Preparation and Characterization of MoSi$_2$/WSi$_2$ Composites from MASHSed Powder

Jianguang Xu$^{1,*}$, Yuchen Wang$^{1,2}$, Baicheng Weng$^1$ and Fang Chen$^3$

$^1$School of Materials Engineering, Yancheng Institute of Technology, Yancheng, Jiangsu 224051, P. R. China
$^2$School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, Guilin, Guangxi 541004, P. R. China
$^3$School of Physics and Electronic Science, Hunan University of Science and Technology, Xiangtan, Hunan 411201, P. R. China

MoSi$_2$ based materials are considered to have potential for use in high temperature structural part. In this work, MoSi$_2$/WSi$_2$ composites have been successfully prepared by pressureless sintering from mechanically-assisted combustion synthesized powders. The size of green powders shows great impact on the properties of sintered samples. The sample obtained from smaller powders has finer microstructure, and its Vickers hardness, flexural strength and fracture toughness were as high as 10.78 GPa, 327.21 MPa and 7.32 MPa m$^{1/2}$, respectively. The morphologies of the fractured surface of the composites revealed the mechanism to improve the mechanical properties of MoSi$_2$ matrix. Moreover, this composite exhibits good oxidation resistance at low temperature. A continuous SiO$_2$ layer was formed after exposure to air at 500°C for 120 hours, which could prevent further oxidation of the composite. [doi:10.2320/matertrans.M2014370]

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1. Introduction

MoSi$_2$ has attracted great research interest due to its rather low density (6.28 g·cm$^{-3}$), high melting point, high electrical conductivity and very good oxidation resistance at high temperature.$^{[1-4]}$ It is useful in such applications as high temperature heating elements and potential structural parts at elevated temperature. However, monolithic MoSi$_2$ shows extreme brittleness and poor impact strength at lower temperature, and has low strength and creep resistance at elevated temperature (>1200°C). It is proven that compound with a second phase or alloying with other elements is a good method to strengthen and toughen MoSi$_2$. Significant property improvement has been readily gained through alloying MoSi$_2$ with WSi$_2$.$^{[5-7]}$ Grain-size engineering—specifically, reduction of grain sizes into the nanometer regime—offers another potentially useful way for optimizing the properties of MoSi$_2$. Grain boundaries rather than dislocations in nanocrystalline materials govern the mechanical behavior, resulting in enhancement of mechanical properties. The fracture toughness of nanocrystalline MoSi$_2$ is as high as 4.8 MPa·m$^{1/2}$. Much more property enhancement might be expected of nanocrystalline MoSi$_2$/WSi$_2$.

The mechanical alloying is the most common method reported to date that yields nanocrystalline MoSi$_2$/WSi$_2$.$^{[6,9,10]}$ However, some unexpected impurities such as Fe would be introduced to products during the mechanical alloying process, and WSi$_2$ cannot completely form a solid solution with MoSi$_2$. This would decrease the oxidation resistance of MoSi$_2$. An alternative way to obtain MoSi$_2$/WSi$_2$ is combustion synthesis (also known as Self-propagating high temperature synthesis, or SHS)$^{[5,11-17]}$ The advantages in the SHS method lie in its low cost, high purity and transition rate. Unfortunately, for the Mo-Si-W mixture, ignition is difficult without additional activation.$^{[12]}$ Primarily, this is due to the thermodynamic limitation, i.e. a low reaction enthalpy or the relatively low adiabatic combustion temperature of this mixture. Moreover, coarse particles will be obtained through SHS in most situations.

Recently, Bernard and Gaffet proposed a new variation of the SHS method.$^{[13,14]}$ The so-called MASHS (mechanically-assisted self-propagating high temperature synthesis) method consists of a high-energy ball milling step followed by a self-sustaining reaction. This process combines the advantages of mechanical alloying and self-propagation high temperature synthesis. Thus this method has been used to synthesize intermetallics, ceramics and composites.$^{[16-19]}$ Additionally, it was applied successfully to produce pure nanocrystalline (88 nm) MoSi$_2$.$^{[15]}$ In this study, this work presented preparation and characterization of MoSi$_2$/WSi$_2$ composites from MASHSed powders. The composites showed excellent mechanical properties and good oxidation resistance at lower temperature.

2. Experimental Procedure

98.5% pure Mo powder with a particle size range 2–5 µm, 99.4% pure Si powder with an average size of 10 µm and 99% pure W powder with an average size of 8.5 µm were used as starting raw materials. A mixture of Mo, W and Si powders was prepared according to the composition of 20 vol% WSi$_2$ and 80 vol% MoSi$_2$. The details of the MASHS technique for the in-situ WSi$_2$/MoSi$_2$ powder preparation have been published elsewhere.$^{[20]}$ The as-synthesized powder was milled using a conventional planetary ball mill (QM-ISP4) at 300 rpm speed for 1 h. Agate balls with diameter of 5 mm were used as the milling media, and the weight ratio of the balls to the powders’ mixture was 10 : 1. Then the powders were sieved and uniaxially pressed at 200 MPa. The pressed green compact was placed in a graphite crucible and pressureless sintered at 1550°C for 1 h in vacuum. The as-received samples were machined into 3 mm × 4 mm × 36 mm bars.

The morphologies of sintered products were studied by using scanning electron microscopy (SEM) with an energy dispersive X-ray spectrometer (EDS). Sintered sample...
densities were measured by the Archimedes method. The flexural strength was measured at room temperature using the three-point bending test with a span length of 30 mm and a cross-head speed of 0.5 mm·min⁻¹. The Vickers hardness (HV) and fracture toughness (KIC) were measured on polished specimens using Vicker’s diamond indenter under 294 N for 15 s. KIC values were calculated by using the equation reported by Anstis et al. Cyclic oxidation behavior of the composite at 500°C in air during 120 h exposure time was investigated by TGA. One cyclic consisted of heating at a particular temperature for 1–20 h followed by cooling to room temperature in the air.

3. Results and Discussions

3.1 Mechanical properties

The XRD and SEM results of as-prepared powders by MASHS technique have been published elsewhere, which shows the structure of these powders could be considered as aggregates (0.3 to 3 µm) composed of nanometric crystallites of (Mo,W)Si2. The crystallite size of (Mo,W)Si2 was 143.4 nm.

The densities, mechanical properties of the sintered samples and a MoSi2/WSi2 composite were listed in Table 1. The size of as-synthesized powders shows a great effect on the densities and mechanical properties of samples. For example, WMS2 has better mechanical properties than other samples, which was obtained from the smallest powders. Especially, the density, the flexure strength, the Vicker’s hardness and the fracture toughness of WMS2 are 96.49%, 327.21 MPa, 10.78 GPa and 7.32 MPa·m¹/², respectively. Moreover, these values are also superior to those of MoSi2/WSi2 composite, which was obtained through pressureless sintering of MoSi2/WSi2 powders by normal SHS. These results illustrate that, high-density MoSi2/WSi2 composites with excellent mechanical properties can be obtained by pressureless sintering from MASHSed powders. It’s because the MASHSed powder has stronger sintering activity due to their small size and fresh surface, especially nanometric crystallite size.

Figure 1 shows the fractured surfaces of WMS1 and WMS2. It can be observed from Fig. 1 that WMS2 has finer grains than WMS1. Moreover, the edge of some grains of WMS1 still keep smooth and some holes in WMS1 still keep connected, which indicated that WMS1 did not fully sinter and led to the relative low density. On the other hand, the grains of WMS2 connected tightly and left only a few independent holes in its structure, which indicates that it has almost sintered completely. It’s because the green powders of WMS2 had relatively small size, which could facilitate the sintering process greatly. We can also see that the fractured surface of WMS2 is much more tortuous and has more intergranular fracture than that of WMS1, resulting in the significant improvement of flexural strength and fracture toughness. All our samples have better mechanical properties than monolithic MoSi2 due to the solid solution strengthening.

3.2 Cyclic oxidation behavior

Figure 2 shows the cyclic oxidation curve of WMS2 at 500°C. During the initial 5 h of the oxidation process, it can be observed a relatively rapid increase in weight of sample WMS2. At that stage, the surface of MoSi2/WSi2 would be
oxidized to MoO$_3$, WO$_3$, and SiO$_2$ at the same time and might generate an oxide layer, which led to the observed increase of the sample weight. However, the oxide layer is not continuous and dense. The oxidation process can be very quick due to the fine grains of the sample, which possessed a large surface area. After approximately 5 h, the weight gain decreased. This was probably due to the formation of an oxide layer not completely covering the entire matrix at this stage, and MoO$_3$ and WO$_3$ would evaporate from the surface. Then the weight gain increased again. The oxidation continued and the silicon oxide film layer of protection gradually covered the entire matrix material, and hence the entry of oxygen became difficult. As a result, the sample weight was stable after 50 h. The sample that were oxidized in air for 120 h at 500°C was analyzed using SEM. It can be seen from Fig. 3 there is an oxide layer with some cracks and holes covering MoSi$_2$/WSi$_2$ composite. Especially, a few areas such as point A are not covered by the oxide layer, which contain less oxygen than other areas such as point B based on EDS results (Table 2). Moreover, the proportion of Mo and W atoms is more than that of Si atoms, which indicates Mo$_5$Si$_3$ and W$_5$Si$_3$ were formed during the oxidation procedure. It is because the O$_2$ is difficult to diffuse to the inner side of the sample, and Mo$_5$Si$_3$ and W$_5$Si$_3$ is preferably formed at low P$_{O_2}$. Because MoO$_3$ has a higher vapour pressure than that of WO$_3$, MoO$_3$ is more easily to diffuse to the surface and evaporate. Thus it can be seen that there are more W atoms at point A area. It can be seen from the oxidation results, there is no “pesting” phenomenon of the MoSi$_2$/WSi$_2$ composite, and the composite shows good low-temperature oxidation resistance. It is because in our high density samples, grain boundaries are the main route for oxygen diffusion. Oxygen is difficult to diffuse to inner side of the sample. After the MoO$_3$ and WO$_3$ were evaporated from the sample surface at the initial oxidation stage, a continuous SiO$_2$ layer was finally formed, which could prevent the further entry of oxygen. It can be convinced there are no needle-shaped MoO$_3$ and WO$_3$ are detected on the sample surface from Fig. 3. The EDS results of point B also show that the sample surface is mainly composed of SiO$_2$. Moreover, because the oxidation experiment was carried out on wet air, the protective oxide layer was easier formed on wet air than dry air.

**4. Conclusion**

In this work, MoSi$_2$/WSi$_2$ composite powder with nanostructure has been successfully synthesized by mechanically-assisted combustion synthesis method. This process includes a ball-milling process followed by combustion synthesis. The as-synthesized powder was pressureless sintered and showed very excellent sintering activity. The relative density, flexural strength, Vicker’s hardness and fracture toughness of the sintered samples are up to 96.49%, 327.21 MPa, 10.78 GPa and 7.32 MPa m$^{1/2}$, respectively. The WSi$_2$/MoSi$_2$ composite also exhibits good low-temperature oxidation resistance.

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