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Synthesis and mechanical properties of $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$–x vol% SiC composites fabricated via SHS-HP

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ABSTRACT

$(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$–SiC composites were consolidated via vacuum HP sintering from the mixture of $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ powder and SiC nanoparticles. The $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ powder was prepared by self propagating synthesis (SHS). The effects of SiC content on the ambient temperature mechanical properties and microstructure of the SHS-HP composites were investigated. The results show that the indentation fracture toughness, bending strength and Vickers hardness of $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$–*x* vol % SiC composites increase gradually with the increase of SiC content. The grain size and relative density of the composites decrease gradually with increase of SiC content. $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$–15 vol% SiC composite exhibits excellent mechanical properties: Vickers hardness 12.62 GPa, fracture toughness 5.01 MPa $m^{1/2}$, bending strength 472 MPa. With the addition of SiC, the fracture mode transforms from a mixed mode of transcrystalline and intercrystalline fracture to mainly transcrystalline fracture.

1. Introduction

Molybdenum disilicide ($MoSi_2$) has been regarded as a potential high-temperature structural material. Despite excellent elevated temperature resistance to oxidation, high melting point (2030 °C), and low density (6.28 g cm^{-3}), it has not been utilized as the high-temperature structural material due to its intrinsic limitation in properties such as low ductility at room temperature and low strength at high temperatures (> 1200 °C) [1]. For example, the fracture toughness of $MoSi_2$ is in the range of 0.8–2.4 MPa $m^{1/2}$ at room temperature [2] and the 0.2% offset yield strength of $MoSi_2$ is about 20 MPa at 1600 °C [3,4]. Thus, the key material issue associated with $MoSi_2$ is the improvement in the room temperature toughness and high temperature strength.

The presence of metallic bonding in $MoSi_2$ opens the possibility of alloying to improve the mechanical properties, and over the years, the composite approach has been developed to toughen and strengthen structural ceramics, and many of the approaches developed for ceramics may also be applied to $MoSi_2$ [5]. The first principles calculations indicate that the effects of substitution of Mo by Nb, and substitution of Si by Al are found to be particularly beneficial to the enhancement of ductility [6]. Wang [7] investigated the relationship of the valence electronic structure and mechanical properties of $MoSi_2$ co-alloy with Nb and Al, and the results indicated that the ductility and toughness of Nb and Al co-containing alloys may be increase remarkable but the strength and hardness of alloys were dramatic decline. Dasgupta [8] reported that the room temperature fracture toughness of Nb (1 al%) and Al (4 al%) co-substituted $MoSi_2$ composite is 4.05 MPa $m^{1/2}$ which is improved by about 21.6%, but the average Vickers hardness is 874 Hv which is decreased by about 13.2% compared to pure $MoSi_2$ (989 Hv). Sharif [9,10] reported that Nb and Al single alloying of $MoSi_2$ composites exhibited concurrent enhanced room temperature ductility and higher elevated temperature strength. These investigations suggest that alloying may be a means to increase room temperature fracture toughness and high temperature strength of $MoSi_2$. Moreover, Esmaeily [1] reported that in order to simultaneously improve the mechanical properties (such as flexural strength, hardness and fracture toughness) of $MoSi_2$, secondary additions have been attempted. Significant increase has been reported with ceramics reinforcements such as SiC, ZrO_2, TiC additions [11–13]. $MoSi_2$ is thermodynamically stable with mullite and a variety of other ceramic reinforcements, including TiC, ZrO_2, Al_2O_3, TiB_2, SiC and Si_3N_4 [13–18]. Among these reinforcements, SiC is considered to be significantly effective due to its good compatibility [1] and high thermal stability [19] with $MoSi_2$.

Self-propagating high temperature synthesis (SHS, named as Combustion Synthesis) is a rapid and green method for preparing materials by chemical reactions between powder components [20]. It offers several advantages such as high efficiency and energy saving. So

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far, over 500 compounds have been reported to be synthesized by SHS, such as borides, carbides, nitrides, silicides etc. [21].

In the present study, the alloying and composite approaches have simultaneously tried to apply the toughen and strengthen $MoSi_2$, and $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ alloys were synthesized via SHS, using Mo, Si, Nb and Al powders as the starting raw materials. The dense $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$-SiC composite was prepared by vacuum hot pressing (HP) the mixture of $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ and SiC nano-particles. The SHS mode and combustion temperature of $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ were investigated. The ambient temperature mechanical properties (such as bending strength, Vickers hardness, and fracture toughness) and microstructure of the HP composites are investigated.

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, Qiangshun Specialty Products Co. Ltd., China) powders with atomic ratio of 0.94: 1.94: 0.06: 0.06 were ball-milled (QM-ISP 2CL, Nanjing NanDa Instrument Plant, China) for 240 min at 450 rounds per minute, and 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. Then the SHS reaction was conducted in a steel combustion chamber, under pure argon (99.99%, 0.1 MPa) atmosphere [20]. The ignition was accomplished by a red hot molybdenum coil. A color CCD video camera was used to record the images of combustion synthesis. AVS Video Remaker software was applied to analyze the combustion images and the combustion mode. Thermocouple wires (WRe3-WRe25 with a diameter of 0.1 mm) were placed inside a small hole drilled at the bottom of green compacts to record the combustion synthesis temperature with a frequency of 300 Hz. The schematic diagram of experimental combustion synthesis setup is summarized in Fig. 1. The synthesized $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ porous monoliths were ground to powders (−100 mesh). Then, the powders and 0, 5, 10 and 15 vol% SiC nano-particles (40 nm, 99.9% purity, Beijing Gold Island Technology Co., Ltd., China) were ball-milled for 240 min at 450 rounds per minute as before, respectively.

$(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$–$x$ vol% SiC (x=0, 5, 10, 15) mixtures were consolidated by vacuum hot pressed sintering at 1400 °C and 27.5 MPa for 1.5 h and the hot pressing produces were singed as C0, C5, C10 and C15, respectively.

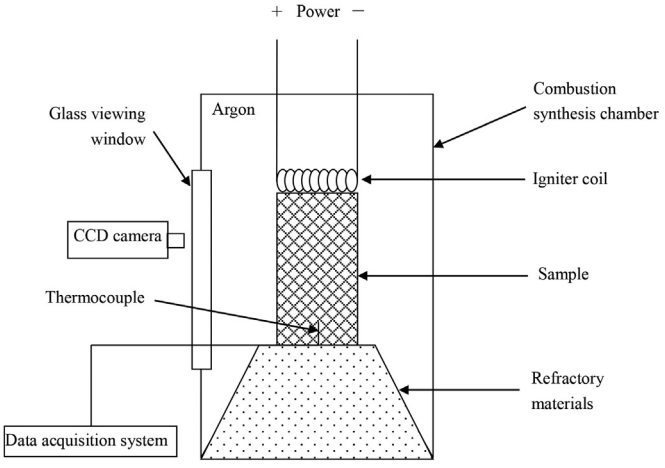

Fig. 1. Schematic diagram of experimental combustion synthesis setup.

The sintered disks (φ50 mm×5 mm) were cut into test specimens of 22 mm×3 mm×4 mm by wire-electrode cutting. The surface of specimens was polished to mirror finish. The SHS and HP products were identified by X-ray diffraction (XRD) on a Bruker D8 ADVANCE XRD machine with Cu target (λ=0.15406 nm). The theoretical density was calculated using the rule of mixtures. The real densities of hot pressing composites were measured by Archimedes's method (Matsuhaku QL-120C, Taiwan China). The relative densities of the composites were calculated from the measured and theoretical densities. The Vickers hardness (H_v) and fracture toughness (K_{IC}) were measured on polished specimens using Vickers's diamond indenter under 98 N for 15 s (Laizhou Huayin HVS-50, China). K_{IC} was calculated by using the equation reported by Anstis [22] (hardness imprints and the cracks emanating from the imprints) on polished sections by Olympus metallographic micrograph (PMG 3, Japan). Bending strength was measured through three-point-bending test using an 18 mm span and a crosshead speed of 0.5 mm min^{-1} (CSS-44300 electronic universal testing machines, Shenzhen Xinsansi, China), and at least five specimens were tested for each condition. The microstructure of the composites was observed by FEI Quanta TM 250 scanning electron microscope with energy-dispersive spectroscopy (EDS, Quantax 400-10). The SEM images were utilized to quantitatively determine the content of reaction phase in Cx (x=0, 5, 10 and 15) composites by Image J2x software.

In order to measure the grain size of matrix of Cx (x=0, 5,10 and 15), the polished surface was etched in a solution consisting of distilled water (40 ml), nitric acid (20 ml) and hydrofluoric acid (10 ml). The microstructures of chemically etched surface were examined by Olympus metallographic micrograph. The average grain sizes were determined by Nano Measure software accompanied with the SEM images.

3. Results and discussion

3.1. Synthesis and microstructure

$(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ alloys are successfully synthesized via SHS. Fig. 2 shows the combustion images, it can be seen that the combustion synthesis reaction is ignited locally at the point where the green compact contacts with the ignition coil, and then quickly spreads to the top plane of the cylindrical compact before t=0.96 s. The heat generated in combustion makes the reaction self-sustained (t=0.96–3.40 s), and the flame-front propagates along a spiral trajectory till it reaches the bottom of the compact, which is determined as the unstable state combustion mode.

Fig. 3 shows the actual combustion temperature profile, XRD patterns and SEM micrograph of $(Mo_{0.94}Nb_{0.06})(Si_{0.97}Al_{0.03})_2$ alloy. It can be seen that in Fig. 3a, the temperature of the sample rapidly increases from ambient temperature to 1526 °C in 0.25 s, which is caused by combustion. The maximum combustion temperature of 1526 °C is higher than the melting point of silicon (1414 °C) and aluminum (660 °C) but lower than that of niobium (2468 °C) and molybdenum (2617 °C) [23–26]. Therefore, Si and Al melt under the high combustion temperature, and then forms a solution of Si and Al in the vicinity of Mo and Nb particles, indicating a solid-liquid reaction mechanism.

XRD results (Fig. 3b) show the major peaks match with the standard peaks of tetragonal $C11_b$-$MoSi_2$ (PDF No. 41-0612) and a trace of Mo_5Si_3 can also be detected, indicating that molybdenum silicides are formed via SHS reaction. Typically, Mo_5Si_3 is formed along with $MoSi_2$ during different synthesis routes, such as spark plasma sintering [1], SHS [27], and mechanical alloying [28]. This is due to that the raw powders containing a small volume of oxygen [17], sintering of such powders results in a small volume fraction of amorphous silica in the final product. Consumption of Si to form SiO_2 renders the material slightly Mo-rich leading to the formation of