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Technical note

A ternary compound additive for vacuum densification of β-silicon carbide at low temperature

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Abstract

The thermal decomposition behavior of a ternary carbide compound (Al_4SiC_4) was investigated under vacuum conditions. Decomposition of Al_4SiC_4 occurred above 1450 °C, resulting in the formation of SiC and carbon phases in the matrix, with some losses of Al. To simultaneously obtain the densification and refinement of SiC, the potential of the compound as a sintering additive for low-temperature sintering of SiC was evaluated and compared to cases of SiC with Al_4C_3 and Al_2O_3 additives. SiC that was almost entirely densified with fine and elongated grains was successfully formed using a 10 wt% Al_4SiC_4 additive by hot pressing at 1700 °C for 2 h in a vacuum. During the densification, the decomposition behavior of the Al_4SiC_4 was strongly related to the densification behavior of the SiC.

Keywords: Carbides; SiC; Powders-solid state reaction; Sintering; Al_4SiC_4

1. Introduction

The high covalency of Si–C bonds and the low self-diffusion coefficient of SiC make it difficult to sinter pure SiC to high densities. For example, without any additives, the theoretical density could only be achieved at 2500 °C by hot pressing under a pressure of 50 MPa.[1] Various oxide additives such as Al_2O_3,[2] Al_2O_3–Y_2O_3 (YAG),[3,4] and Al_2O_3–Y_2O_3–CaO[5] have been utilized in an attempt to decrease the sintering temperature of SiC. When these additives are added, the consolidation steps take place through liquid phase sintering, accompanied by the formation of an interphase at the grain boundaries.[6] However, the interphase shows lower corrosion resistance than SiC.[6]

To obtain a high density and to minimize the degradation of corrosion resistance, consolidation of SiC has been achieved with non-oxide sintering aids, such as B–C[6,7] and Al–B–C[8,9] systems. Boron has been shown to be a very efficient additive for low-temperature sintering of SiC, but liquid phases such as borosilicate glass[6] or melts of $Al_8B_4C_7$[9] were reported to form during heating, which may decrease corrosion resistance of the sintered SiC. The fabrication of a fully dense SiC with a non-oxide additive in the absence of boron is very difficult at temperature as low as 1700 °C. Al and Al_4C_3 have been shown to be effective sintering aids for SiC, thus SiC to which Al has been added can be sintered without pressure to high densities (>95% theoretical density) at temperature ≥1850 °C.[9] Recently, a ternary compound (Al_4SiC_4) has received widespread attention because of its combination of unique properties, including a low crystal density (3.03 g/cm^3) and a high melting temperature (>2080 °C).[10,11] In addition, this ternary compound shows outstanding oxidation and corrosion resistance due to the formation of dual oxide layers, with the formation of mullite at the inner layer and alumina at the outer layer.[10,11]

The objective of this work is to investigate the thermal decomposition behavior of the ternary carbide compound (Al_4SiC_4) in a vacuum condition and to evaluate the potential of the compound as a sintering additive for SiC densification at low temperature compared to SiC coupled with binary carbide (Al_4C_3) or aluminum oxide (Al_2O_3) additives in a vacuum condition.

2. Experimental procedure

Commercial aluminum (Al, Kojundo Chemical Lab. Co., Japan), silicon (Si, Kojundo Chemical Lab. Co., Japan), and carbon black (carbon black, MA-600B, Mitsubishi Chem., Tokyo,

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Japan) powders were selected as raw materials to synthesize Al_4SiC_4. The molar ratio of Al, Si, and C was 4:1:4, as required in reaction (1):

$$4Al + Si + 4C \rightarrow Al_4SiC_4 \quad (1)$$

The raw powders were homogeneously mixed with ethyl alcohol for 10 min by an ultrasonifier (GSD-300T, SMT Co., Japan) and dried at 60 °C for 24 h in a vacuum dryer. The powder mixture was placed into a carbon mold and the gap between the mold and the carbon cap was tightly sealed using a BN slurry to minimize vaporization of the metallic gases. Subsequently, the powder was calcined at 1700 °C for 2 h in flowing Ar.

The phase identifications of the as-synthesized powder and the post-treated powders at various temperatures for 30 min in a vacuum of $<7 \times 10^{-3}$ Pa were determined by X-ray diffractometry (XRD, RINT-UltimaIII, Rigaku Co., Japan) using Cu K_α radiation (wavelength of 1.54056 Å). Chemical compositions (Al, Si, and C elements) of all powders were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 3300DV, PerkinElmer, Wellesley, MA) and an infrared absorption method (CS 444-LS, Leco, St. Joseph, MI).

To achieve SiC densification with the Al_4SiC_4 additive, commercially available nanoβ-SiC powders (T-1 grade, Sumitomo Osaka Cement Co., Japan) with a mean particle size of 30 nm containing around 3 wt% free carbon and 0.45 wt% oxygen were mixed with 2 or 10 wt% of the as-synthesized Al_4SiC_4 powder and ethyl alcohol for 24 h using a planetary mill. A SiC ball and jar apparatus was used to minimize contamination during the milling.

To compare the case of SiC with an Al_4SiC_4 additive, mixtures of SiC and 7.82 wt% aluminum carbide (Al_4C_3, Kojundo Chemical Lab. Co., Japan) or 11.08 wt% aluminum oxide (Al_2O_3, Kojundo Chemical Lab. Co., Japan) powders were also prepared using the same method described above. The molar volume of Al in the powder mixtures of SiC–7.82 wt% Al_4C_3 and SiC–11.08 wt% Al_2O_3 systems was identical to that in the mixture of the SiC–10 wt% Al_4SiC_4 system. The slurry was dried at 60 °C for 24 h using a vacuum dryer and then sieved through a 150 μm mesh.

The powder mixtures were hot-pressed at 1700 °C for 2 h under a pressure of 60 MPa in vacuum. In all of the cases, the consolidated samples were cooled down to room temperature by turning off the power. During sintering, the change of the dimension along the press direction was recorded to monitor the densification behavior of the powder mixture. The relative densities of the samples were calculated by Archimedes' method based on theoretical densities determined using the rule of mixture. The sintered samples were polished and plasma-etched in a mixture of CF_4 and 8% O_2. The microstructure of the samples was observed by scanning electron microscopy (SEM, JSM-6700F, JEOL Ltd., Japan).

3. Results and discussion

Fig. 1 shows XRD patterns of Al_4SiC_4 powder synthesized at 1700 °C for 2 h in flowing Ar and powders post-treated at various temperatures for 30 min in vacuum. The phase identification of the as-synthesized powder indicated the presence of X-ray pure single-phase Al_4SiC_4, and the chemical composition of the powder was nearly identical with the stoichiometric value of Al_4SiC_4. Most of the powders remained as Al_4SiC_4, but C and SiC peaks were detected after post-heating above 1450 °C in the vacuum. To investigate the decomposition behavior of Al_4SiC_4 in detail, chemical composition analyses for Al, Si, and C in all of the powders were determined using the ICP-AES and infrared absorption methods, as shown in Fig. 2. The chemical contents of Al, Si, and C in the powders post-treated up to 1350 °C were almost identical to those in the as-synthesized Al_4SiC_4. However, the Al content decreased but C and Si contents increased with an increase of the post-treatment temperature above 1450 °C. The results clearly indicated that the decomposition of Al_4SiC_4 occurred above 1450 °C in the vacuum. The decomposition occurred more intensely with increasing temperature.

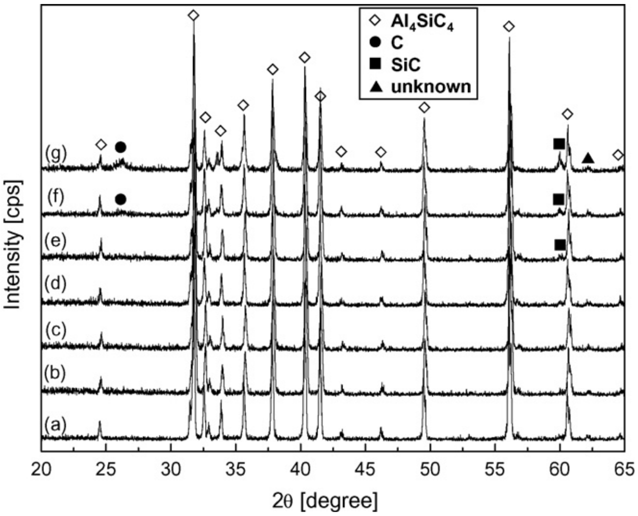

Fig. 1. XRD patterns of (a) Al_4SiC_4 powder synthesized at 1700 °C for 2 h in flowing Ar and powders post-treated at (b) 1150, (c) 1250, (d) 1350, (e) 1450, (f) 1550 and (g) 1650 °C for 30 min in vacuum, respectively.

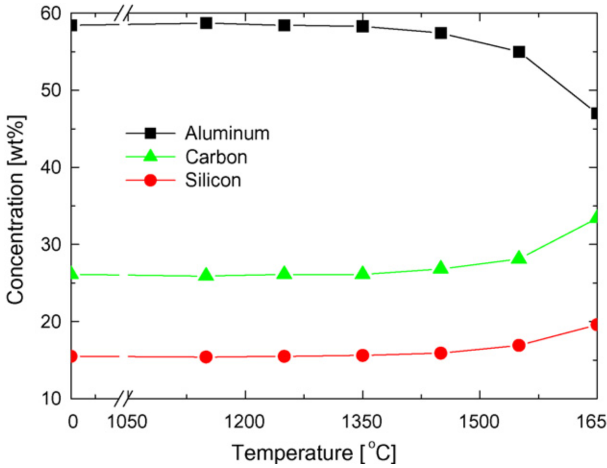

Fig. 2. Evolution of the Al, Si, and C concentration in Al_4SiC_4 powders, post-treated for 30 min in vacuum, as a function of the temperature.

From a crystallographic perspective, Al_4SiC_4 can be described as an Al_4C_3-type crystal with hexagonal 4H-SiC-type structural units alternatively stacked along the *c*-direction.[12] Liao et al.[12] reported that the mechanical properties of Al_4SiC_4 are dominated by the Al_4C_3-type structural units. The strength values of Al_4SiC_4 (tensile strength $\sigma = 20$ GPa, shear strength $\tau = 18$ GPa) are closer to that of Al_4C_3 ($\sigma = 21$ GPa, $\tau = 22$ GPa), but differ significantly from the corresponding values of 4H-SiC ($\sigma = 48$ GPa, $\tau = 38$ GPa).[12] The above discussion indicates that the decomposition of Al_4SiC_4 originates from breaking the bonds of the Al_4C_3-type unit because the Al–C bonds are considerably weaker than the Si–C bonds in Al_4SiC_4; this is clearly supported by the increased carbon and silicon contents seen after the decomposition. Itatani et al.[10] reported that the thermal decomposition of a hot-pressed Al_4SiC_4 compact by reaction (2):

$$Al_4SiC_4 \rightarrow 3Al_{(g)} + SiC_{(s)} + 3C_{(s)}, \tag{2}$$

occurred at 1900 °C in Ar after heating for 1 h, leaving the SiC and carbon phases in the matrix. However, the onset temperature of reaction (2) decreased significantly to 1450 °C in a vacuum.

The decomposition behavior of Al_4SiC_4 at low temperature in a vacuum condition has never been reported. Inoue et al.[13,14] prepared sintered Al_4SiC_4 and composites consisting of SiC and Al_4SiC_4 at 1700 °C in a vacuum using a spark plasma sintering method, but they did not report any decomposition behavior of Al_4SiC_4 up to 1700 °C. Unlike our experiment, they applied the relatively high pressure of 80 MPa to the densification of the mixture during heat-treatment. It is well known that the pressure during heat-treatment significantly inhibits the decomposition of Al_4SiC_4 by restraining the partial pressure of vapour species because the decomposition temperature of aluminum-based compounds was reported to depend on the partial pressure of aluminum vapour.[15] Therefore, the decomposition of Al_4SiC_4 occurred at 1800 °C with the formation of $Al_4Si_2C_5$ and C phases in their experiment because of the vaporization of Al. However, in our study, the Al_4SiC_4 started to decompose at a much lower temperature (1450 °C) than the value reported previously.

Al has been shown to be an effective sintering aid for SiC and free carbon originating from reaction (2) is also useful for removing oxygen impurities and retarding grain growth of the SiC.[7,16] Therefore, Al_4SiC_4 is expected to be useful as a sintering additive for SiC to obtain a dense specimen with a fine microstructure. Fig. 3 shows the shrinkage curves of SiC containing Al_4SiC_4 (10 and 2 wt%), Al_4C_3, and Al_2O_3 additives as a function of temperature. The onset temperature of shrinkage (OTS) of the SiC–10 wt% Al_4SiC_4 system (≈1425 °C) was 125 °C lower than the value of the SiC–Al_4C_3 system (≈1550 °C) because Al_4SiC_4 is weaker than Al_4C_3, which consequently leads to a lower decomposition temperature.[12] Compared to SiC–10 wt% Al_4SiC_4 (Fig. 3(a)) and SiC–Al_4C_3 (Fig. 3(b)) systems, the SiC–2 wt% Al_4SiC_4 (Fig. 3(c)) and SiC–Al_2O_3 (Fig. 3(d)) systems did not show rapid densification behaviors at low temperature and the relative densities of the SiC with the 2 wt% Al_4SiC_4 and Al_2O_3 were 80.89% and 87.18%, respectively. However, the relative densities of SiC with 10 wt% Al_4SiC_4 and 7.82 wt% Al_4C_3 were 99.42% and 96.77%, respectively. This indicates that addition of 2 wt% Al_4SiC_4 and Al_2O_3 additives was not sufficient to achieve high densification of SiC at low temperature, even though there were thermal decomposition of Al_4SiC_4 and formation of a SiO_2–Al_2O_3 liquid (eutectic temperature: 1595 °C).[17] Indeed, the SiO_2 layer on SiC and Al_2O_3 layers on Al_4SiC_4 could be efficiently removed by carbothermal reduction reactions through the incorporation of excess carbon and vacuum. In particular, the SiO_2 volume fraction in the SiC starting powder is relatively low, and the carbothermal reduction reaction for SiO_2 removal starts to proceed at 1300 °C.[18] Moreover, the degassing of by-product gas species from the carbothermal reaction of SiO_2 may even be easy under vacuum because SiC densification does not progress at 1300 °C. This means that liquid phase sintering involving SiO_2–Al_2O_3 eutectic melts is negligible for determining effective mechanism in vacuum densification of SiC, because single Al_2O_3 phase is very stable up to 1700 °C.[19]

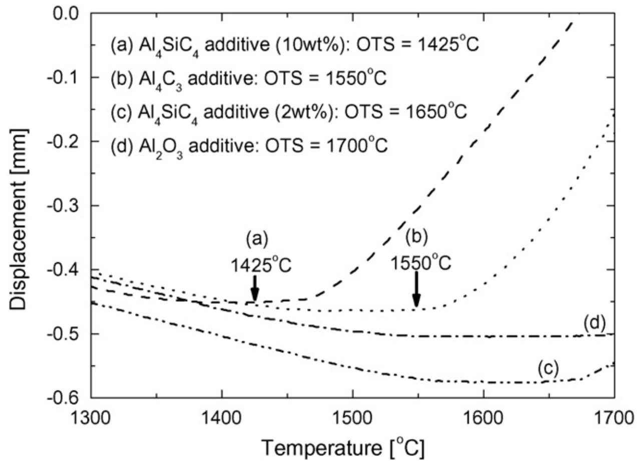

Fig. 3. Sintering curves as a function of temperature under a 60 MPa applied load for (a) 10 wt% Al_4SiC_4, (b) Al_4C_3, (c) 2 wt% Al_4SiC_4, and (d) Al_2O_3 powders used as sintering additives for SiC densification. OTS indicates the onset temperature of shrinkage.

Except for dissolution–reprecipitation of SiC in the melts, the SiC densification with Al_4SiC_4 doping could be achieved through the following mechanism: dissolution of Al in the SiC lattice to form a solid solution and a decrease in the interfacial energy at the grain boundaries of SiC by an activator.[20] In the case of the SiC–10 wt% Al_4SiC_4 system, the onset temperature of shrinkage was nearly identical to the decomposition temperature of Al_4SiC_4. This indicates that the thermal decomposition of Al_4SiC_4 induced the initiation of SiC consolidation. The Al derived from the decomposition appeared to act as an activator of SiC densification at a low temperature. Zhou et al.[9,21] reported that most of the Al activators resided at the grain boundaries of the SiC grains with strong interfacial strength, while a very small amount of Al dissolved into the SiC lattice because of its low solubility in SiC (0.5 wt% at 2000 °C).[22] The amount of Al used in this study was much higher than the value reported by Zhou et al., which implied that a large amount of Al may segregate at the grain boundary. Consolidation of SiC was also

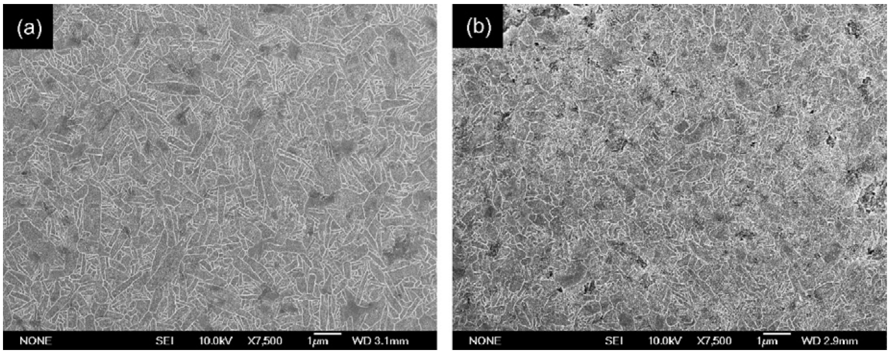

Fig. 4. SEM images of the SiC bodies sintered with (a) Al_4SiC_4 and (b) Al_4C_3 additives at 1700 °C for 2 h under a pressure of 60 MPa at a heating rate of 50 °C min^{-1}.

carried out using a 2 wt% Al_4SiC_4 additive. The additive content (Al content: 1.17 wt%) was designed to be much higher than the solubility limit of Al in SiC so that lattice diffusion by dissolution of the Al into the SiC could be fully activated. However, the densification of the system was clearly suppressed compared to the system containing 10 wt% Al_4SiC_4. This indicates that the main effect of Al heavy doping on SiC densification at low temperature seems to be enhancement of grain boundary diffusion by Al segregation at the grain boundary, because the solubility of Al in SiC is hardly altered. Therefore, the decisive mechanism for high densification of SiC could be explained that Al segregated at the grain boundaries modifies the properties of the grain boundaries by enhancing grain boundary diffusion. This explanation is more plausible than the lattice diffusion mechanism which involves the introduction of defects into the structure of SiC in heavily Al_4SiC_4-doped SiC system.[23]

Fig. 4 shows SEM images of the plasma-etched surface of the sintered SiC containing the 10 wt% Al_4SiC_4 or Al_4C_3 additives. Almost fully dense microstructure with fine and elongated grains was obtained after sintering at 1700 °C when using the Al_4SiC_4 additive; however, the specimens containing the Al_4C_3 additives contained some pores. The lower sintering onset temperature with the Al_4SiC_4 made a greater degree of densification possible,[20] because the Al content was constant in both samples. The very small amount of Al which formed during the decomposition of the ternary compound most likely induced the elongation of the SiC grains by dissolution into SiC grains.[7,22] Such a elongated microstructure can improve fracture toughness attributed to crack bridging and crack deflection.[24]

4. Conclusions

The decomposition of Al_4SiC_4 occurred above 1450 °C under vacuum conditions and originated from the breaking of bonds inside the Al_4C_3-type unit in the Al_4SiC_4 structure, which was clearly supported by the increased carbon and silicon contents seen after the decomposition. The potential of the compound as a sintering additive for low-temperature sintering of SiC was evaluated under vacuum. Highly dense SiC with fine and elongated grains could be obtained at 1700 °C using the 10 wt% Al_4SiC_4 additive. SiC densification at low temperature may result from modification of the properties of the grain boundaries by the Al activator resulting in enhanced grain boundary diffusion. We conclude that Al_4SiC_4 is a very effective sintering additive for concurrently obtaining SiC densification and refinement at low temperature. The resulting SiC is expected to show high corrosion resistance at high temperature due to minimization of the liquid phase.

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