends to be uniform. On this condition, the advantages of overall heating and low temperature fast burning for microwave sintering have been presented remarkably. On the condition of low temperature sintering, the grain growth is inhibited that is beneficial to exhibit the fine-grain strengthening.

But, when the sintering time is too high, as 650 °C, the microwave E-field will more easily result in the local focusing effects nearby the interface, the sintering neck and other areas, which will reduce the uniformity of the temperature inside the composite [27]. It has been demonstrated by the schematic diagram of figure 7.

At the same time, liquid aluminum appears, the fluidity of the aluminum matrix is greatly increased, and a more serious aluminization phenomenon occurs, which leads to the uneven distribution of B$_4$C particles in the matrix, the interface pores become larger to a certain extent. The compactness has been decreased significantly. Furthermore, the grain size become larger that at low sintering temperature.
3.2. Al$_3$BC phase at the interface

Figure 8 shows the XRD pattern of B$_4$Cp/Al composites at different sintering time (sintering temperature is 580 $^\circ$C). The crystal phases of Al, B$_4$C, Al$_3$BC($s$) can be detected. When the sintering time is 30 min, a small amount of Al$_3$BC($s$) phase is formed through the chemical reaction between the Al and B$_4$C, that can be expressed by formula (3): 3Al($s$) + B$_4$C($s$) → Al$_3$BC($s$) + 3B($s$).

According to its expression of Gibbous free energy, it belongs to an endothermic reaction. That is to say, a high local temperature may induce the reaction. The heat in the system comes from multi approaches as (a) microwave absorption and conversion, (b) internal free charge movement driven by E-field and (c) aided heating by SiC absorbing layer. For 30 min sintering, the time is not enough for the heat diffusion. Some areas with high local temperature may become the reaction sites between the Al and B$_4$C particles. The generated Al$_3$BC($s$) becomes a new phase in composites.

When the sintering time is 45 min, the diffraction peaks of the Al$_3$BC($s$) phase are significantly reduced, indicating that partial Al$_3$BC($s$) phase has been decomposed. That can be explained by the uniform temperature distribution and few locations with high temperature. The thermodynamic condition is not suitable for the Al$_3$BC($s$) generation, but appropriate for its decomposition. Therefore, few Al$_3$BC($s$) phases can be seen in the 45 min sample.

When the sintering time is extended to 60 min or 75 min, the application time of microwave field to B$_4$C particles increases. The actual sintering temperature, especially at the interface, is higher than the set sintering temperature. At this time, the Al$_3$BC($s$) phase diffraction peak reappeared in the XRD pattern. It can be concluded that on the condition of uniform temperature distribution, the Al$_3$BC($s$) phase is easily formed.

Figure 9 shows the XRD pattern of B$_4$Cp/Al composites with different sintering temperatures (sintering time is 45 min). The results show that when the sintering temperature is 450 $^\circ$C, due to the low sintering temperature, insufficient penetration depth of microwave, temperature gradients and uneven temperature distribution are apparent. On this condition, the B$_4$C particles tend to react with the aluminum matrix, and the transition phase Al$_3$BC($s$) is formed. The formation rate of Al$_3$BC($s$) crystals is enhanced with the increase of sintering temperature because of the endothermic performance of Al–B$_4$C chemical reaction. When the sintering temperature is 580 $^\circ$C, under the coupling actions of microwave field, SiC microwave absorbing aided heating and microwave E-field, the temperature in the sample distribute uniformly and the temperature gradient disappears. On the basis of previous analysis, part of the generated Al$_3$BC($s$) transition phase will be decomposed and its amount decreased. When the sintering temperature is 650 $^\circ$C, the Al$_3$BC($s$) phase diffraction peaks in the composite material emerge again due to the uneven temperature distribution, especially in some hyperthermal areas, the molten aluminum with high active energy will accelerate the Al$_3$BC($s$) generation.

Figure 10 illustrates the SEM and EDS diagrams of optimized 45 min, 580 $^\circ$C B$_4$Cp/Al composite about the interface characteristic. According to XRD patterns, an Al$_3$BC phase will be generated in the composite on special condition during microwave sintering. As shown in figure 10(b) that reveals the main elements that composes the pointed phase marked in figure 10(a), there are Al, B, and C elements in the phases. It is determined as the Al$_3$BC phase on the basis of atomic ratios.

Figure 11 displays the surface SEM same with figure 9(a). In order to further confirm the existence of the Al$_3$BC($s$) phase. The distribution of each element around the B$_4$C particles is obtained. There is a small mixed
region of B, C, and Al about 1 μm x 1 μm at the interface between the B\textsubscript{4}C particles and the Al matrix. the framed phase, therefore, is confirmed as the Al\textsubscript{3}BC transient phase.

The effect of Al\textsubscript{3}BC\textsubscript{(s)} phase can be analyzed as positive mainly and negative factors. (1) It is formed at the B\textsubscript{4}C/Al interface, which improves the wettability between the B\textsubscript{4}C particles and the Al matrix; (2) It fills the pores between B\textsubscript{4}C/Al and reduces the porosity, which increases the compactness of the composite; (3) Being a hard second phase, it can play the role of strengthening and improve the strength of the composite; (4) But at the same time, its generation will reduce the cleanliness of the interface between the B\textsubscript{4}C particles and the Al matrix, which is determinantal to the interface bonding and plastic toughness of the composite material.

3.3. Nanoindentation

Figure 12 demonstrates the nanoindentation test result. It aims to investigate the properties evolution for interface strength, two typical samples as 30 min, 450 °C (figures 12(a), (b)) and 45 min, 580 °C (figures 12(c), (d)) composites are selected to be subjected the \textit{in situ} nanoindentation test. The nanoindentation result can act as a reference to the macroscopic mechanical properties.

Using the Oliver and Pharr theorem [28], the load-displacement curve can be analyzed to obtain the nanohardness (H) and elastic modulus (E). According to the maximum load $P_{\text{max}}$, the maximum displacement $h_{\text{max}}$, the residual displacement $h_{\text{r}}$ after complete unloading, and the slope $S$ at the top of the unloading curve, the nanohardness $H$ of the material can be calculated by the formula:

$$H = \frac{P_{\text{max}}}{A}$$

Figure 9. XRD patterns of B\textsubscript{4}C\textsubscript{p}/Al composites with different sintering temperatures.

Figure 10. Regional SEM of B\textsubscript{4}C\textsubscript{p}/Al composites (×8000) and EDS.
In the formula: $P_{\text{max}}$ is the maximum load in mN; $A$ is the contact area between the indenter and the sample, in mm$^2$; $h_c$ is the indentation depth of the indenter, $h_{\text{max}}$ is the maximum indentation depth; $\varepsilon$ is a parameter.

$$A = f(h_c^2) = 24.56h_c^2$$  \hfill (5)

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}$$  \hfill (6)

$$S = \left( \frac{dp}{dh} \right)_{h = h_{\text{max}}}$$  \hfill (7)

Figure 11. Surface scanning metallography of $B_4C_{\phi}$/Al composite.
related to the shape of the indenter, for Berkovich type Indenter, \( \varepsilon = 0.75 \); \( S \) is the slope of the curve at the maximum indentation depth. The elastic modulus \( E \) of the material can be calculated by the formula:

\[
\frac{1}{E_i} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu^2}{E}
\]

\[
E_r = \frac{\Pi^{1/2}S}{2\beta A^{1/2}}
\]

In the formula: \( E_i \) and \( \nu_i \) are the elastic modulus and Poisson’s ratio of the indenter. For natural diamond indenter, \( E_i \) and \( \nu \) are 1114 GPa and 0.07, respectively; \( E_r \) is the reduced elastic modulus, which is caused by the total elastic deformation of the indenter and the sample. \( E \) is the elastic modulus of the measured material, \( \nu \) is the Poisson’s ratio of the measured material; \( \beta \) is a constant related to the geometry of the indenter.

The hardness and elastic modulus of the interface have been extracted from the relationship between the interface load \( (P) \) and the indentation depth \( (h) \) to characterize the interface strength of the composite [29]. It is demonstrated by table 4.

The interface hardness and elastic modulus of the 45 min, 580 °C composites are significantly higher than those of the 30 min, 450 °C composites one. For 30 min, 450 °C composite, the sintering time is short and the sintering temperature is low, there is more residual gas remaining between the particles and the matrix, resulting in larger interface pores and difficult to eliminate, resulting in low bonding strength of particles and matrix.

On the condition of optimized sintering time and temperature, both the interface wettability and the interface bonding strength have been improved. Due to the little amount of Al\(_3\)BC\(_3\) in the interface exhibits as the characteristic as high cleanliness, small and narrow interface pores, and high interface bonding.
3.4. Compactness

Figure 13 shows the effects of sintering time (Figure 13(a), sintering temperature is fixed at 580 °C) and sintering temperature (Figure 13(b), sintering time is fixed at 45 min) on the compactness of B₄Cp/Al composites. For B₄Cp/Al composites, because the wettability of B₄C ceramic particles and Al matrix is poor, it is difficult to achieve satisfactory compactness and a dispersed microstructure. In the research, the microwave sintering plays an apparent role in compactness and dispersion of microstructure. The B₄C particles are the main phases to absorb microwave. The microwave field is propagated and distributed along the pores besides the action of penetration depth. On an optimized sintering parameter (45 min, 580 °C), the temperature gradient will be disappeared and overall heating be realized.

From the perspective of the effect of sintering time, when the sintering time is 30 min, the microwave sintering time is shorter. The residual gas in the pores of the composite material is difficult to fully dissipate, which inhibits the substance migration of particles. On this condition, the sintering neck grows slowly and the sintering proceed insufficiently, which lead to the incomplete elimination of pores inside the material and lower compactness as 86.4%.

When the sintering time is increased to 45 min, the temperature gradient has disappeared, that is accompanied by the full dissipation of residual gas and uniform of particles and insufficient substance diffusion. The compactness is raised to 93.2%, that has been enhanced by 7.9% in comparison to the 30 min sample.

When the sintering time is 60 min, the sintering time is too long and the grains continue to grow, making the grains coarse and sizes difference. The compactness is lowered to 91.5%. On the condition of 75 min, the sintering time is too long to get a valuable sample, the aluminum matrix particles are partially liquefied, and the internal pores are filled, so that the compactness is further enhanced to 93.9%, a little higher than that of 45 min sample. But the microstructure segregation has become apparent, which is detrimental to the mechanical properties.

From the perspective of the effect of sintering temperature, when the sintering temperature is 450 °C (87.2% compactness) and 520 °C (89.4% compactness), the lower temperature is not conducive to the exhaust of the residual gas adsorbed on the particle surface, hinders the migration and diffusion. When the sintering temperature is 580 °C the compactness is relatively high. For 650 °C sample, it is close to the melting point of aluminum, in the hyperthermal areas, a part of liquid aluminum appears. The pores between the B₄C particles and the Al matrix are filled and compactness increase continuously to 93.8%. Nevertheless, too high sintering temperature will result in the grain coarsening and microstructure segregation.

Table 4. Nanoindentation results for two state B₄Cp/Al composites.

| Sample                  | Hardness (GPa) | Elastic modulus (GPa) |
|-------------------------|----------------|-----------------------|
| 30 min, 450 °C composite| 6.474          | 107.873               |
| 45 min, 580 °C composite| 8.494 (↑31.2%) | 142.537 (↑33.0%)      |

**Figure 13.** Effect of sintering time: (a) and sintering temperature; (b) on the density of composites.
3.5. Hardness

The effects of sintering time (figure 14(a), sintering temperature is 580°C) and sintering temperature (figure 14(b), sintering temperature of 45 min) on the Vickers hardness are shown in figure 14. The loading load is 1 kg. The results show that 30 min sample has the lowest hardness of 77.4HV₁, which corresponds to the much residual gas and insufficient sintering. The Vickers hardness of 45 min sample is utmost as 112.5HV₁ that is 45.3% higher than the 30 min sample. It is attributed to its optimized conditions involving few residual pores, few Al₃BC and sufficient sintering. For the 60 min (95.8HV₁) and 75 min (89.6HV₁) samples, the grains continue to grow, resulting in a continuous decrease in the Vickers hardness of the composite material.

As for the effect of the sintering temperature, for the 450°C sample, due to the low penetration depth of the microwave and the low diffusion rate of the substance, the hardness is low (73.2HV₁). This is mainly due to the small number of pores, low density, and insufficient sintering. It is difficult to achieve a sufficient metallurgical bonding between B₄C particles and Al matrix. With the increase from 450°C to 520°C, the positive effect of microwave gradually increases, that is, it accelerates the removal of residual gas, sintering propagation and formation of tight metallurgical bonding between particles. The hardness is increased from 73.2HV₁ of 450°C sample to 87.7HV₁ of 520°C. On the condition of 580°C sintering temperature, being an optimized condition, both the compactness and the Vickers hardness arrived at the utmost. The 112.5HV₁ hardness is increased by 53.6% in comparison to the 450°C sample. In the 650°C sample, part of the liquid aluminum is generated, the fluidity of the aluminum matrix is greatly increased, which results in the microstructure segregation and grain coarse. The hardness (97.6HV₁), thereafter, is been lowered down.

4. Conclusion

The 20 vol% B₄Cp/Al composite was fabricated by microwave sintering after high-energy ball milling and cold isostatic pressing. The sintering time (30 min, 45 min, 60 min, and 75 min) and sintering temperature (450°C, 520°C, 580°C and 650°C) were the main parameters to influence the microstructure and properties of composite material. The results show that:

1. On the optimized condition of 580°C sintering temperature and 45 min sintering time, the residual pores are few. The B₄C particles distribute uniformly in the matrix and the B₄C/Al interface is clean with little transient Al₃BC(α) phase and with tough metallurgical combination. The properties reach the utmost among all the samples. The nanoindentation test results show that the interface hardness and elastic modulus are 8.494 GPa and 142.537 GPa respectively. The compactness is 93.2% and hardness is 112.5 HV.

2. On the condition of apparent temperature gradient in unoptimized samples, certain amounts of Al₃BC(α) phase will generate at the local interface. As a second phase, it strengthens the composite material, but when the amount of Al₃BC(α) phase is large, it will reduce the cleanliness and bonding strength of the B₄C/Al interface.
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