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Fabrication and mechanical properties of \((\text{Mo}_{0.9}\text{W}_{0.1})(\text{Si}_{0.4}\text{Al}_{0.6})_2\) composites reinforced by TiC

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Abstract

TiC-(\(\text{Mo}_{0.9}\text{W}_{0.1})(\text{Si}_{0.4}\text{Al}_{0.6})_2\)) composites were prepared from Mo, W, Si, Al and TiC powders via self-propagating high-temperature synthesis and hot pressing. The propagation mode of the combustion synthesis reaction and the influence of different TiC contents (0, 5, 10, 15, 20, 25 and 30 vol\%) on the mechanical properties of \((\text{Mo}_{0.9}\text{W}_{0.1})(\text{Si}_{0.4}\text{Al}_{0.6})_2\) were investigated. The results showed that the combustion propagation mode was steady from 0.00 to 2.06 s and unsteady from 2.06 to 6.45 s. The composites were mainly composed of MoSi2 (C11\(_b\)) and TiC. The bending strength, Vickers hardness, and fracture toughness of the 0–30 vol\% TiC-(\(\text{Mo}_{0.9}\text{W}_{0.1})(\text{Si}_{0.4}\text{Al}_{0.6})_2\)) composites were 270–433 MPa, 9.60–14.85 GPa and 6.40–9.73 MPa \(\cdot\) m\(^{1/2}\), respectively. These results indicated that TiC doping could effectively improve the mechanical properties of \((\text{Mo}_{0.9}\text{W}_{0.1})(\text{Si}_{0.4}\text{Al}_{0.6})_2\).

1. Introduction

With the rapid development of aerospace technology, it is urgent to study new high-temperature structural materials. In this regard, molybdenum disilicide (MoSi2) with C11\(_b\) structure is considered one of the most promising high-temperature structural materials because of its high melting temperature of 2030 \(^\circ\)C, moderate density of 6.24 g cm\(^{-3}\), high thermal conductivity and no phenomenon of pesting [1–4]. However, MoSi2 has poor mechanical properties, such as low bending strength and low fracture toughness at room temperature, which limits its further application [5–8].

Currently, many researchers have focused on addressing the poor mechanical properties of MoSi2, and two methods have been commonly applied to address these problems. One of the effective methods to improve the mechanical properties is to form MoSi2-based solid solution alloys with other elements, such as Al, W, Ti, Ta, and Zr [9, 10]. Among alloying additions, the substitution of Al at Si-sites in MoSi2 is highly beneficial because this not only improves the brittleness of MoSi2 at room temperature but also significantly inhibits the degradation of MoSi2 due to oxidation. For example, Mitra et al reported that the fracture toughness of MoSi2 increased with increasing Al substitution and reached a maximum of 4.67 MPa \(\cdot\) m\(^{1/2}\) [11]. However, it was reported that the addition of Al in MoSi2 would decrease the Vickers hardness of MoSi2 [12]. Compared to Al addition, W addition has the opposite effect, decreasing the fracture toughness of MoSi2 but increasing the hardness and strength [9]. Recently, many studies have focused on multiple alloying, which provides better comprehensive mechanical properties than single alloying [13–15]. For example, Dasgupta et al reported that Nb/Al co-substituted MoSi2 exhibited a marked improvement in mechanical properties compared to pure MoSi2 [16]. The other method for improving the mechanical properties is to prepare MoSi2-based composites with reinforcements such as SiC and TiC [17, 18]. SiC is one of the most widely studied reinforcements because it significantly improves the fracture toughness and the oxidation resistance of MoSi2 at high temperatures [19]. However, microcracks are formed due to the large difference in the thermal expansion coefficients between SiC and MoSi2, resulting in a certain reduction in mechanical properties [20]. Amazingly, TiC has a thermal expansion coefficient of \(7.7 \times 10^{-6} \text{K}^{-1}\), which is similar to that of MoSi2 \(8.5 \times 10^{-6} \text{K}^{-1}\); hence, TiC-MoSi2 composites have better mechanical properties than SiC-MoSi2 composites [19, 21].
According to the research findings presented above, reinforcing W/Al co-substituted MoSi_2 alloy with TiC is expected to provide further increases in mechanical properties. Therefore, the objective of this study is to research novel TiC-(Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 composites (x = 0, 5, 10, 15, 20, 25 and 30 vol%) that are produced by self-propagating high-temperature synthesis (SHS) and hot pressing. The propagation mode of the combustion synthesis reaction and the influence of the volume fraction of TiC on the mechanical properties of (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 are reported.

2. Experiment

2.1. Preparation of (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2

Herein, TiC-(Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 composites are produced by SHS and hot pressing. The process flow diagram is shown in figure 1. First, the (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 matrix was prepared by SHS. Stoichiometric amounts of Mo powders (1.5 μm, 99.95% purity), W powders (2 μm, 99.90% purity), Si powders (3 μm, 99.99% purity), and Al powders (<5 μm, 99.99% purity) were ball milled with anhydrous ethanol in a poly tetra fluoroethylene (PTFE) jar at 200 rpm for 4 h. After ball milling, the mixed slurries were dried at 100 °C for 12 h in a vacuum drying cabinet. The dried powders were sieved with #200 meshes and then pressed into pellets with a diameter of 50 mm at 30 MPa. The combustion synthesis reaction was conducted by heating a molybdenum coil under vacuum (−0.1 MPa). The synthesized porous pellets were ground with an agate mortar and pestle, and then the (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 powders were sieved with #200 meshes to obtain the (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 matrix.

2.2. Preparation of composites

The (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 powders and TiC powders were used to prepare TiC-(Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 composites with different nominal compositions (as shown in table 1). The TiC was ultrasonically dispersed in polyethylene glycol solution for 15 min before use. The powders were wet mixed, and then the mixture slurries were ball milled in a PTFE jar for 6 h at 200 rpm, in which the ball-to-powder ratio was 6:1; the ball milling process was followed by a drying process. The dried mixtures were placed in a graphite mould with a diameter of 50 mm and
heated at 8 °C min^{-1} by hot pressing. From 200 °C to 1200 °C, the pressure was 10 MPa, followed by a pressure of 30 MPa from 1200 °C to 1600 °C. The mixtures were finally sintered at 1600 °C and 30 MPa for 1 h under vacuum.

2.3. Characterization
The SHS process was recorded with a high-speed camera. The crystalline phases of the composites were identified via x-ray diffraction (XRD, Bruker D8 Advance x-ray diffractometer) using Cu Kα radiation and energy-dispersive spectroscopy (EDS). Recorded XRD patterns were used for calculation of grain size. A universal testing machine was used to determine the bending strength of the composites. The Vickers hardness of the composites was determined with a Vickers hardness tester (VH1150) under a load of 98.07 N and a holding time of 15 s. The relative density of the composites was determined with the Archimedes method. The fracture toughness of the composites was determined using the indentation fracture technique.

3. Results and discussion
3.1. Observation of the SHS process
The recorded SHS process images of (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 from green body to final products are shown in figure 2. The molybdenum coil, which contacted the green body, was heated and then the top-left edge of the green body was ignited. Subsequently, the combustion wave spread from the left edge to the right edge and then traversed the entire sample along a spiral trajectory. The combustion wave uniformly traversed downwards during the period 0.00–2.06 s; however, the wave unevenly traversed downwards from 2.06 to 6.45 s. The main reason for this phenomenon was that combustion synthesis progress was determined by the heat generated from the combustion synthesis reaction zone and the heated molybdenum coil

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At the beginning of the combustion synthesis reaction (0.00–2.06 s), the heat generated from the heated molybdenum coil and combustion synthesis reaction zone supported the steady propagation of the combustion wave. After 2.06 s, however, the combustion synthesis reaction became self-sustained as the heat from the heated molybdenum coil faded. The heat from the self-sustaining reaction was insufficient to maintain the steady propagation of the combustion wave [23]. Therefore, the combustion mode was considered unsteady from 2.06 to 6.45 s.

3.2. Phase analysis
Figure 3(a) represents the XRD patterns of the (Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 matrix produced by SHS. As illustrated in this figure, most of the diffraction peaks were the MoSi_2 (C11b) phase (PDF01-072-6181). Peaks of Mo (Si, Al)_2(C40) were also found, perhaps due to the supersaturated solid solution of Al in MoSi_2(C11b) [24]. In addition, there were few peaks of Mo_5Si_3, which was considered to be a result of selective oxidation above 1000 °C for MoSi_2 [25, 26]. Figure 3(b) shows the XRD patterns of the TiC-(Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})_2 composites produced by hot pressing. When the volume fraction of TiC was 0%, impurities such as C40 and Mo_5Si_3 were still detected. However, only the peaks of the C11b phase and TiC phase were detected after the introduction of TiC, and no impurity was observed. Of course, the peaks of TiC became stronger as the volume fraction of TiC increased.
The EBSD and EDS mapping images for the 20 vol% TiC-(Mo_{0.9}W_{0.1})(Si_{0.4}Al_{0.6})\textsubscript{2} composite are shown in figure 4. The chemical elements Mo, Si, Al, W, Ti, C and O were detected in these images. In part I, Mo and Si had the highest concentrations, and W was distributed uniformly. Combined with the XRD results, part I was considered to be MoSi\textsubscript{2} with C11\textsubscript{b} structure. Compared to part I, part II had the same situation but was brighter; this part was speculated to be Mo\textsubscript{5}Si\textsubscript{3}. The Mo\textsubscript{5}Si\textsubscript{3} phase was not detected via XRD, which was probably due to its small volume fraction in the composite [27]. In part III, the concentrations of Ti and C were higher than those in parts I and II. In addition, the concentrations of Mo, Si, and Al in part III were low. Thus, part III was considered to be TiC. Part IV had the highest concentrations of Al and O, whereas the concentrations of Mo and Si were low; hence, this part may be Al\textsubscript{2}O\textsubscript{3}. This finding was consistent with published results, in which Al-substituted MoSi\textsubscript{2} had two phase microstructures of Al\textsubscript{2}O\textsubscript{3} and MoSi\textsubscript{2} [11].

3.3. Mechanical properties at room temperature
Figure 5 represents the results of the average grain size and bending strength of the composites. These results showed that there was a monotonous decrease in the average grain size as the volume fraction of TiC increased. This result indicated that TiC served as a second phase that could retard the migration of the grain boundary,
which is beneficial to grain refinement [28]. When the volume fraction of TiC was 0%, the bending strength was 270 MPa. As the volume fraction of TiC increased, the bending strength increased further. As the volume fraction of TiC increased to 20%, the bending strength reached a maximum of 433 MPa, which was approximately 60.37% higher than that of the (Mo0.9W0.1)(Si0.4Al0.6)2 matrix. Afterwards, the bending strength decreased slightly as the volume fraction of TiC increased. Reports have shown that the C11b structure has greater deformability and more slip systems than the C40 phase, resulting in stronger fracture strength of the corresponding composites [29]. Moreover, grain refinement of the matrix would improve the fracture strength [30]. Therefore, the increase in strength was perhaps due to the decrease in the C40 phase and the grain refinement of the matrix.

Figure 6 shows the Vickers hardness and fracture toughness of the TiC-(Mo0.9W0.1)(Si0.4Al0.6)2 composites. When the volume fraction of TiC was 0%, the Vickers hardness was 9.6 GPa. As the volume fraction of TiC increased, the Vickers hardness increased. When the volume fraction of TiC was 25%, the maximum Vickers hardness was 14.85 GPa. Afterwards, the Vickers hardness decreased slightly as the volume fraction of TiC increased further. The variation in the Vickers hardness was in compliance with the rule of mixtures, which is described by the following formula [31]:

\[ H = V_f H_f + (1 - V_f) H_m \]  

(1)

where \( H \) is the Vickers hardness of the TiC phase, \( H_m \) is the Vickers hardness of the matrix phase, and \( V_f \) is the volume fraction of TiC. The Vickers hardness was 27.5 GPa for TiC [25] and 9.6 GPa for (Mo0.9W0.1)(Si0.4Al0.6)2.
The black dashed line in figure 6 represents the Vickers hardness of the TiC-(Mo$_{0.9}$W$_{0.1}$)(Si$_{0.4}$Al$_{0.6}$)$_2$ composites calculated by the theoretical formula, which shows the same trend as the black line. It has been reported that experimental Vickers hardness is closely related to the relative density of composites [32]. According to the relative density of the TiC-(Mo$_{0.9}$W$_{0.1}$)(Si$_{0.4}$Al$_{0.6}$)$_2$ composites in table 2, TiC had a positive effect on the relative density: the relative density mostly reached above 95% or 97%. However, the relative density of the composites decreased when the volume fraction of TiC was 30%. Therefore, the decrease in Vickers hardness was perhaps explained by the decrease in relative density when the volume fraction of TiC was 30%.

The fracture toughness ranges from 6.40 to 9.73 MPa $\cdot$ m$^{1/2}$ in figure 6. When the volume fraction of TiC was 0%, the fracture toughness was 6.40 MPa $\cdot$ m$^{1/2}$; the fracture toughness increased as the volume fraction of TiC increased. When the volume fraction of TiC increased to 20%, the composites exhibited the highest fracture toughness of 9.73 MPa $\cdot$ m$^{1/2}$. Afterwards, the fracture toughness decreased slightly as the TiC volume fraction increased. Figure 7 shows the crack propagation behaviour in the 20 vol% TiC-(Mo$_{0.9}$W$_{0.1}$)(Si$_{0.4}$Al$_{0.6}$)$_2$ composite. Crack deflection and crack branching have been demonstrated as the main toughening mechanisms for
MoSi$_2$-matrix composites [33, 34]. These mechanisms could sophisticate the crack propagation paths and increase the energy required for crack propagation [35–37]; this phenomenon would increase the fracture toughness.

Peng et al reported that the fracture toughness of Mo-Si-W composites was 2.97 MPa · m$^{1/2}$, which is 13.0% less than that of pure MoSi$_2$ [9]. Zhang et al studied the formation of Mo-Si-Al composites by mechanical alloying and heat treatment techniques and reported that the maximum fracture toughness was approximately 7.2 MPa · m$^{1/2}$ when the Al content was 8.5% [38]. Lan et al characterized 20 vol% TiC-MoSi$_2$ composites with the hot pressing method and reported a fracture toughness of 5.2 MPa · m$^{1/2}$ for the composites and 3.2 MPa · m$^{1/2}$ for pure MoSi$_2$ [20]. Compared to these cases, the TiC-(Mo$_{0.9}$W$_{0.1}$)(Si$_{0.4}$Al$_{0.6}$)$_2$ composites has notably higher fracture toughness.

4. Conclusion

This study investigated xTiC-(Mo$_{0.9}$W$_{0.1}$)(Si$_{0.4}$Al$_{0.6}$)$_2$ (x = 0, 5, 10, 15, 20, 25 and 30 vol%) composites produced by SHS and hot pressing with Mo, Si, W, Al and TiC powders as the raw materials. The combustion synthesis reaction progressed under the combined effect of the heat from the heated molybdenum coil and the combustion synthesis reaction zone during 0.00–2.06 s; the combustion propagation mode was steady in this period. Then, the combustion synthesis reaction became self-sustained after 2.06 s, and the combustion propagation mode was unsteady. Analysis of the XRD and EDS results showed that the composites were mainly MoSi$_2$ with C11$_2$ structure and TiC. In addition, the composites contained a small amount of Al$_2$O$_3$ and Mo$_2$Si$_2$. TiC served as the second phase, which effectively improved the mechanical properties, including the Vickers hardness, bending strength and fracture toughness, of the composites. The 20 vol% TiC-(Mo$_{0.9}$W$_{0.1}$)(Si$_{0.4}$Al$_{0.6}$)$_2$ composite exhibited the highest bending strength of 433 MPa, a high Vickers hardness of 14.71 GPa and the maximum fracture toughness of 9.73 MPa · m$^{1/2}$. The crack deflection and crack branching were the main toughening mechanisms of the composites in this study.

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