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Rapid synthesis and consolidation of nanostructured $(Mo,W)Si_2$ by high-frequency induction heated sintering and its mechanical properties

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A dense nanostructured $(Mo,Ti)Si_2$ compound was simultaneously synthesized and sintered by the high frequency induction heating method within 2 minutes from mechanically activated powder of Mo, W and Si. A highly-dense $(Mo,Ti)Si_2$ compound was produced under simultaneous application of a 80 MPa pressure and the induced current. The mechanical properties and microstructure were investigated.

Key words: $(Mo,W)Si_2$, Mechanical properties, Sintering, Nanostructured materials.

Introduction

$MoSi_2$ 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 ºC), high modulus (440 GPa), good oxidation resistance in air, a relatively low density (6.24 g/cm^3) [1], and the ability to undergo plastic deformation above 1200 ºC [2]. Combined with good thermal and electric conductivities, these properties have led to the utilization of $MoSi_2$ as a heating element material in high-temperature furnaces operating in air up to about 1700 ºC [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 nanomaterials 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 $(Mo,W)Si_2$ (within 2 minutes) starting with high energy ball milled nanopowder. The mechanical properties and grain sizes of the resulting nanostructured $(Mo,W)Si_2$ 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 tungsten (< 0.5 μm, Daegu Tec. 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 (8 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]:

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

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after an instrumental correction; $B_{crystalline}$ and B_{strain} are the FWHM caused by the grain size and internal stress, respectively; k is a constant

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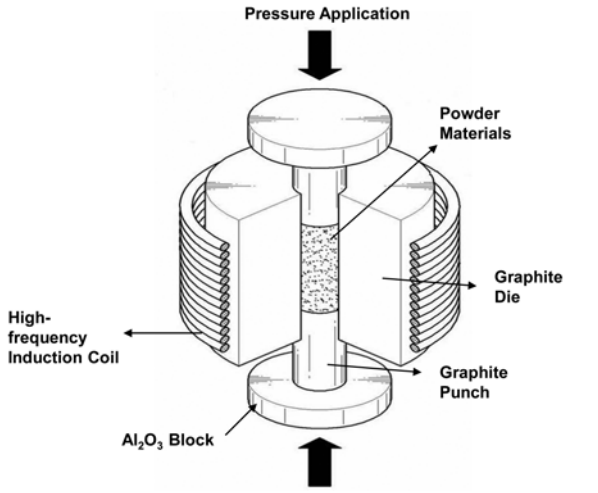

Fig. 1. Schematic diagram of the apparatus for high-frequency induction heating.

(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 = 45 mm, inside diameter = 20 mm, and height = 40 mm) and then introduced into the high-frequency induction heated sintering system, shown schematically in shown in Fig. 1. 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.%), HNO_3 (30 vol.%), and H_2O (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.

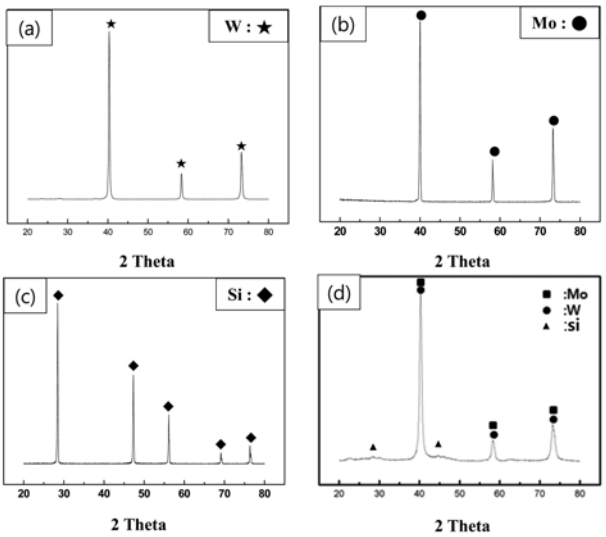

Fig. 2. XRD patterns of raw materials; (a) W, (b) Mo, (c) Si, (d) milled 0.5Mo-0.5W-2Si powders.

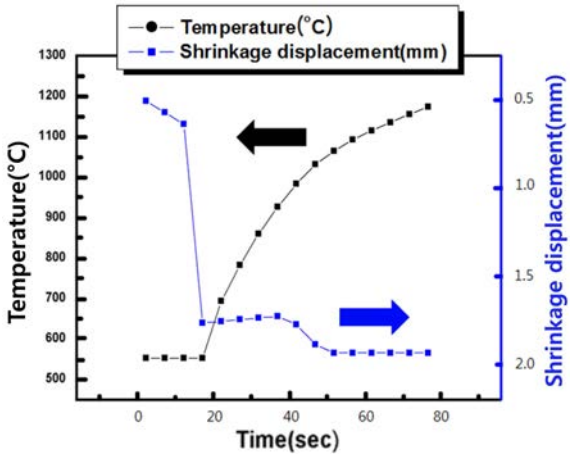

Fig. 3. Variations of temperature and shrinkage displacement with heating time during synthesis and densification of (Mo,W)Si_2.

Results and Discussion

Fig. 2 shows XRD patterns of raw powders and milled 0.5Mo-0.5W-2Si powders. In Fig. 2(d), Only Mo, W, and Si peaks were observed, as marked on the Fig. 2(d). 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 crystallize sizes became very fine by milling. The average grain size of Mo, and W measured by Suryanarayana and Grant Norton's formula [19] was about 32 nm, respectively.

The variations in shrinkage displacement and temperature of the surface of the graphite die with heating time during the synthesis and densification of (Mo,W)Si_2 are shown Fig. 3. As the induced current

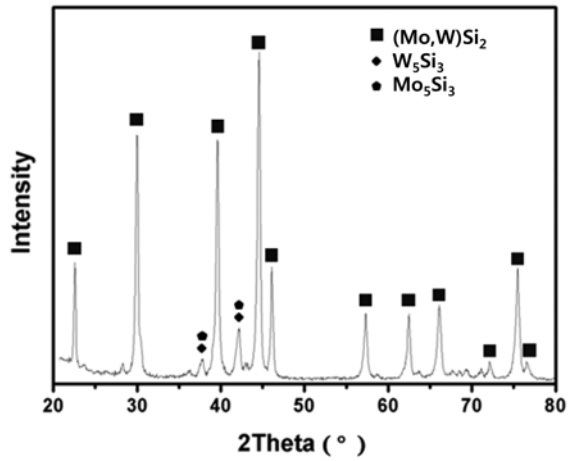

Fig. 4. XRD patterns of the specimen sintered at 11500 ºC from milled 0.5W-0.5Mo-2Si powders.

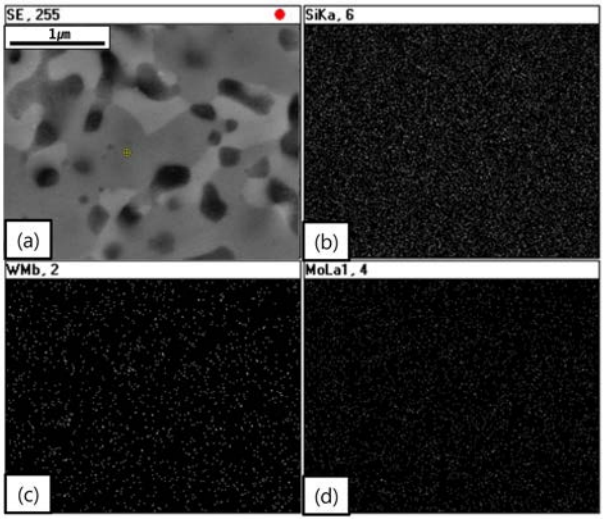

Fig. 5. FE-SEM image and X-ray mapping of (Mo,W)Si2 sintered at 11500 ºC.

was applied the shrinkage displacement increased gradually with temperature up to about 550 ºC, and then abruptly increased. Fig. 4 displays the XRD pattern of a specimen sintered at 1150 ºC from high-energy ball-milled 0.5Mo + 0.5W + 2Si powders. X-ray diffraction analyses of this sample showed peaks of $(Mo,W)Si_2$, as indicated in Fig. 4. And minor phases (Mo_5Si_3 and W_5Si_3) observed by X-ray diffraction analyses, as show in Fig. 4. The presence of Mo_5Si_3 and W_5Si_3 of the sample suggests a deficiency of Si. It is considered that this observation is related to entrapped oxygen in the pores of the interior portion of the sample during pressing or maybe due to a little oxidation of Si during the heating. The X-ray data (Fig. 2 and Fig. 4) suggest that the interaction between these phases, i.e.,

$$0.5Mo + 0.5W + 2Si \rightarrow (Mo,W)Si_2 \quad (2),$$

is thermodynamically feasible.

The average crystalline size of the sintered $(Mo,W)Si_2$ was determined as 80 nm from Suryanarayana and Grant Norton's formula [19]. A FE-SEM image and X-ray mapping of the etched surface of the sample heated to 1150 ºC under a pressure of 80 MPa is shown in Fig. 5. The microstructure consists of ultra fine phases (gray phase; A point, bright phase; B point, dark phase; C point) in FE-SEM image. The corresponding relative density was about 98%. Fig. 6 shows EDS analysis of A, B. and C point in Fig. 5. Only W, Mo, and Si peaks were detected. X-ray mappings of Mo, W, and Si were uniformly observed at the same point. The milling process is known to introduce impurities from the ball and/or container. However, in this study, peaks of Fe were not identified. The contents of W exists in bright phase (B point in Fig. 5) higher than those in dark phase (C point in Fig. 5). The contrast is due to mass effects.

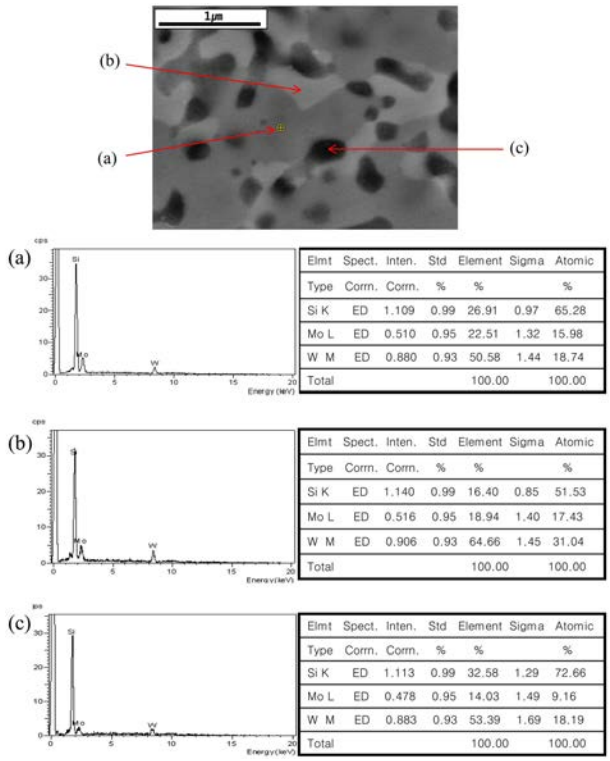

Fig. 6. EDS analysis of (Mo,W)Si2 sintered at 11500 ºC.

The abrupt increase in the shrinkage displacement at the ignition temperature is due to the increase in density resulting from the change in the molar volume associated with the formation of $(Mo,W)Si_2$ from the reactants (Mo, W and Si) and the consolidation of the product.

Vickers hardness measurements were made on polished sections of the $(Mo,W)Si_2$ using a 10 kg load and 15 s dwell time. The calculated hardness value of $(Mo,W)Si_2$ was 1296 kg/mm^2. 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,

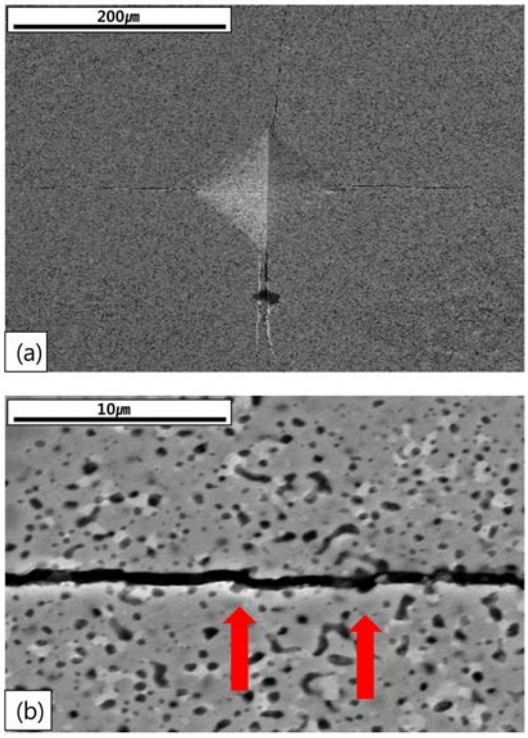

Fig. 7. (a) Vickers hardness indentation and (b) median crack propagating in (Mo,W)Si2 compound.

proposed by Niihara *et al*. [20]:

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

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 4.1 MPa · $m^{1/2}$. These fracture toughness and hardness values of nanostuctured (Mo,W)Si_2 are higher than those (fracture toughness; 2.58 MPa · $m^{1/2}$ hardness; 8.7 Mpa) of micronstuctured $MoSi_2$ [21]. A typical indentation pattern for the (Mo,W) Si_2 compound is shown in Fig. 7(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. 7(b). This shows the crack propagates deflectively (↑).

Summary

Nanopowders of Mo, W and Si were fabricated using high energy ball milling for 10 h. Using the high-frequency induction heated sintering method, (Mo,W)Si_2 was consolidated using the mechanically activated powders of 0.5 Mo, 0.5 W and 2 Si within 2 minutes. The relative density of the composite was 98% for the applied pressure of 80 MPa. The average crystalline size of (Mo,W)Si_2 prepared by this method were about 78 nm. The average hardness and fracture toughness values obtained were 1296 kg/mm^2 and 4.1 MPa · $m^{1/2}$, respectively. These fracture toughness and hardness values of nanostuctured (Mo,W)Si_2 are higher than those of monolithic $MoSi_2$.

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