

Consolidation and mechanical properties of nanostructured (Mo,Ti)Si₂ from mechanically activated powder by high frequency induction heated sintering

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A dense nanostructured (Mo,Ti)Si₂ compound was sintered by the high frequency induction heating method within 2 minutes from mechanically activated powder of Mo, Ti and Si. A highly-dense (Mo,Ti)Si₂ compound was produced under simultaneous application of a 80 MPa pressure and the induced current. The mechanical properties and microstructure were investigated.

Key words: (Mo,Ti)Si₂, Mechanical properties, Sintering, Nanostructured materials.

Introduction

MoSi₂ has been investigated as a potential material for high temperature structural applications and for application in the electronics industry. Its properties provide a desirable combination of a high melting temperature (2020 °C), high modulus (440 GPa), good oxidation resistance in air, a relatively low density (6.24 g/cm³) [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 about 1700 °C [3, 4]. However, as in the case of many such compounds, the current concern about these materials focuses on their low fracture toughness below the ductile-brittle transition temperature [5, 6]. To improve on the mechanical properties of these materials, the fabrication of a nanostructured material and solid solution metal silicides [7-10] have been found to be effective. As nano-materials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid to the application of nanomaterials [11, 12].

Recently, nanocrystalline powders have been produced by high energy milling [13]. 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 [14-16]. 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 method (HFIHSM), which can make dense materials within 2 minutes, has been shown to be effective in achieving not only rapid densification to near theoretical density but also the prohibition of grain growth in nanostructured materials [17, 18].

This paper reports on an investigation on the consolidation of dense nanostructured (Mo,Ti)Si₂ (within 2 minutes) starting with high energy ball milled nanopowder. The mechanical properties and grain sizes of the resulting nanostructured (Mo,Ti)Si₂ are also evaluated.

Experimental procedure

Powders of 99.95% pure molybdenum (< 10 μm, Aldrich Products), 99.5% pure silicon (–325 mesh, Aldrich Products) and 99.5% pure titanium (–325 mesh, Aldrich Products) were used as starting materials. 0.5Mo, 0.5Ti 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 (5 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. A charge ratio (ratio of mass of balls to powder) of 30 : 1 was used. The grain size and internal strain were calculated using Suryanarayana and Grant Norton's formula [19] :

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

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

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(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_s , 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 = 45 mm, inside diameter = 20 mm, and height = 40 mm) and then introduced into the high-frequency induction heated sintering system, shown schematically in reference [18]. The four major stages in the synthesis are as follows: The evacuation of the system to 40 mtorr (stage 1), the application of a uniaxial pressure of 80 MPa (stage 2), the activation of an induced current (frequency of about 50 kHz), which was maintained until densification was attained as indicated by a linear gauge measuring the shrinkage of the sample (stage 3). Temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature (stage 4). The process was carried out under a vacuum of 40 mtorr (5.3 Pa).

The relative densities of the sintered sample 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 scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations at a load of 10 kg and a dwell time of 15 s on the synthesized samples.

Results and Discussion

Fig. 1 shows XRD patterns of raw powders and milled 0.5Mo-0.5Ti-2Si powders. During the high energy ball milling, (Mo,Ti)Si₂ was not synthesized from the powders of 0.5Mo, 0.5Ti, and 2Si. Milling resulted in a significant reduction of the grain size of Mo, Ti, and Si. The average grain size of Mo, Ti, and Si measured by Suryanarayana and Grant Norton's formula [19] was about 54, 35 and 21 nm, respectively.

The interaction between these phases, i.e.,



is thermodynamically feasible.

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the synthesis and densification of (Mo,Ti)Si₂ are shown Fig. 2. As the induced current was applied the shrinkage displacement increased gradually with temperature up to about 550 °C, and then abruptly increased. When the reactant mixture of 0.5Mo + 0.5Ti + 2Si was heated

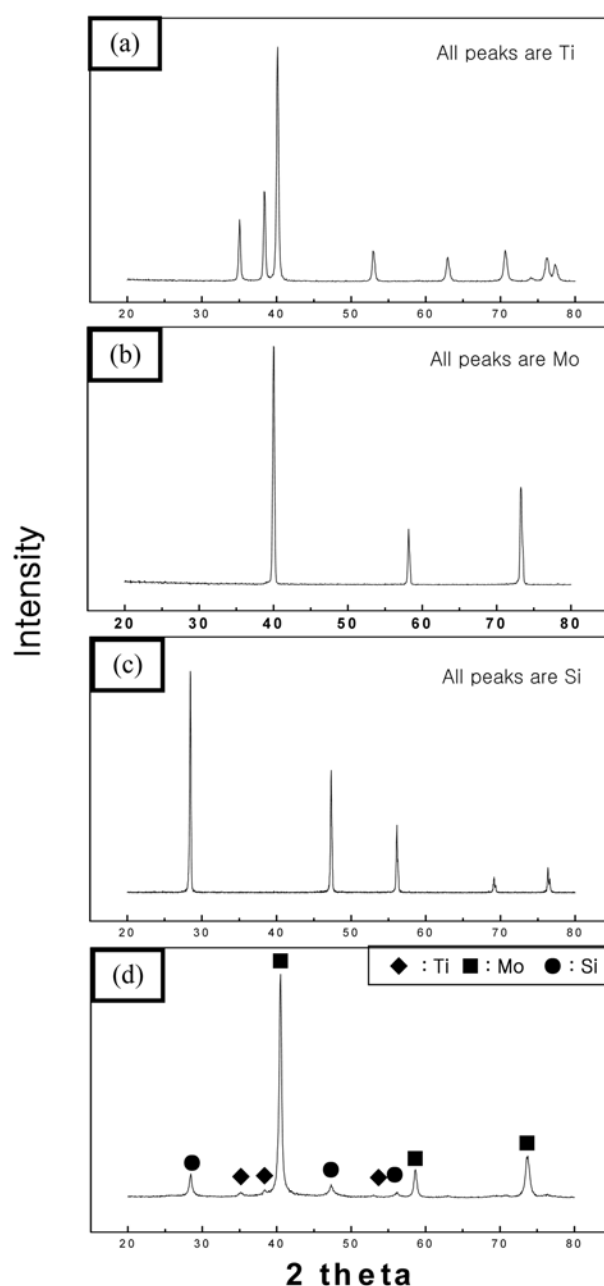


Fig. 1. XRD patterns of raw materials : (a) Ti, (b) Mo, (c) Si, (d) milled 0.5Mo-0.5Ti-2Si powder.

to 550 °C under a pressure of 80 MPa, no reaction took place as judged by the subsequent XRD analysis. Fig. 3 (a), (b), and (c) show the X-ray diffraction results of the powder after milling, the sample heated to 550 °C and the sample heated to 1080 °C, respectively. Fig. 3(a) and Fig. 3(b) exhibit only peaks pertaining to the reactants Mo, Ti and Si. However, when the temperature was raised to 1080 °C, the starting powders reacted with each other producing highly dense products of (Mo,Ti)Si₂. Fig. 4 shows a plot of $B_s \cos \theta$ versus $\sin \theta$ for (Mo,Ti)Si₂ to calculate grain size and strain from Suryanarayana and Grant Norton's formula [19]. The average grain sizes and strains of the sintered (Mo,Ti)Si₂ were determined as 46 nm and 0.0015,

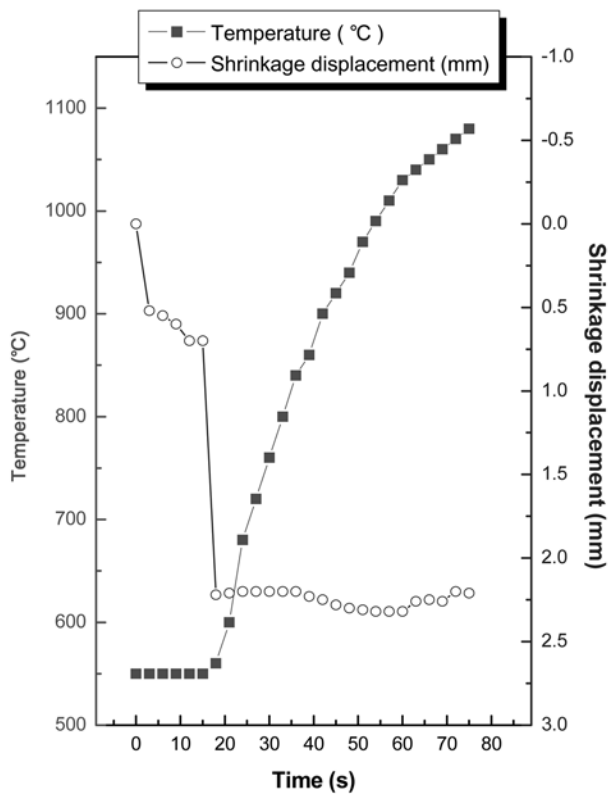


Fig. 2. Variations of temperature and shrinkage displacement with heating time during densification of (Mo,Ti)Si₂.

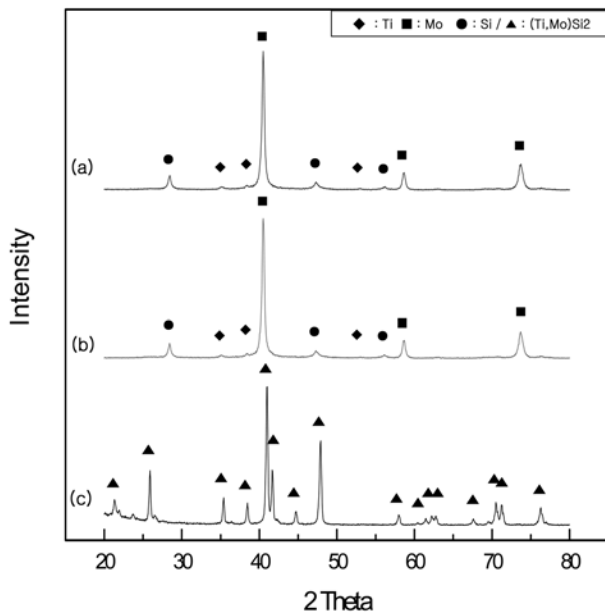


Fig. 3. XRD patterns of the 0.5Ti-0.5Mo-2Si system: (a) after milling, (b) after heating to 550 °C and (c) after sintering at 1080 °C.

respectively.

A FE-SEM image of the etched surface of the sample heated to 1080 °C under a pressure of 80 MPa is shown in Fig. 5. The microstructure consists of nanophases in FE-SEM image. The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density

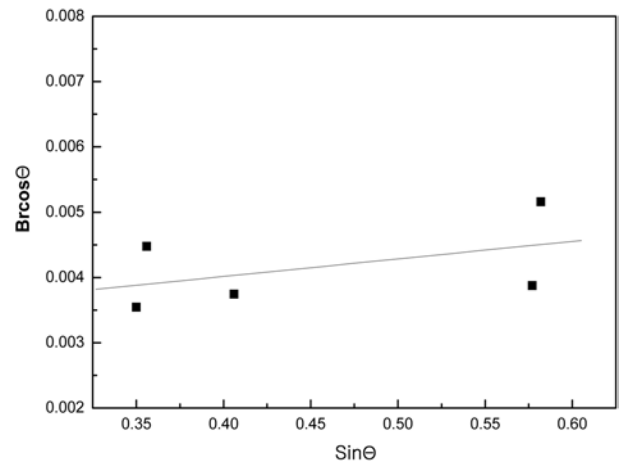


Fig. 4. Plot of $Brcos\theta$ versus $Sin\theta$ for (Mo,Ti)Si₂ sintered at 1080 °C.

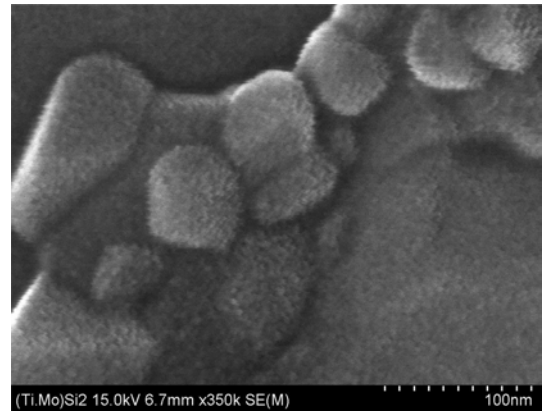


Fig. 5. FE-SEM image of (Mo,Ti)Si₂ sintered at 1080 °C.

resulting from the change in the molar volume associated with the formation of (Mo,Ti)Si₂ from the reactants (Mo, Ti and Si) and the consolidation of the product.

Vickers hardness measurements were made on polished sections of the (Mo,Ti)Si₂ using a 10 kg load and 15 s dwell time. The calculated hardness value of (Mo,Ti)Si₂ was 1020 kg/mm². This value represents an average of five measurements. Indentations with large enough loads produced median cracks around the indent. From the length of these cracks, the fracture toughness can be determined using an expression, proposed by Niihara *et al.* [20] :

$$K_{IC} = 0.023(c/a)^{-3/2} \cdot H_v \cdot a^{1/2} \quad (3)$$

where c is the trace length of the crack measured from the center of the indentation, a is half of the average length of two indent diagonals, and H_v is the hardness. The toughness values were derived from an average of five measurements. The toughness values obtained by this method of calculation is 3.5 MPa·m^{1/2}. These fracture toughness and hardness values of nanostructured (Mo,Ti)Si₂ are higher than those (fracture toughness; 2.58 MPa·m^{1/2} hardness; 8.7 Mpa) of micronstructured MoSi₂ [21]. A typical indentation pattern for the 10MoSi₂-SiC-Si₃N₄ composite is shown in Fig. 6(a). Typically, one to three additional cracks were observed

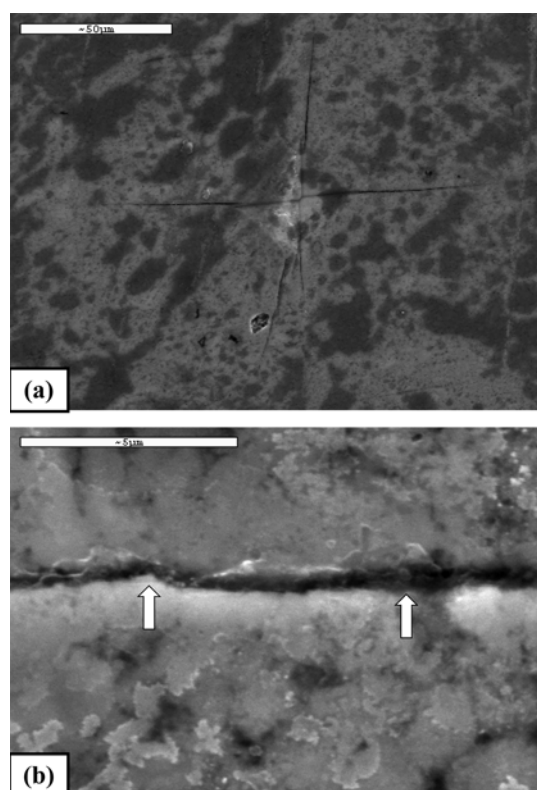


Fig. 6. (a) Vickers hardness indentation and (b) median crack propagating in (Mo,Ti)Si₂ compound.

to propagate from the indentation corner. A higher magnification view of the indentation median crack in the composite is shown in Fig. 6 (b). This shows the crack propagates defectively ($\uparrow$).

Summary

Nanopowders of Mo, Ti and Si were fabricated using high energy ball milling for 10 h. Using the high-frequency induction heated sintering method, (Mo,Ti)Si₂ was consolidated using the mechanically activated powders of 0.5Mo, 0.5Ti and 2Si within 2 minutes. The relative density of the composite was 97% for the applied pressure of 80 MPa. The average grain size and strain of (Mo,Ti)Si₂ prepared by this method were about 46nm and 0.0015, respectively. The average hardness and fracture toughness values obtained were 1020 kg/mm² and 3.5 MPa·m^{1/2}, respectively. These fracture toughness and hardness values of nanostructured (Mo,Ti)Si₂ are higher than those of monolithic MoSi₂.

Acknowledgements

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