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Effect of annealing environment on the crack healing and mechanical properties of $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$

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ABSTRACT

Crack healing of Nb and Al alloyed $MoSi_2$ notched ceramics had been investigated during thermal treatment from 900 to 1500 °C in air, vacuum, argon and nitrogen environments. Notched $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ ceramics showed significant recovery of bending strength after heat treatment in air. Bending strength recovery of 250% was found after heat treatment in air at 1200 °C. Oxide layer formation healed the cracks during annealing in air. Re-sintering was found dominant mechanism of crack healing during annealing in vacuum, argon and nitrogen atmosphere. Bending strength recovery of 208% was found after heat treatment in vacuum at 1200 °C.

1. Introduction

Molybdenum disilicide ($MoSi_2$) has received significant attention for high-temperature structural applications [1–4]. $MoSi_2$ has high melting point (2030 °C), low density (6.24 g cm^{-3}) and excellent high temperature resistance to oxidation [4]. The low fracture toughness at room temperature (2–3 MPa $m^{1/2}$) and poor creep resistance at high temperature (>Brittle–Ductile Transition Temperature) have limited its application in load bearing applications [5,6]. Several approaches have been investigated to improve the fracture toughness at room temperature and creep resistance of $MoSi_2$ at high temperature [7,8]. Most promising routes reported to improve fracture toughness are (I) developing composites and (II) addition of alloying elements [9].

Alloying of $MoSi_2$ has been widely adopted to improve fracture toughness. Alloying of $MoSi_2$ with metals results in formation of metallic–covalent bonds and improves mechanical properties of $MoSi_2$ by promoting the dislocation plasticity at low temperature. Commonly used alloying elements to structural silicides are Nb, V, Cr, Zr, Ta, Re and Al [9–11]. Al addition to $MoSi_2$ has shown significant improvement in oxidation resistance at moderate temperatures [10]. Nb addition improves low temperature deformability and high temperature strength [12]. Nb-alloyed $MoSi_2$ has shown anomalous strengthening behavior with a maximum strength at 1600 °C [13,14]. The co-substitution of Nb and Al in $MoSi_2$ leads to improvement in the oxidation resistance at pest oxidation temperatures, reduction in the hardness and stiffness values and increase in the fracture toughness [11].

Structural ceramics, including $MoSi_2$, are brittle and sensitive to superficial defects such as cracks and pores. The presence of these defects greatly reduces the component reliability. The component reliability can be improved by improving the fracture toughness and/or promoting the defect healing in ceramics. Early researches show that structural ceramics such as SiC [15], Si_3N_4 [16], Al_2O_3 [17], Ti_3AlC_2 [18], UO_2 [19] and $MoSi_2$ [20] exhibit crack healing during carefully devised heat treatment cycle in air. The crack-healing in these structural ceramics is mainly driven by oxidation process at crack surface during heat treatment in air.

Korouš et al. studied the crack healing behavior of pre-cracked SiC ceramics in air from 600 to 1500 °C. They identified formation of SiO_2 in crack healing regions by X-ray diffraction and related it to the observed crack healing phenomenon [21]. Zhang et al. heat treated ZrB_2–SiC composites at 800 °C for 180 min in air. They found that a B_2O_3–SiO_2 glass layer was formed with a 15% increase in strength [22]. Our preliminary work on $MoSi_2$-montmorillonite composite heating elements showed that excellent self-healing occurred with a bending strength recovery from 133 MPa to 345 MPa after heat treatment at 1500 °C for 1 h in air [20].

In contrast to several studies addressing the issue of crack healing in SiC and Si_3N_4 based ceramics and composites, this is the first study reporting the defect and crack healing of $MoSi_2$ based bulk ceramics by oxidation and re-sintering mechanisms at high temperatures. Moreover, we show that contrary to SiC and Si_3N_4 based

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ceramics, $MoSi_2$ ceramics exhibit defect healing properties in non-oxidizing conditions. In order to study the crack healing properties, $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ ceramics were prepared by self-propagation high-temperature synthesis (SHS) and vacuum hot-pressing (HP). The sintered $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ ceramics were pre-cracked by Vickers indentation method and investigated for crack healing in air, vacuum, argon and nitrogen atmospheres from 900 to 1500 °C. Bending strength, crack-healing mechanisms and fracture mode of $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ ceramics are reported.

2. Experimental procedure

Molybdenum (2.0–2.5 μm, 99.9% purity, Zhuzhou cemented carbide group Co. Ltd., China), silicon (−300 mesh, 99.9% purity, WODETAI (Beijing) science and technology development Co. Ltd., China), niobium (−300 mesh, 99.9% purity, Zhuzhou cemented carbide group Co. Ltd., China) and aluminum (100–200 mesh, 99.0% purity, Chinasun Specialty Products Co. Ltd., China) powders with atomic ratio of 0.97:1.94:0.03:0.06 were ball-milled for 240 min at 450 rounds per minute. Absolute ethanol was used as milling media. After milling, the slurry was dried. The powder mixture was cold-pressed into cylindrical compacts of 16 mm diameter and 15 mm height at 200 MPa pressure. The relative density of the compacts was 65% of the theoretical. Combustion synthesis of the compacts was conducted in a steel combustion chamber (in-house manufactured), under pure argon (99.99%, 0.1 MPa) atmosphere [23]. The details of the combustion synthesis process are summarized in Supplementary Information (see SI, Part A). The synthesized $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ porous compacts were ground to powder (−100 mesh). The powder was ball-milled for 240 min at 450 rounds per minute as before.

The ball-milled $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ powder was dried and hot-pressed at 1500 °C at 27.5 MPa for 2 h in vacuum ($<6.0 \times 10^{-2}$ Pa). The sintered $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ has the following properties: fracture toughness (K_{IC}) of 2.5 ± 0.2 MPa $m^{1/2}$, Vickers hardness (Hv) of 10.6 ± 0.1 GPa. The sintered disks (φ50 mm × 5 mm) were used to machine test specimens of 36 mm × 3 mm × 4 mm by wire-electrode cutting. The surface of test specimens was polished to mirror finish. The edges of all the specimens were chamfered to minimize the effect of stress concentration due to machining flaws. Cracks induced by Vickers indentation are used as model cracks for crack healing studies [24]. For this reason, a crack was introduced at the center of the test specimen using a Vickers indenter, at a load of 98 N for 20 s.

Pre-cracked specimens were annealed in air at 900, 1200 and 1500 °C. The specimens annealed at 1200 °C in air exhibited the highest bending strength. To make a comparison, the pre-cracked specimens were annealed at 1200 °C in vacuum ($<2 \times 10^{-2}$ Pa), argon (99.99%, 0.1 MPa) and nitrogen (99.99%, 0.1 MPa). The bending strength of polished, pre-cracked and heat treated $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ specimens was tested by a three-point loading system, using a 30 mm span and a crosshead speed of 0.5 mm min^{-1}, and at least five specimens were tested for each condition. Surfaces and fracture patterns of $(Mo_{0.97}Nb_{0.03})(Si_{0.97}Al_{0.03})_2$ specimens were analyzed by scanning electron microscopy (SEM, FEI Quanta TM 250) equipped with energy-dispersive spectroscopy (EDS, Quantax 400-10). The phase compositions were identified by Bruker D8 Advance X-ray diffractometer (XRD) using Cu Kα (λ = 0.15406 nm) radiation.

3. Results and discussions

The surface SEM micrographs of the indentation are shown in Fig. 1. After indentation, microcracks appear around the indent (Fig. 1a). The semi-elliptical radial surface cracks are 0.5–0.8 μm wide at half-length of the crack and ~100 μm long (the half crack length, c, was measured from the center of the indentation to the crack tip). The effect of crack length on the strength of brittle ceramics is discussed in Supplementary Information (see SI, Part B). After heat treatment at 900 °C in air (Fig. 1b) SiO_2 particles (white) of 5–10 μm appear on the surface, determined by energy dispersive spectroscopy (see SI, Fig. S7). After annealing at 1200 °C (Fig. 1c) in air, the indentation edges passivate and the specimen surface is covered with a discontinuous glass layer. Annealing at 1500 °C (Fig. 1d) show that the cracks and diagonals of the indentation disappear and indent edges passivate. X-ray diffraction (XRD) data (see SI, Fig. S10) confirms that SiO_2 diffraction peaks appear after annealing at 1200 and 1500 °C in air. At 1500 °C, the oxidation happens at a faster rate with accelerated volatilization of MoO_3 and results in reconstitution of SiO_2 [25]. A dense SiO_2 layer forms on the surface at 1500 °C (Fig. 1d). The dense SiO_2 layer inhibits the diffusion of O^{2-}, and Mo_5Si_3 is produced because of the selective oxidation of $MoSi_2$ (see SI,

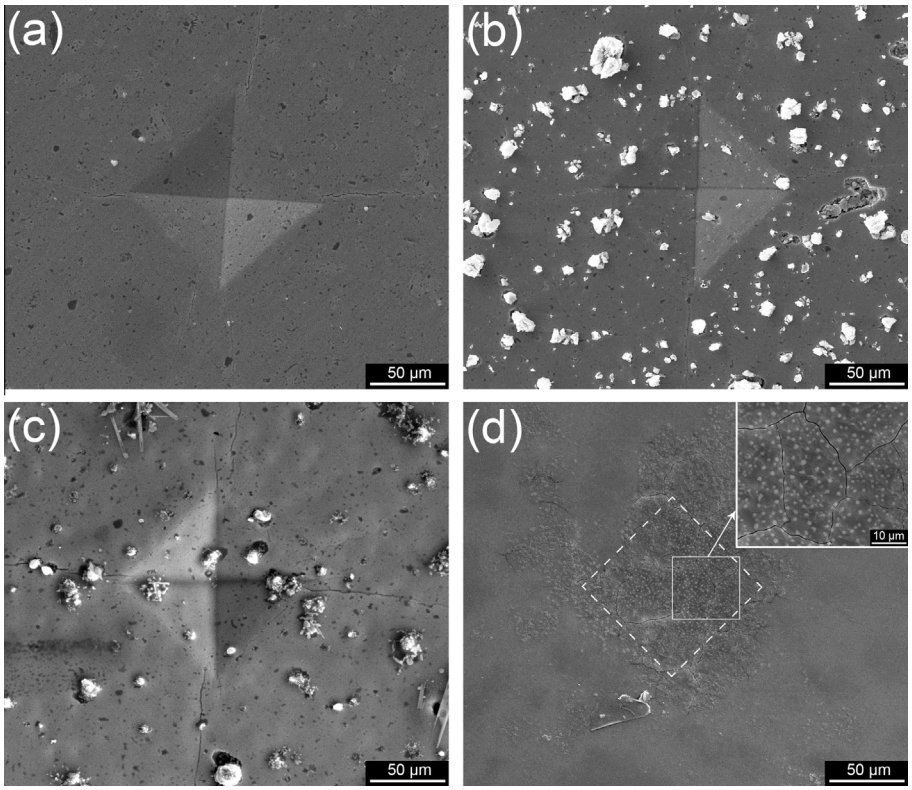

Fig. 1. (a) SEM micrographs of the untreated surface shape; samples at different temperatures for 1 h in air: (b) 900 °C; (c) 1200 °C; and (d) 1500 °C. The inset of (d) is a higher-magnification image of the box.