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Ceramics International 33 (2007) 453–458

CERAMICS INTERNATIONAL

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Mechanical properties of Al_4SiC_4 bulk ceramics produced by solid state reaction

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Received 1 April 2005; received in revised form 31 August 2005; accepted 31 October 2005
Available online 19 January 2006

Abstract

The mechanical properties at ambient and high temperature of Al_4SiC_4 bulk ceramics prepared by solid state reaction were investigated. By increasing the sintering temperature slightly, the room temperature bending strength increased up to 318 MPa, whereas, the fracture toughness decreased with the increase of the sintering temperatures. The high temperature bending strengths of the Al_4SiC_4 ceramics exhibited anomalous increases within certain temperature ranges especially at 1300 °C in air with the highest value of 449.7 MPa, i.e. about 1.5 times of that at room temperature (300 MPa). The self-healing behavior of the flaws on the specimen surface due to the oxidation of the surface layer of the Al_4SiC_4 ceramics is considered to be the main strength-enhancing mechanism at high temperatures.

Keywords: C. Mechanical properties; Al_4SiC_4; High temperature mechanical properties; Self-healing properties

1. Introduction

As one of the promising high-temperature ceramics, Al_4SiC_4 has been under active development for demanding high temperature applications, special refractory materials and high-temperature structural materials for its unique combination of the high melting point (~2080 °C), the low density (3.03 g/cm^3), excellent oxidation resistance and corrosion resistance [1–3]. Recently, some studies have been done on the synthesis of Al_4SiC_4 powders and Al_4SiC_4 bulk ceramics [4,5]. The oxidation behavior, physical properties and the electrical conductivities of this material were also studied [6–8]. However, the mechanical properties, especially the high temperature mechanical properties have not been extensively studied so far. Thus, in this study, the mechanical properties of Al_4SiC_4 ceramics have been investigated, particularly the enhanced mechanism of fracture toughness at room temperature and the increased bending strength at high temperature in air.

2. Experimental procedure

The material used in this work is bulk Al_4SiC_4 ceramics which were fabricated by the solid state reaction process according to the following procedure. The molar ratio of Al, graphite and SiC conversed from polycarbosilane (PCS) was 4:3:1 as required by Eq. (1):

$$4Al + 3C + SiC \rightarrow Al_4SiC_4 \quad (1)$$

The pre-mixed powders of Al and graphite were homogeneously dispersed in the PCS solution using a magnetic stirring apparatus for 20 min. The resulting slurry was gently heated to remove the solvent. Subsequently, the mixture was compacted under 10–20 MPa, and calcined in a tube furnace with flowing argon at 1100 °C for 60 min. The baked body was ball-milled into powders which were compacted in a graphite sleeve with BN coated in the inner wall, and hot pressed at different temperatures: 1700 °C for 2 h then at 1800 °C for 1 h ($Al_4SiC_4$1700), at 1800 °C for 2 h then at 1900 °C for 1 h ($Al_4SiC_4$1800) and 1900 °C for 2 h then at 2000 °C for 1 h ($Al_4SiC_4$1900), respectively, with the pressure of 25 MPa and under Ar. The specimens prepared by this process are almost pure and dense.

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0272-8842/$32.00
doi:10.1016/j.ceramint.2005.10.009

Table 1
Mechanical properties of Al_4SiC_4 ceramics at room and high temperatures

Specimen	Relative density (%)	Bending strength (MPa)	Fracture toughness ($MPa\ m^{1/2}$)	High temperature bending strength (MPa)		
				1000 °C	1200 °C	1300 °C
$Al_4SiC_4$1700	91.7	240.3 ± 11.4	4.23 ± 0.02			
$Al_4SiC_4$1800	95.3	297.1 ± 22.4	3.98 ± 0.05	385.4 ± 35.1	388.3 ± 79.1	449.7 ± 25.6
$Al_4SiC_4$1900	97.4	318.8 ± 22.3	3.70 ± 0.09			

The specimens parallel to the hot-pressing axis were cut to various sizes for mechanical tests. The room temperature and high temperature bending strength tests in air atmosphere or in vacuum were conducted by three point bending method using an Instron instrument. Specimens with dimensions of 3 mm × 4 mm × 36 mm (30 mm outer span) were cut by means of a diamond saw. After grinding on all sides, the tensile surfaces were polished to a 1 μm finish and the tensile edges were beveled. The specimens were loaded with a crosshead speed of 0.5 mm/min. The single-edge-notched-beam (SENB) method was used for the fracture toughness measurement at room temperature on notched specimens of 2 mm × 4 mm × 20 mm (16 mm outer span), with a cross-head speed of 0.05 mm/min. The strength and fracture toughness data summarized in Table 1 are the mean values of six specimens. The density was measured by the Archimedes water-immersion technique. The microstructure and the surface of the testing specimens were observed using SEM and TEM, respectively.

3. Results and discussion

3.1. Microstructure

The typical microstructure of Al_4SiC_4 ceramics is shown in Fig. 1. One of the most obvious microstructural characteristics is that the Al_4SiC_4 grains have 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 grains is shown clearly. The formation of plate-like morphology can be attributed to its hexagonal crystal structure testified by its SAED (see Fig. 1(b and d)) [9]. The length of these grains is 2–5 μm (Fig. 1(a)) and the thicknesses of the Al_4SiC_4 grains range about 1 μm (Fig. 1(c)). Defects like stacking faults were observed by TEM in the Al_4SiC_4 grains. Fig. 1(d) indicates that the stacking faults are parallel to the basal plane {0 0 0 1}.

3.2. Mechanical properties of Al_4SiC_4 ceramics at room temperature

The room temperature mechanical properties of this material including bending strength and fracture toughness are summarized in Table 1, and the corresponding curves of bending strength and fracture toughness versus sintering temperatures can be seen in Fig. 2. The bending strengths slightly increase with increasing sintering temperatures, which may be due to its favorable effect of the densification on these ceramics (as shown in Table 1). The room temperature bending strength of Al_4SiC_4 ceramic reached the maximum value of 330 MPa for $Al_4SiC_4$1900. Surely this value is not very high compared with other ceramics; the reasonable explanation is

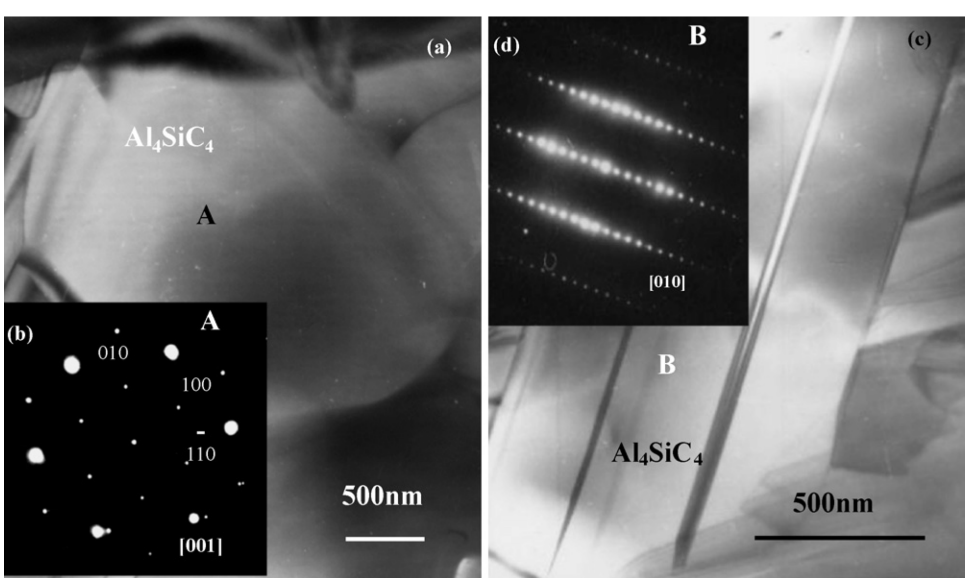

Fig. 1. TEM micrograph observation Al_4SiC_4 1800 ceramics. (a) Perpendicular to the hot-pressing axis, (b) corresponding SAED of area A; (c) parallel to the hot-pressing axis and (d) corresponding SAED of area B.

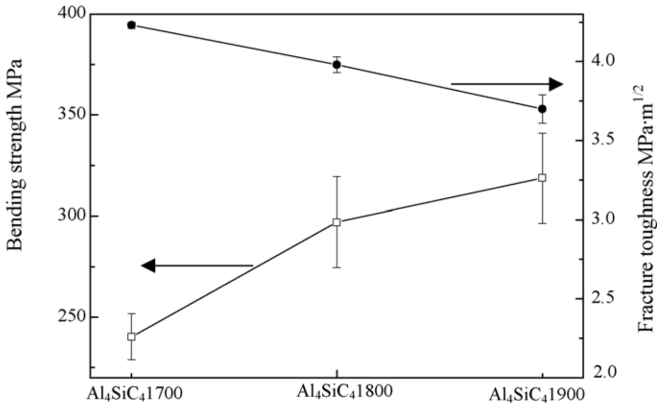

Fig. 2. Bending strengths and fracture toughness of Al_4SiC_4 ceramics sintered at different temperatures.

that the Al_4SiC_4 grains are more anisotropic, as shown in Fig. 1. So there must exist a high level of interfacial stresses between grains due to the difference between thermal expansions coefficients in different directions. With increasing sintering temperatures, however, another remarkable aspect is that the fracture toughnesses of Al_4SiC_4 ceramics continuously decreases. For Al_4SiC_4 bulk ceramics, the toughness of $Al_4SiC_4$1700 is 4.2 MPa $m^{1/2}$ and that of $Al_4SiC_4$1900 is 3.70 MPa $m^{1/2}$. A possible explanation will be discussed as follows.

The typical fracture surface of an Al_4SiC_4 ceramic is shown in Fig. 3, which displays the mixed inter- and intra-granular fracture behavior. Some pull-out of the plate-like grains can also be observed in the $Al_4SiC_4$1700 specimen (labeled with arrows). Moreover, comparing with $Al_4SiC_4$1900, the inter-granular fracture of the $Al_4SiC_4$1700 was often happened resulting from the weak interfacial bonding. Fig. 4(a–c) shows that graphite phases appear in the $Al_4SiC_4$1700 specimen at the interface of Al_4SiC_4 grains. It has a thickness of 0.1–0.5 μm. Some microcracks occur around the graphite (Fig. 4(a)) or at the tip of the graphite (Fig. 4(b)) (labeled with arrows). Graphite phases shaped like a wedge have been observed. The intergranular fracture was often formed along the interfaces between Al_4SiC_4 grains and carbon grains,

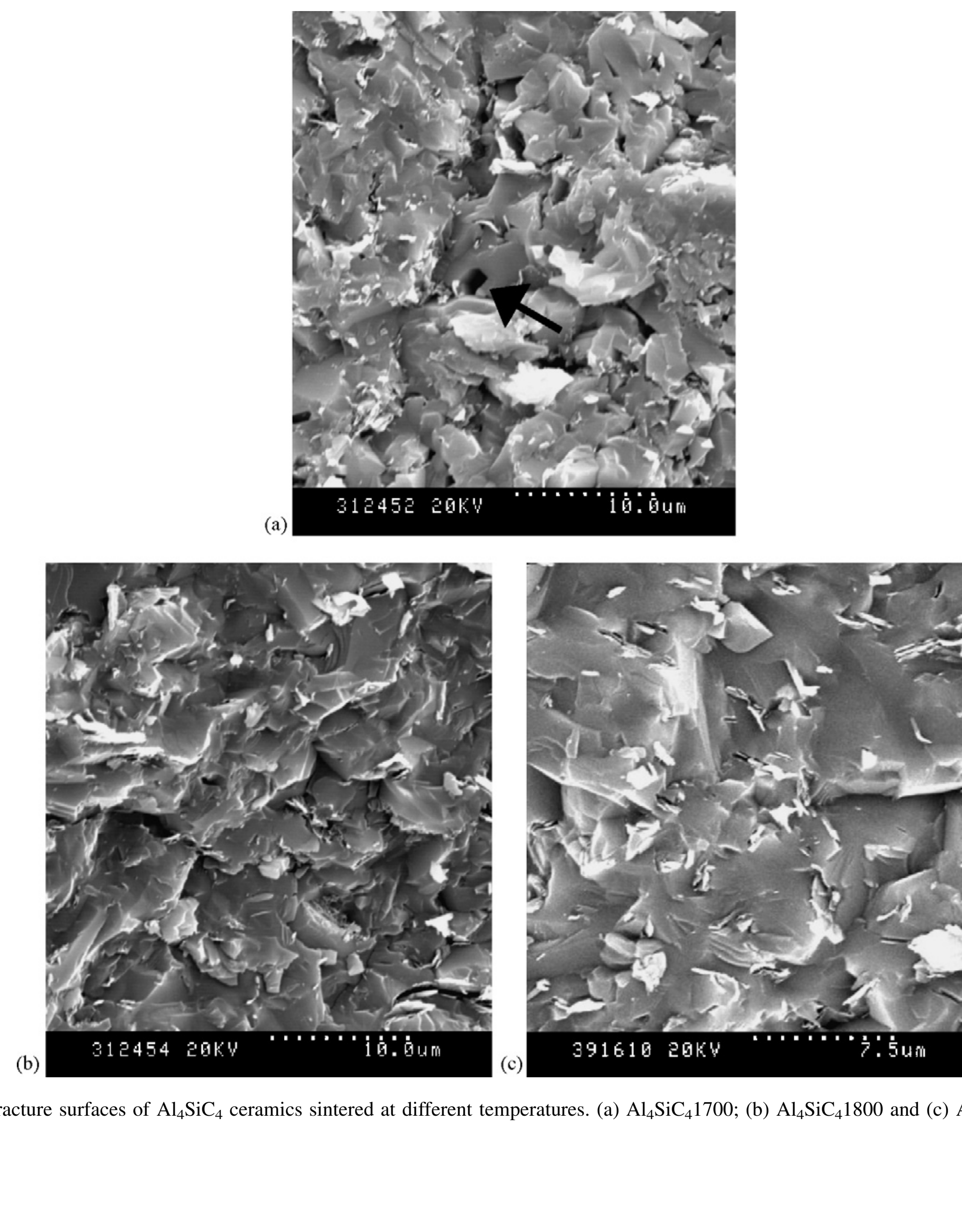

Fig. 3. Fracture surfaces of Al_4SiC_4 ceramics sintered at different temperatures. (a) $Al_4SiC_4$1700; (b) $Al_4SiC_4$1800 and (c) $Al_4SiC_4$1900.

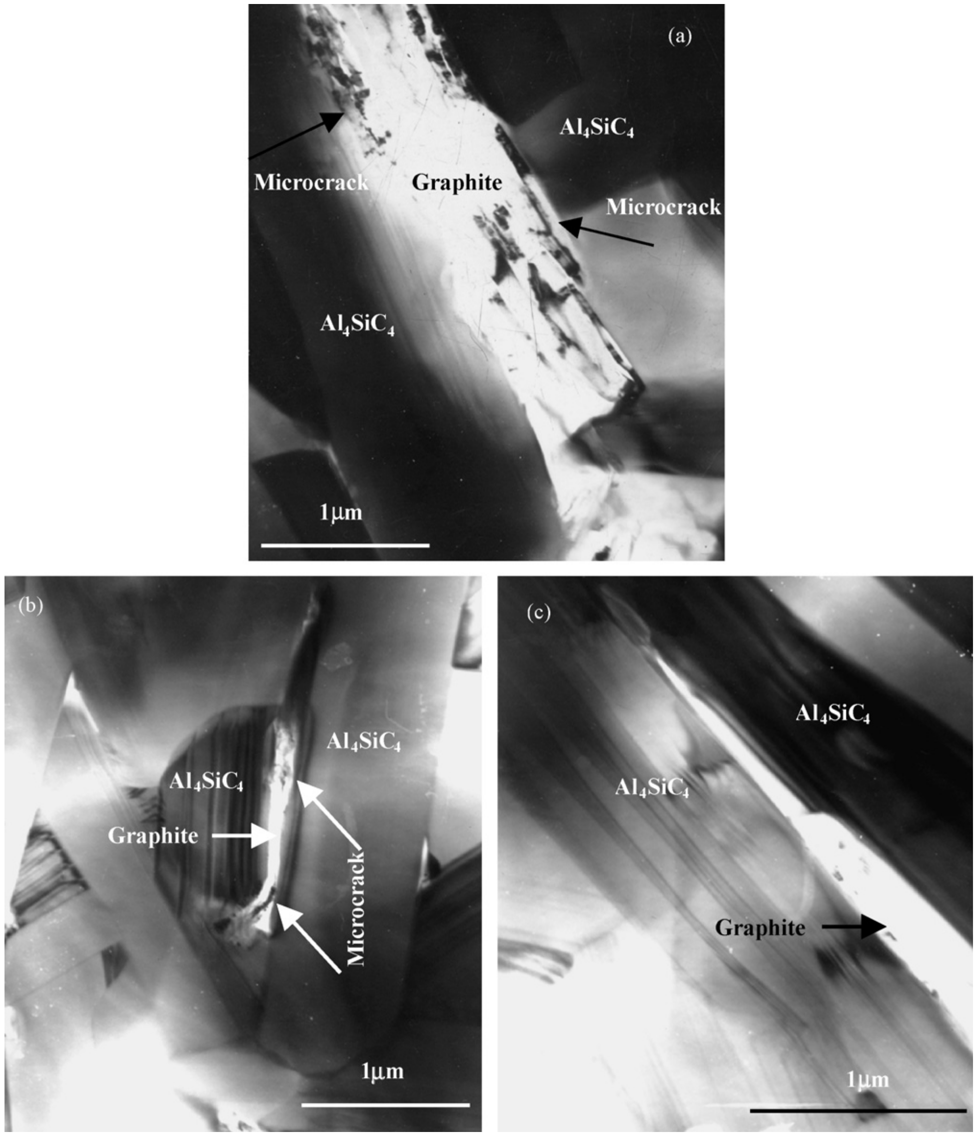

Fig. 4. TEM observations of $Al_4SiC_4$1700 ceramic. (a) Graphite phase with microcracks; (b) graphite phase with microcracks at the tip and (c) graphite phase as the weak interface.

which can be attributed to their weak interfacial bonding. The toughening by weak interfaces has been well documented in a number of materials [10–14] including graphite toughened B_4C/TiC [13] and fibrous ceramic composites [14]. The low cracking resistance of interfaces in these materials was triggered by the layer structure of graphite which, on the application of stress, fractures readily along their basal plane [15,16]. In addition, there existed a large residual stress field related to the mismatch of the thermal expansion coefficients between graphite grains ($2.5 \times 10^{-6}\ K^{-1}$) [17] and Al_4SiC_4 ceramics ($6.2 \times 10^{-6}\ K^{-1}$) [6]. The thermal expansion coefficient of Al_4SiC_4 is much greater than that of graphite, which generates a compressive radial stress on the graphite grains, and a tensile hoop stress to the matrix. It is the interfacial stress that affects cracks, rendering the cracks propagate tortuously along the interfaces, thereby producing toughening effects.

3.3. High temperature bending strength of Al_4SiC_4 ceramics

The increased bending strength of Al_4SiC_4 bulk ceramics from room temperature to 1300 °C in air can be seen in Table 1. For Al_4SiC_4 bulk ceramics, at 1000 °C, the bending strength is 385 MPa, an increase of 30% over that at room temperature (300 MPa). Such strength value was maintained for the most part up to 1200 °C, followed by an anomalous gain in strength at 1300 °C with a very high value of 450 MPa, an increase of 50% over that at room temperature (300 MPa). In the authors' knowledge, it is a novel property that the bending strength of such material remains increasing up to 1300 °C in air.

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 [18]. Another factor be considered is the crack-healing on the surface

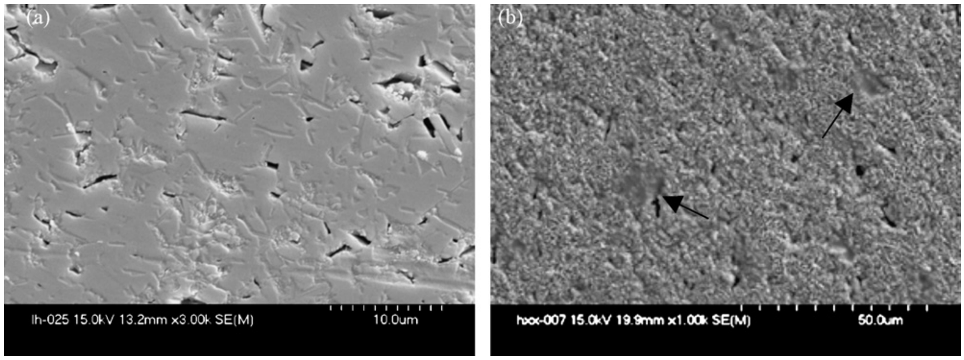

Fig. 5. Surface morphologies of the specimen after the high temperature bending testing. (a) 1000 °C and (b) 1300 °C in air.

of the specimens due to oxidation. Fig. 5(a and b) shows the SEM morphologies of the Al_4SiC_4 specimen surface after bending test at 1000 and 1300 °C, respectively. From this figure we can see that there were a lot of narrow pores or cracks on the surface of the specimen tested at 1000 °C. Whereas, the self-healing of the flaws on the surface of the specimen was visible by the viscous flow of the glass due to oxidation at 1300 °C (labeled with arrows in Fig. 5(b)), which might be a new mechanism that was not present in graphite resulting in a large increase of the high temperature strength.

To verify the above hypothesis that the crack-healing played an important role on the higher temperature strength gain, a test of high temperature bending strength in vacuum was conducted at 1300 °C. Fig. 6(a) shows the results of the bending strength in air and in vacuum, respectively. The bending strength in vacuum (about 270 MPa), is almost the same than that at room temperature. The surface morphologies of Al_4SiC_4 ceramics tested in air and in vacuum (Fig. 6(b and c)) were investigated, respectively. The specimen tested in air at 1300 °C shows a rugous, glassy feature in the surface because of oxidation. X-ray and EDS analysis (not shown here) reveal that the oxidation layer is composed of Al_2O_3 and amorphous oxide, of aluminosilicate glass. Differently, in vacuum condition, a number of large pores were observed in the tested specimen surface (Fig. 6(c)), which decreased the fracture stress more or less. So, it is reasonable to conclude that the enhanced mechanism in bending strength at high temperatures would be attributed to the self-healing behavior of the flaws in the surface

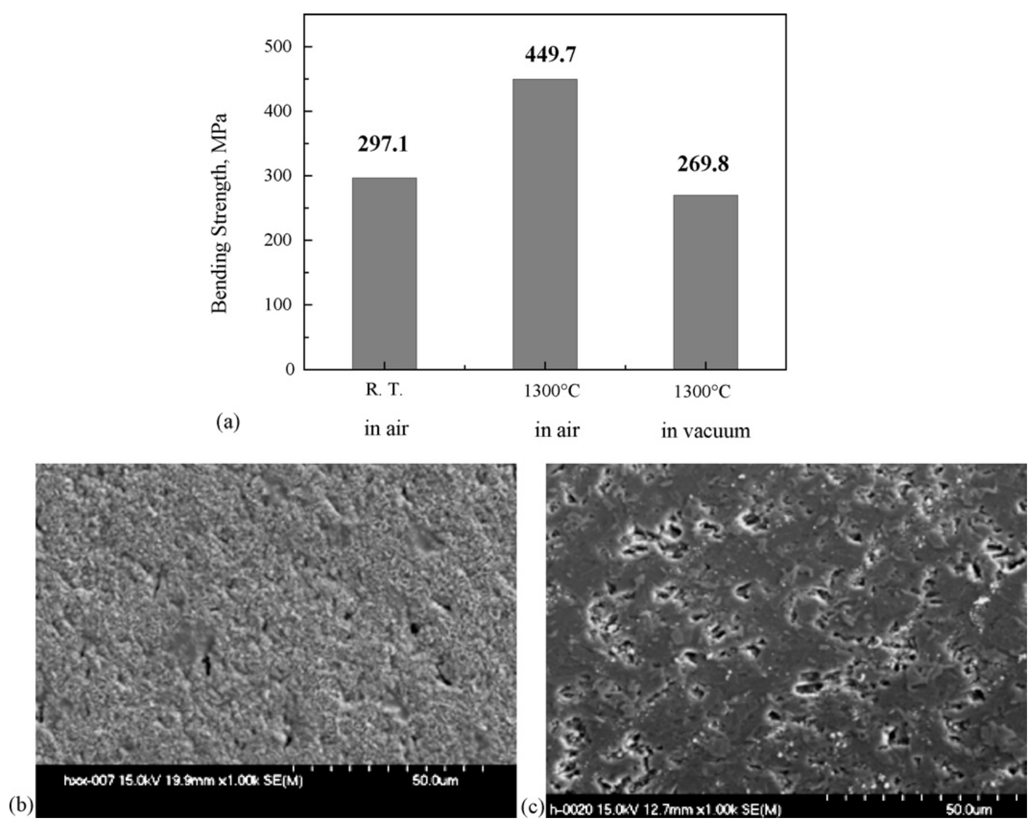

Fig. 6. Bending strengths tested at RT and high temperatures at different testing environments and corresponding surface morphologies observations of Al_4SiC_4 ceramics. (a) Bending strengths, (b) tested at 1300 °C in air and (d) tested at 1300 °C in vacuum.

caused by oxidation similar to Mullite/SiC [19], Al_2O_3/SiC [20] and SiC [21].

4. Conclusions

Microstructure, mechanical properties and the corresponding enhanced mechanism of Al_4SiC_4 ceramics in toughness at room temperature and in bending strength at higher temperatures in air were investigated. The toughening mechanism is caused by the weak interfaces and interfacial strain fields. At high temperatures, the bending strength of Al_4SiC_4 ceramics increases with increasing test temperatures up to 1300 °C. The strength value is 450 MPa at 1300 °C in air, which was about 1.5 times of that at room temperature (300 MPa). The self-healing behavior of the flaws on the specimen surface due to the oxidation of the surface layer of the Al_4SiC_4 ceramics is considered as the main enhancement mechanism at high temperatures.

Acknowledgements

The authors would gratefully acknowledge the help of the ceramics group of Harbin Institute of Technology, and wish to express their appreciation to the teachers, at the Center of Analysis and Measurement, for the help in experiments.

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