Simultaneous Synthesis and Consolidation of Nanostructured MoSi₂-NbSi₂ Composite by High-Frequency Induction Heated Sintering and Its Mechanical Properties

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Abstract The current concern about these materials (MoSi₂ and NbSi₂) focuses on their low fracture toughness below the ductile-brittle transition temperature. To improve the mechanical properties of these materials, the fabrication of nanostructured and composite materials has been found to be effective. Nanomaterials frequently possess high strength, high hardness, excellent ductility and toughness, and more attention is being paid to their potential application. In this study, nanopowders of Mo, Nb, and Si were fabricated by high-energy ball milling. A dense nanostructured MoSi₂-NbSi₂ composite was simultaneously synthesized and sintered within two minutes by high-frequency induction heating method using mechanically activated powders of Mo, Nb, and Si. The high-density MoSi₂-NbSi₂ composite was produced under simultaneous application of 80MPa pressure and an induced current. The sintering behavior, mechanical properties, and microstructure of the composite were investigated. The average hardness and fracture toughness values obtained were 1180 kg/mm² and 3 MPa·m^{1/2}, respectively. These fracture toughness and hardness values of the nanostructured MoSi₂-NbSi₂ composite are higher than those of monolithic MoSi₂ or NbSi₂.

Key words composite, mechanical properties, sintering, nanostructured materials.

1. Introduction

MoSi₂ and NbSi₂ have been investigated as potential materials for high-temperature structural applications and for use in the electronics industry. Their properties provide a desirable combination of a high melting temperature, high modulus, good oxidation resistance in air, a relatively low density,¹⁾ and the ability to undergo plastic deformation above 1200 °C.²⁾ Combined with good thermal and electric conductivities, these properties have led to the utilization of MoSi₂ as a heating element material in high-temperature furnaces operating in air up to approximately 1700 °C.^{3,4)} However, as in the case of many similar compounds, the current concern about these materials (MoSi₂ and NbSi₂) focuses on their low fracture toughness below the ductile-brittle transition temperature.⁵⁻⁷⁾ To improve the mechanical properties of these materials, the fabrication of a nanostructured material and

composite material⁸⁻¹¹⁾ have been found to be effective. As nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid to their potential application.^{12,13)}

Recently, nanocrystalline powders have been produced by high-energy milling.^{14,15)} The sintering temperature of high-energy mechanically milled powder is lower than that of unmilled powder due to the increased reactivity, internal and surface energies, and surface area of the milled powder, which contribute to its so-called mechanical activation.¹⁶⁻¹⁸⁾ The grain size in sintered materials becomes much larger than that in pre-sintered powders due to rapid grain growth during a conventional sintering process. Therefore, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the high-frequency induction-heated sintering (HFIHS) method, which can make dense materials within 2 minutes, has been

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shown to be effective in achieving not only rapid densification to near theoretical density, but also the prohibition of grain growth in nanostructured materials.¹⁹⁻²¹⁾

This paper reports on the rapid synthesis and consolidation of dense nanostructured MoSi₂-NbSi₂ composite starting with high-energy ball-milled nanopowders. The mechanical properties and grain sizes of the resulting nanostructured MoSi₂-NbSi₂ composite were also evaluated.

2. Experimental Procedures

Powders of 99.95 % pure molybdenum (< 10 μm, Aldrich Products), 99.5 % pure silicon (–325 mesh, Aldrich Products), and 99.8 % pure niobium (–325 mesh, Alfa Products) were used as starting materials. 0.5Mo, 0.5Nb, and 2Si powder mixtures were first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm and for 10 h. Tungsten carbide balls (9 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. A charge ratio (ratio of ball mass to powder) of 30:1 was used. The grain size was calculated using Suryanarayana and Grant Norton's formula²²⁾:

$$B_r(B_{\text{crystalline}} + B_{\text{strain}}) \cos \theta = k\lambda / L + \eta \sin \theta \quad (1)$$

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after an instrumental correction; $B_{\text{crystalline}}$ and B_{strain} are the FWHM caused by the grain size and internal stress, respectively; k is a constant (with a value of 0.9); λ is the wavelength of the X-ray radiation; L and η are the grain size and internal strain, respectively; and θ is the Bragg angle. The parameters, B and B_r , follow the Cauchy's form with the relationship $B = B_r + B_s$, where B and B_s are the FWHM of the broadened Bragg peaks and the standard Bragg peaks of the samples, respectively.

After milling, the powder was placed in a graphite die (outside diameter = 35 mm, inside diameter = 10 mm, and height = 40 mm), and then introduced into the induced current-activated sintering system, shown schematically in Fig. 1. The four major stages in the synthesis are as follows: evacuation of the system to 40 mtorr (stage 1), application of a uniaxial pressure of 80 MPa (stage 2), activation of an induced current, which was maintained

Fig. 1. Schematic diagram of the high-frequency induction-heated sintering apparatus.

until densification was attained as indicated by a linear gauge measuring the shrinkage of the sample (stage 3), and cooling the sample to room temperature (stage 4). The samples were densified by heating to a sintering temperature of 1200 °C with heating rate of 1000 °C/min. Temperatures were measured by a pyrometer focused on the surface of the graphite die. The process was carried out under a vacuum of 40 mtorr (5.3 Pa).

The relative densities of the sintered samples were measured by the Archimedes method. Microstructural information was obtained from product samples, which were polished and etched for 1 minute at room temperature using a solution composed of HF (10 vol.%), HNO₃ (30 vol.%), and H₂O (60 vol.%). Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations with a load of 5 kg and a dwell time of 15 s on the synthesized samples.

3. Results and Discussion

Fig. 2 shows SEM images of the raw powders used. Nb and Si have angular shapes, while Mo has a round

Fig. 2. SEM images of raw materials: (a) Nb, (b) Mo, and (c) Si.

Fig. 3. XRD patterns of raw materials: (a) Nb, (b) Mo, (c) Si, and (d) milled 0.5Mo-0.5Nb-2Si powder.

shape. XRD patterns of raw powders and milled 0.5Mo-0.5Nb-2Si powders are shown in Fig. 3. In Fig. 3(d), only Mo, Nb, and Si peaks were observed, as marked. Therefore, it is obvious that no chemical reaction occurred between the component powders during milling. Nevertheless, the peaks of the powders are significantly wide, suggesting that their grain sizes became very fine due to the milling. The average grain sizes of Mo, Nb, and Si measured by Suryanarayana and Grant Norton's formula²²⁾ were about 77, 25, and 16 nm, respectively. Fig. 4 shows a SEM image of milled powders, X-ray mapping, and EDS analysis. The milled powders have a very fine grain size and some agglomeration. In X-ray mapping, Mo, Nb, and Si distributed uniformly. In EDS, only Mo, Nb, and Si peaks were detected. The milling process is known to introduce impurities from the ball and/or container. However, in this study, peaks of Fe and W were not identified.

The interaction between these phases, i.e.,

is thermodynamically feasible, as shown in Fig. 5.

The variations in shrinkage displacement and temperature of the surface of the graphite die upon heating

Fig. 4. SEM image, X-ray mapping, and EDS of the milled 0.5Mo-0.5Nb-2Si powder.

Fig. 5. Temperature dependence of the Gibbs free energy change by interaction of the 0.5Mo+0.5Nb+2Si.

during the synthesis and densification of MoSi₂-NbSi₂ composite are shown in Fig. 6. As the induced current

Fig. 6. Variations of temperature and shrinkage displacement with heating time during synthesis and densification of the MoSi₂-NbSi₂ composite.

Fig. 7. XRD patterns of the 0.5Nb-0.5Mo-2Si system heated at 1200 °C.

was applied, the shrinkage displacement increased slowly with temperature up to 700 °C, and then abruptly increased. Fig. 7 shows the X-ray diffraction result of the sample heated to 1200 °C. The reactant peaks of Mo, Nb, and Si were not detected and only product peaks of MoSi₂ and NbSi₂ were observed. The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density resulting from the change

Fig. 8. FE-SEM image of MoSi₂-NbSi₂ composite sintered at 1200 °C.

in the molar volume associated with the formation of MoSi₂ and NbSi₂ from the reactants (Mo, Nb, and Si) and the consolidation of the product.

The average grain size of MoSi₂ and NbSi₂ measured by Suryanarayana and Grant Norton's formula²²⁾ was about 168 and 110 nm, respectively. A FE-SEM image of the etched surface of the sample heated to 1200 °C under a pressure of 80 MPa is shown in Fig. 8. The microstructure consists of nanophases in the FE-SEM image. The corresponding relative density is 98 %. The role of the current during sintering and/or synthesis has been the focus of several attempts to provide an explanation for the observed sintering enhancement and the improved product characteristics. The role played by the current has been broadly interpreted by several groups. The effect has been explained by rapid heating due to Joule heating at contacts points, the presence of plasma in pores separating powder particles, and the intrinsic contribution of the current to mass transport.²³⁻²⁶⁾

Vickers hardness measurements were made on polished sections of the MoSi₂-NbSi₂ composite using a 5-kg load and 15-s dwell time. The calculated hardness value of the MoSi₂-NbSi₂ composite was 1180 kg/mm². This value represents an average of five measurements. Indentations with large enough loads produced median cracks around the indentations. The length of these cracks permits an estimation of the fracture toughness for the material. From the length of these cracks, fracture toughness values can be determined using the formula developed by Anstis et al.,²⁷⁾ which is

$$K_{IC} = 0.016(E/H)^{1/2} \cdot P/C^{3/2} \quad (4)$$

where E is Young's modulus, H is the indentation hardness, P is the indentation load, and C is the trace length of the crack measured from the center of the

Fig. 9. (a) Vickers hardness indentation and (b) median crack propagation in the MoSi₂-NbSi₂ composite.

indentation. The modulus was estimated by the rule of mixtures for the 0.52 volume fraction of MoSi₂ and the 0.48 volume fraction of NbSi₂ using $E(\text{MoSi}_2) = 204 \text{ GPa}^{28)}$ and $E(\text{NbSi}_2) = 362 \text{ GPa}^{29)}$. As in the case of hardness values, the toughness values were derived from the average of five measurements. The toughness value obtained by this method of calculation is $3 \text{ MPa}\cdot\text{m}^{1/2}$. These fracture toughness and hardness values of the nanostructured MoSi₂-NbSi₂ composite are higher than those (fracture toughness; $2.58 \text{ MPa}\cdot\text{m}^{1/2}$ hardness; 8.7 MPa) of the microstructured MoSi₂³⁰⁾ or those (fracture toughness; $2.5 \text{ MPa}\cdot\text{m}^{1/2}$ hardness; 876 kg/mm^2) of the nanostructured NbSi₂.⁷⁾ A typical indentation pattern for the MoSi₂-NbSi₂ composite is shown in Fig. 9(a). Typically, one to three additional cracks were observed to propagate from the indentation corner. A higher magnification view of the indentation median crack in the composite is shown in Fig. 9(b). This shows that the crack propagates in a deflective manner ($\uparrow$). This is believed to suggest that NbSi₂ and MoSi₂ in the composite may deter the propagation of cracks.

4. Summary

Mo, Nb and Si nanopowders were fabricated using high-energy ball milling for 10 h. Using the high-frequency induction-heated sintering method, a MoSi₂-NbSi₂ composite was consolidated using the mechanically activated powders of 0.5Mo, 0.5Nb, and 2Si within two minutes. The relative density of the composite was 98 % for the applied pressure of 80 MPa. The average grain sizes of MoSi₂ and NbSi₂ in MoSi₂-NbSi₂ composite sintered by HFIHS method were determined as 168 and 110 nm, respectively.

The average hardness and fracture toughness values obtained were 1180 kg/mm^2 and $3 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. These fracture toughness and hardness values of the nanostructured MoSi₂-NbSi₂ composite are higher than those of monolithic MoSi₂ or NbSi₂.

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