

Increased high temperature strength and oxidation resistance of Al_4SiC_4 ceramics

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Abstract

Al_4SiC_4 bulk ceramics were synthesized by reaction hot-pressing using Al, graphite powders and polycarbosilane (PCS) as starting materials. The present work confirmed that this process was an effective method for the preparation of Al_4SiC_4 ceramics having high relative density and well-developed plate-like grains. The mechanical, thermal properties and oxidation behaviors of the Al_4SiC_4 ceramics were also investigated. The flexural strength, fracture toughness (K_{IC}) and Vickers hardness at room temperature were 297.1 ± 22 MPa, 3.98 ± 0.05 MPa $\text{m}^{1/2}$, 10.6 ± 1.8 GPa, respectively. The high-temperature bending strength showed an increasing trend with increasing test temperatures, with the value of 449.7 ± 26 MPa at 1300°C . The thermal expansion coefficient was $6.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the temperature range from 200°C to 1450°C . The isothermal oxidation of Al_4SiC_4 ceramics at 1200 – 1600°C for 10–20 h revealed that it had excellent oxidation resistance. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Al_4SiC_4 is a ternary carbide with a low crystal density (3.03 g/cm^3), a higher melt point ($>2700^\circ\text{C}$), and outstanding oxidation resistance.^{1–4} Recently, Al_4SiC_4 powders were prepared by Yamamoto with aluminum, silicon and carbon black as raw materials.⁴ Inoue et al.³ synthesized bulk Al_4SiC_4 from the mixture of aluminum, silicon, and carbon and the mixture of Kaolin, aluminum and carbon as raw materials by a two-step method, namely synthesis of Al_4SiC_4 powders, followed by the pulse electronic current sintering. They investigated some of the thermal properties and the electrical conductivities of this material.^{5–6} However, most properties of this material, such as mechanical properties at room temperature and high temperatures and detailed oxidation behaviors, have not been well characterized.

In the present work, we developed a novel route to obtain bulk Al_4SiC_4 ceramics and investigated the mechanical and thermal properties of such material prepared with aluminum,

natural graphite and polycarbosilane (PCS) as raw materials. The purpose of using PCS is that the SiC powder coming from pyrolysis of PCS has very high activity which can promote the formation of Al_4SiC_4 and its densification. Moreover, reaction hot-pressing technique was used to integrate the synthesis of the Al_4SiC_4 and its densification into one event. As far as we are aware, the reports of the microstructure analysis and the room temperature and the high temperature mechanical properties of this material have not been observed in any other paper. The application prospects for Al_4SiC_4 ceramic are also discussed at the end of this paper.

2. Processing

Bulk polycrystalline Al_4SiC_4 ceramic specimens with final dimension of $\phi 55 \times 5 \text{ mm}^3$ were fabricated by means of a reaction hot-pressing method based on the overall reaction equation:



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Commercially available natural graphite powders with an average particle size of 50 μm , aluminum powders with an average particle size of 10 μm and polycarbosilane (PCS, which purity is above 98%) with an average molecular weight of about 2000 were used as the starting materials, where PCS was used to pyrolyse into SiC in the high temperature treatment. The molar ratio of Al, C, SiC converted from PCS was 4:3:1 as required by the Eq. (1). In the process, the Al, graphite mixed powders and PCS solution (solved in the tetrahydrofuran (THF) solvent) were firstly homogenized on a magnetic stirring apparatus for 20 min. The resulting slurry was gently heated to remove the solvent. Then the mixture was calcined at 1100 $^{\circ}\text{C}$ for 30 min in a tube furnace under flowing argon to realize the pyrolysis of PCS into SiC. The baked body was crashed and milled into powders that were placed in a graphite die with an inner diameter of 55 mm for hot-pressing. The hot-pressing was conducted under flowing argon atmosphere in a graphite heating furnace at the temperature of 1800–1900 $^{\circ}\text{C}$. The furnace was firstly heated to 1800 $^{\circ}\text{C}$ at the rate of 30 $^{\circ}\text{C min}^{-1}$, and held for 2 h under a pressure of 25 MPa to realize the reactions, and then was increased to 1900 $^{\circ}\text{C}$, holding for 1 h for densification. The density of the Al_4SiC_4 bulk ceramic determined by Archimedes' method was 2.89 g/cm^3 , which was 95.4% of theoretical value which comes from the XRD unit cell.

3. XRD analysis

XRD was used to identify the reaction products. Fig. 1 shows the X-ray diffraction patterns of the calcined powders (Fig. 1a) and the sintered specimen (Fig. 1b). For the products of calcinations, the major products are Al_4C_3 and SiC, so the main reactions can be summarized by the following equations:

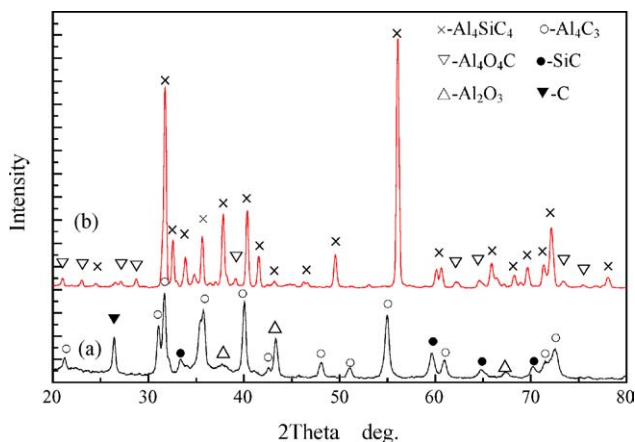


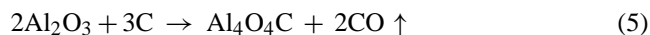
Fig. 1. XRD patterns of the calcined powders and sintered Al_4SiC_4 ceramic: (a) the calcined powders and (b) the sintered Al_4SiC_4 ceramic.

The reaction temperature between aluminum and carbon was about at the melting point of the aluminum, as reported by Kennedy.⁷ If the reactions were complete, the phases detected by XRD would be only Al_4C_3 and SiC. However, XRD analysis indicated the presence of other phase: C and Al_2O_3 . Al_2O_3 was the product of reaction between Al and oxygen, where oxygen came from both the oxide film on the aluminum and the oxygen impurity of the PCS.⁸ Because a small part of Al was consumed to react with oxygen, excessive graphite was left in the pre-pyrolysis products.

Al_4SiC_4 was formed in the sintered ceramic (Fig. 1b), which was thought to be the reaction product of Al_4C_3 and SiC:



The standard Gibbs energy for Eq. (4) changes from positive to negative at 1106 $^{\circ}\text{C}$. Consequently, Al_4SiC_4 ceramic would form at a temperature above 1106 $^{\circ}\text{C}$.³ Moreover, beside Al_4SiC_4 as a main phase, a second phase $\text{Al}_4\text{O}_4\text{C}$ (The assessment of quantity of the $\text{Al}_4\text{O}_4\text{C}$ phase was calculated to be 3–5 wt.% on the basis of XRD peak intensity) was also detected in the sintered materials (Fig. 1b). In Inoue's work,³ $\text{Al}_4\text{O}_4\text{C}$ was also found, and was attributed to reduction of Al_2O_3 by carbon, as shown in Eq. (5).



Based on thermodynamic data,⁹ the Eq. (6) could proceed toward the right. Related reactions were likely to be the following:



The content of $\text{Al}_4\text{O}_4\text{C}$ would decrease when the temperature is above 1600 $^{\circ}\text{C}$ with the removal of CO gas at this temperature, as follows:⁹



However, in our experiment, compared the composition phases of the specimens prepared at different sintering temperature, the decomposed temperature of $\text{Al}_4\text{O}_4\text{C}$ is above 1700 $^{\circ}\text{C}$, corresponding discussion will be made in other paper.

4. Microstructural observation

Fig. 2a and b show the SEM micrographs of the polished and the thermal etching surface parallel to the pressing axis of the hot pressed Al_4SiC_4 ceramic. The sintered product achieved about 95.4% relative density. The typical plate-like grains can be seen from Fig. 2b (parallel to the hot-pressing axis). Fig. 2c is the fractured surface of Al_4SiC_4 ceramic, which shows a rough and flaky surface morphology, indicating that the Al_4SiC_4 ceramic has a mixture mode of intergranular and transgranular fracture.

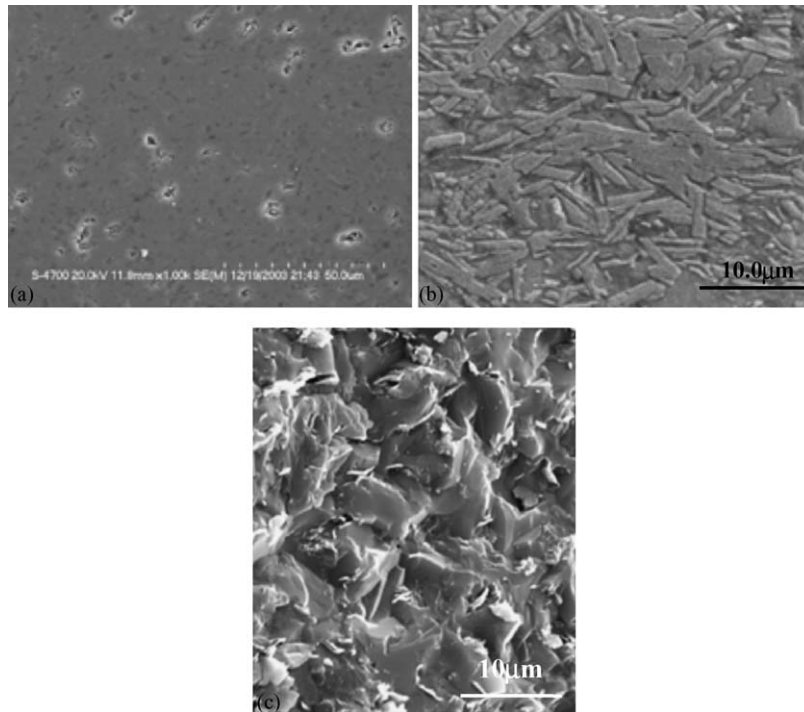


Fig. 2. SEM micrograph observations Al_4SiC_4 ceramics: (a) the polished surface, (b) the heat eroded surface and (c) the fractured surface.

Fig. 3a and b show the further microstructure analysis by TEM observation on the Al_4SiC_4 grains. One of the most obvious microstructure characteristics is that the Al_4SiC_4 grain has different morphologies on the planes perpendicular and parallel to the hot-pressing axis, from which a plate-like morphology with straight edges of the Al_4SiC_4 grain was obvious. The formation of plate-like morphology can be attributed to its hexagonal crystal structure.¹⁰ The thicknesses of the Al_4SiC_4 grains range from 200 nm to 1 μm (Fig. 3b) and the length of these grains are 2 μm ~5 μm (Fig. 3a). Defects like stacking faults were observed by TEM in the Al_4SiC_4 grains. The crystal forming of the

Al_4SiC_4 was thought to stack by the three hexagonal layers, Al_2C_2 , SiC and Al_2C , alternately along the $[0001]$ direction forming hexagonal close packing,¹ which implied that the stacking fault would exist between the layers with the growth of the Al_4SiC_4 grains.¹¹ Fig. 3c is the selected area electron diffraction, which indicates that the stacking faults are parallel to the basal plane $\{0001\}$. It is worth to make out that Fig. 3b is a selected photo to show the morphology of the Al_4SiC_4 grain, the stacking faults in the Al_4SiC_4 grain and the graphite phase. In fact, there is only a small amount of graphite phase in the final specimen.

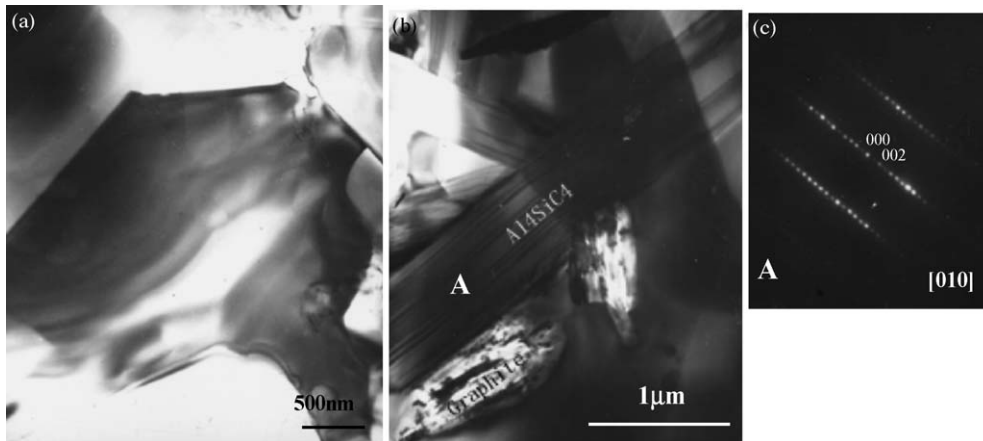


Fig. 3. TEM micrograph observation Al_4SiC_4 ceramics: (a) perpendicular to the hot-pressing axis, (b) parallel to the hot-pressing axis (c) corresponding SAED pattern.

5. Mechanical properties

The specimens perpendicular to the hot-pressing axis were cut to various sizes for mechanical property tests. The room temperature and elevated temperature flexural strength tests in air atmosphere were conducted by three point bending method using an Instron instrument with rectangular bars of 3 mm × 4 mm × 36 mm (30 mm outer span), and a crosshead speed of 0.5 mm/min in air. The single-edge-notched-beam (SENB) method was used for the fracture toughness measurement on notched specimens of 2 mm × 4 mm × 20 mm, with a crosshead speed of 0.05 mm/min. The Vickers hardness was finished at the load of 5 kg on the polished surface. The properties values are listed in Table 1, where each data point presents an average of five to six measured values.

The room temperature flexure strength of Al₄SiC₄ ceramic is 300 MPa. This value is not very high compared with Ti₃SiC₂ and Ti₃AlC₂ (shown in Table 2); the reasonable explanation is that the grain is much more anisotropic (Fig. 3). So there must exist a high level of interfacial stresses between grains when cooling from sintering because of the difference between thermal expansions coefficients in different directions. The fracture toughness of this material is 3.98 MPa m^{1/2}. From the fracture surface (Fig. 2c) we can see the fracture mode displayed mixed inter- and intra-granular behavior. Fig. 4 shows the crack propagation path following hardness indentation. The transgranular fracture was the main fracture mode. Slight crack deflection can also be seen.

Table 1
Properties of Al₄SiC₄ ceramic

Al ₄ SiC ₄	Values
Density (g/cm ³)	2.97
Relative density (%)	95.4
Flexure strength (MPa)	R.T. 297.1 ± 22.4 1000 °C 385.4 ± 35.2 1200 °C 388.3 ± 39.8 1300 °C 449.7 ± 26.4
Fracture toughness (<i>K</i> _{IC}) (MPa m ^{1/2})	3.98 ± 0.05
Vickers hardness (GPa)	10.6 ± 1.8
Thermal expansion (× 10 ⁻⁶ °C ⁻¹) (200–1450 °C)	6.2 ± 0.3

Table 2
Comparison of properties of ternary carbides

	Al ₄ SiC ₄	Ti ₃ SiC ₂	Ti ₃ AlC ₂
Theoretical density (g/cm ³)	3.038	4.53	4.21
Relative density (%)	95.4–97 ³	99 ¹⁸	99 ¹⁶
Mechanical properties			
Bending strength (MPa)	297.5	260–600 ^{18,19}	375 ¹⁶
Fracture toughness (<i>K</i> _{IC})	3.98	8.5 ¹⁹	7.2 ²⁰
Vickers hardness (GPa)	10.6	4 ¹⁸	3.5 ¹⁶
Thermal expansion coefficient (× 10 ⁻⁶ °C ⁻¹)	6.2	10 ¹⁸	9.2 ¹⁶

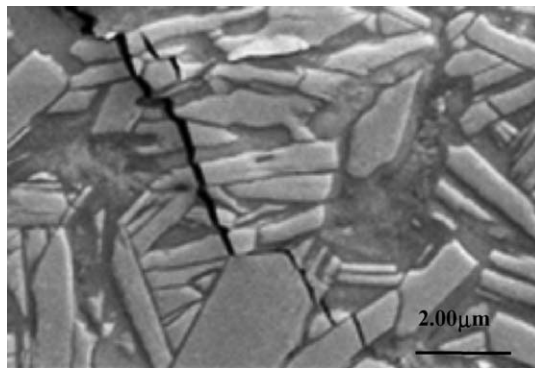


Fig. 4. The hardness indentation of Al₄SiC₄ ceramic.

The Vickers hardness of the Al₄SiC₄ bulk ceramic was measured to be 10.6 ± 1.8 GPa, which is much higher than these of Ti₃SiC₂ and others (shown in Table 2). The lower hardness of Ti₃SiC₂ is attributed to the planar Si layers linked together by TiC octahedral, forming a highly deformable basal slip plane.¹² However, in the crystal structure of Al₄SiC₄, such a weak connective layer may not exist.¹

Fig. 5 shows the elevated temperature bending strengths of Al₄SiC₄ bulk ceramic from R.T. to 1300 °C in air. It is interesting to note that the strength is increasing with increasing test temperatures. The bending strength at 1300 °C was 450 MPa, which was about 1.5 times that at room temperature (300 MPa). Such increased strength is thought to be mainly related with the release of the residual thermal stress as mentioned above, with the same mechanism as occurs in graphite materials.¹³ Another factor should be considered, that is the formation of oxides on the surface of the specimens. As we detected, the surface of the high temperature tested Al₄SiC₄ was covered with a layer of aluminosilicate glass, the detailed results will appear in other papers. Obviously any micro-cracks on the surface of the specimens, a main source of fracture, would be healed by viscous flow of

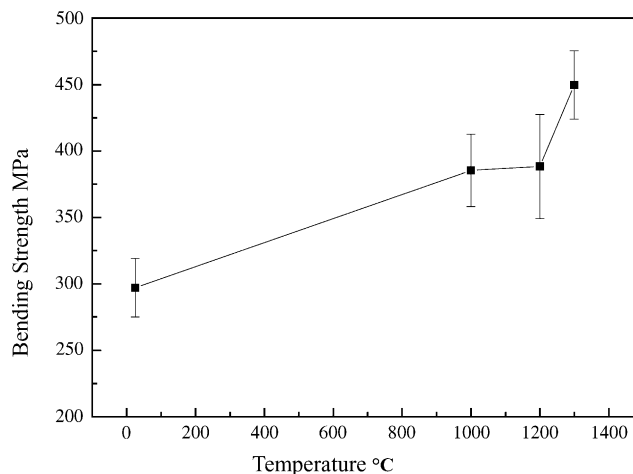


Fig. 5. The bending strength with the room temperature and the high elevated temperature in air.

the glass at the test temperature. This is a new mechanism that is not present in graphite, resulting in a large level of increment of elevated temperature strength. The phenomenon that strength increased with increasing temperature was also found in SiC, by Keppeler et al.¹⁴, where the reason was attributed to a softening and a subsequent stress relief through viscous flow of the grain boundary phase throughout the specimens. This is not according with the present case, because there was not glass phase in the grain boundary, which was verified using the electron diffraction technology in the TEM observation. Surely, the HRTEM would be used to investigate the grains- boundary phase in the next work.

6. Thermal expansion coefficient

The thermal expansion coefficient of Al_4SiC_4 bulk ceramic was measured from 200 °C to 1450 °C with a specimen size of 5 mm × 5 mm × 55 mm, and a temperature rate of 10 °C/min. The expansion direction was parallel to the hot press plane of the specimen. To avoid oxidation, the sample was covered with a layer of graphite powders and the whole run process was carried out under Ar.

In the temperature range of 200–1450 °C, the average thermal expansion coefficient of Al_4SiC_4 bulk ceramic was measured to be $(6.2 \pm 0.3) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. This value is lower than that of other ternary carbides, for example, Ti_3SiC_2 ($9.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$),¹⁵ Ti_3AlC_2 ($(9.0 \pm 0.2) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$).¹⁶

7. Oxidation behavior

The isothermal oxidation tests were carried out in a high temperature furnace in the temperature range 1000–1600 °C for 10–20 h. The specimens were cut to the size of 10 mm × 4 mm × 3 mm and were suspended with a Pt wire into the furnace assembled with an electronic balance when the temperature reached to the required temperatures. The

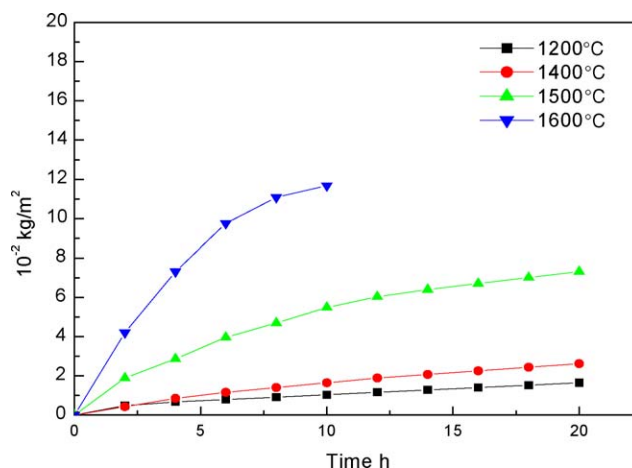


Fig. 6. Weight change of Al_4SiC_4 ceramics as a function of oxidation time.

mass of the specimen was recorded at time intervals of 30 min. The accuracy of thermobalance was ± 0.1 mg. XRD, SEM and EDS were used to examine the microstructure of the oxidized samples.

For high-temperature material application, one of the most important properties of the materials is its oxidation resistance. Therefore, it is necessary and important to study the oxidation behavior of this material at elevated temperatures. Fig. 6 shows the oxidation kinetics curves of the Al_4SiC_4 ceramic. The weight change was less than $7.31 \times 10^{-2} \text{ kg/m}^2$ when oxidized for 20 h at 1200–1500 °C. Even at the oxidation temperature as high as 1600 °C, the final gain change after oxidation for 10 h is only $12.38 \times 10^{-2} \text{ kg/m}^2$, indicating that Al_4SiC_4 has an excellent oxidation resistance. As comparison, the weight changes of Al_4SiC_4 ceramics were far less than those of Ti_3SiC_2 ,¹⁷ indicating that Al_4SiC_4 ceramic has an excellent oxidation resistance. The oxidation kinetics of Al_4SiC_4 was fitted a parabolic rate law with the calculated activation energy of $220 \pm 20 \text{ kJ mol}^{-1}$ for the oxidation process from 1200 °C to 1600 °C.

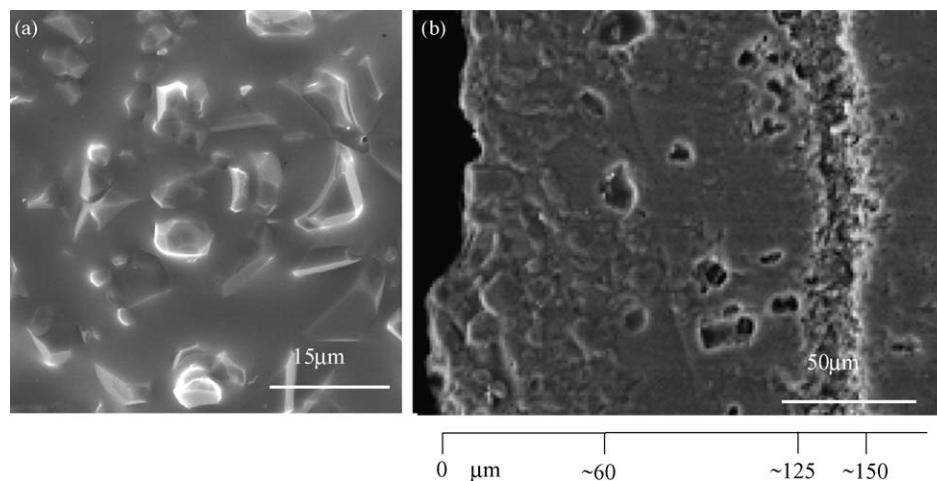


Fig. 7. The typical surface and cross-sectional observations of the oxidized samples at 1600 °C for 10 h: (a) the oxide surface and (b) the cross-sectional scale.

XRD and SEM analysis of phase compositions of the oxide surface and the oxide morphologies revealed that: (1) for the specimens oxidized at 1200 °C and 1400 °C for 20 h, the scales of the sample oxidized consisted of Al_4SiC_4 , Al_2O_3 and aluminosilicate glass, indicating that a very thin layer of Al_4SiC_4 ceramic was oxidized at these test temperatures; (2) when the specimens was oxidized at 1500 °C, only Al_2O_3 and aluminosilicate glass remained on the oxide surface; (3) for the specimens oxidized at 1600 °C and above, in addition to Al_2O_3 and aluminosilicate glass, a new phase of mullite occurred (shown in Fig. 7a). Fig. 7b shows the typical cross-sectional morphologies of the Al_4SiC_4 ceramic oxidized at 1600 °C for 10 h. A three-layer scale was clearly identified: a reaction layer near to the substrate with a large quantity of small size pores; a middle layer with a few large-sized pores and an outer layer with a rather high relative density. The detailed characteristics of the oxidation scale and the mechanism of the oxidation of the Al_4SiC_4 ceramic will be discussed in other papers.

8. Summary and technological importance

In this work, dense Al_4SiC_4 ceramic was prepared through a reaction hot-pressing route; moreover the microstructure and properties were characterized. An excellent oxidation resistance and an increased high-temperature strength have been found. These merits together with its high melting point, high chemical stability and its low density, low thermal expansion coefficient render Al_4SiC_4 ceramic a likely candidate for a high-temperature structural material and for a high-performance refractory material.

Surely, Al_4SiC_4 is a relatively new material. The improving of the mechanical properties and its potential application has yet to be realized. For example, we noted that the relative density of the Al_4SiC_4 ceramic was not very high, resulting in a value of the R.T. mechanical property which was far from optimized (for clear comparison of the properties of Al_4SiC_4 with other ternary carbides, we summarized the properties of some carbides and listed them in Table 2). Therefore, once the formation mechanisms are better understood, it is not unreasonable to expect enhancements in the mechanical properties and others properties.

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