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Letter

Low-temperature synthesis of α- and β-MoSi$_2$ powders using Na

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ABSTRACT

Molybdenum disilicide powders were prepared by heating a mixture of Mo and Si powders with Na metal. The single phases of β-MoSi$_2$ and α-MoSi$_2$ powders were obtained at 873 K and 1073 K, respectively. The preparation temperature of the single phase α-MoSi$_2$ powder was 500 K lower than that of the conventional solid state reaction method using Mo and Si powders. The grain size of both MoSi$_2$ powders was less than 2 μm, and their shape was angular and irregular.

1. Introduction

MoSi$_2$ and its composites are promising materials for high-temperature structural applications because of their high melting temperature (above 2173 K) and oxidation resistance [1–3]. Two crystallographic polytypes of MoSi$_2$ are known. The difference between the structures of both polytypes is in the stacking sequence of close-packed MoSi$_2$ layers. ABAB stacking is α-MoSi$_2$ (C11$_b$-type, tetragonal *I*4/*mmm*) and ABCABC stacking is β-MoSi$_2$ (C40-type, hexagonal *P*6$_2$22) [4].

α-MoSi$_2$ is conventionally synthesized by arc melting [5] or by siliciding molybdenum powders [6,7] or by combustion synthesis method [8,9]. The siliciding process requires high temperature above 1573 K in order to ensure a complete formation of α-MoSi$_2$ [6,7]. Recently, a mechanical alloying (MA) process has been applied to synthesize α-MoSi$_2$ powder at lower temperatures [10–13]. Although contamination from the milling media or from the gas environment is generally unavoidable in the MA process, the process combined a short duration high energy ball milling and low-temperature isothermal annealing or self-propagation high-temperature synthesis were applied successfully to prepare α-MoSi$_2$ powder and compact with high purity [13,14].

β-MoSi$_2$ powders have been prepared as mixtures with α-MoSi$_2$, Mo, or an amorphous phase by MA [8–10,13] and by plasma spray methods [15,16] under non-equilibrium conditions. β-MoSi$_2$ thin films were fabricated by annealing Mo and Si layers deposited on thermally oxidized Si wafers at 873 K [17], by annealing Mo films deposited on Si substrates at 773–963 K [18,19], and by As-ion implantation to Mo films deposited on Si substrates [20].

In our previous studies, powders and bulks of SiC and β-FeSi$_2$ were prepared from elemental sources with Na [21–24]. The preparation temperatures of SiC (900–1000 K) and β-FeSi$_2$ (773–1173 K) were lower than those of conventional synthesis methods. In the present study, we report low-temperature synthesis of α- and β-MoSi$_2$ powders by heating a mixture of Mo and Si powders with a piece of Na metal at 773–1173 K.

2. Experimental procedures

The mixture of Mo and Si powders which weighed to be in a molar ratio of Mo:Si = 1:2 (total mass: 115 mg, Mo powder: Nilaco, 99.9%, 2–5 μm, Si powder: Koujundo Kagaku, 99.999%, <75 μm) was loaded into a sintered BN crucible (φ6 × 13 mm in inner volume, Showa Denko, 99.5%) with and without 115 mg (5 mmol) of Na metal (Nippon Souda, 99.95%) in an Ar gas-filled glove box (MBraun, O$_2$, H$_2$O <1 ppm). The crucible was sealed in a stainless steel tube (SUS316, an inner diameter of 11 mm, a length of 80 mm) with stainless steel caps as shown in Fig. 1 in the glove box.

The tube was heated to predetermined temperatures (773–1173 K) for 12 h with an electric furnace. After heating, the sample was cooled in the furnace by shutting off the electric power to the furnace. The stainless steel tube was cut in the globe box and the sample was taken out of the tube. The Na left in the crucible was removed by reaction with 2-propanol and ethanol at ambient temperature.

The crystalline phases in the prepared samples were identified by powder X-ray diffraction (XRD; Rigaku Co., RINT-2200) with pyrolitic graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). The morphology of the samples was observed with a scanning electron microscope (SEM; Philips, ESEM XL30). The elements of Mo, Si, and Na in the sample were analyzed by using inductively coupled plasma optical emission spectroscopy (ICP-OES).

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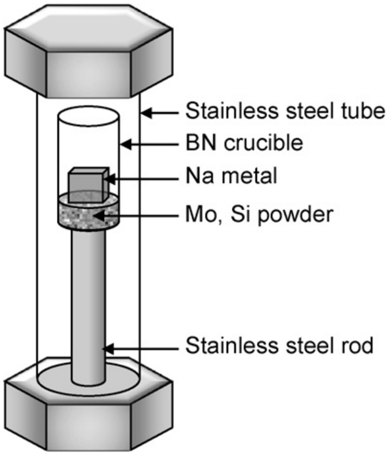

Fig. 1. Schematic drawing of the container for $MoSi_2$ powder synthesis.

3. Results and discussion

Fig. 2 shows the XRD patterns of the powder samples prepared by heating the mixture of Mo and Si without Na at 1173 and 1073 K for 12 h. The source materials of Mo and Si were the main phases and small amounts of Mo_5Si_3 and α-$MoSi_2$ were present in the sample prepared at 1173 K. Weak peaks observed at 25.8°, 34.4°, 39.5°, and 52.1° in the XRD patterns did not correspond to the source materials and their oxide phases. Molybdenum disilicide was not formed at 1073 K and below this temperature.

The XRD patterns of the samples prepared by heating a mixture of Mo and Si with Na from 773 to 1173 K are shown in Fig. 3. The main phase in the sample obtained at 1173 K was α-$MoSi_2$ but a small amount of Mo_5Si_3 was also formed. Only the single phase of α-$MoSi_2$ was synthesized at 1073 K. The samples prepared at 973 and 923 K were a mixture of α-$MoSi_2$ and β-$MoSi_2$. Only the single phase of β-$MoSi_2$ was obtained at 873 K. No reaction was occurred at 773 K. The molar ratios of Mo:Si confirmed by ICP-OES for the single phase powders of α-$MoSi_2$ and β-$MoSi_2$ were 1:1.99(1) and 1:2.00(5), respectively. These ratios indicated the stoichiometry of $MoSi_2$ within the standard deviations. 0.28 and 0.08 at.% of Na were detected in the powders of α-$MoSi_2$ and β-$MoSi_2$, respectively.

The powder XRD pattern of α-$MoSi_2$ obtained at 1073 K was analyzed by the Rietveld method with the program RIETAN-FP [25]. The crystal structure of α-$MoSi_2$ reported by Harada et al. [26] was used as the initial model. The *R*-indexes of the analysis were 0.1068 (R_{wp}) and 0.0068 (R_F). The refined lattice parameters (tetragonal $a = 3.20453(4)$ and $c = 7.84712(10)$ Å) almost agreed with the reported ones ($a = 3.2064(2)$ and $c = 7.8478(8)$ Å [26]).

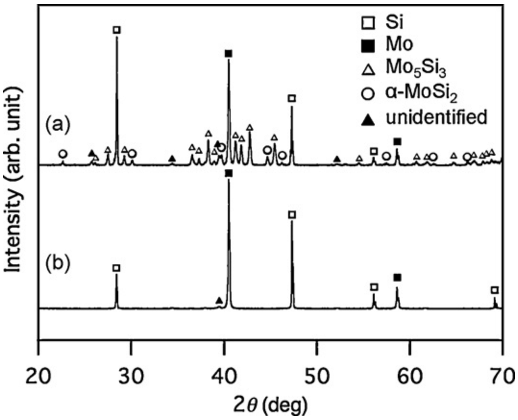

Fig. 2. Powder XRD patterns of the samples prepared by heating the mixture of Mo and Si without Na at 1173 K (a) and 1073 K (b) for 12 h.

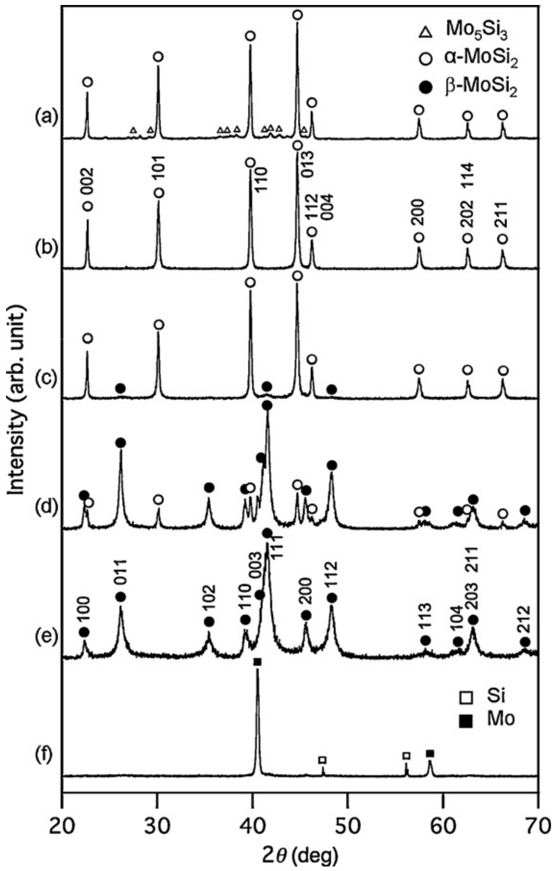

Fig. 3. Powder XRD patterns of the samples prepared by heating the mixture of Mo and Si with Na at 1173 K (a), 1073 K (b), 973 K (c), 923 K (d), 873 K (e), and 773 K (f) for 12 h.

A mixture of α- and β-$MoSi_2$ has been prepared by plasma spray [15]. The hexagonal lattice parameters of β-$MoSi_2$ in the mixture were $a = 4.61$ and $c = 6.55$ Å. The lattice parameters of β-$MoSi_2$ prepared by As-ion implantation through the Mo film deposited on a Si substrate were $a = 4.613$ and $c = 6.424$ Å [20]. These lattice parameters were close to those measured for the β-$MoSi_2$ single phase powder prepared with Na at 873 K ($a = 4.5979(3)$ and $c = 6.5721(5)$ Å). The relative XRD peak intensities could be explained with a disordered model derived from the enantiomorphic structure of β-$MoSi_2$ [4].

Deevi observed no chemical reaction between Mo and Si powders by hot pressing at 1473 K and 24 MPa [6]. α-$MoSi_2$ was synthesized by heating at and above 1573 K in his experiment. Angelescu reported the preparation of α-$MoSi_2$ by solid-state reaction at and above 1573 K, and no reaction below 1373 K [7]. The temperature of α-$MoSi_2$ formation in the present study was 923 K, and 650 K lower than the temperatures in the previous studies. According to the phase diagram of the Na–Si system [27], Na content of the liquid phase ranges from 50 to about 85% at and over 953 K, and the liquidus temperature decreases from 953 to 368 K with increasing Na content from 85 to 100%. Since the solubility of Mo in liquid Na is negligibly small, for example, less than 0.5 ppm at 800 °C [28], α- and β-$MoSi_2$ powders were formed by a reaction between Mo grains and Si dissolved

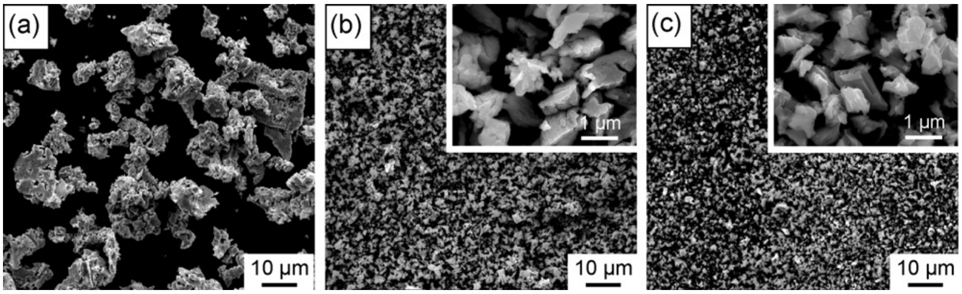

Fig. 4. Scanning electron micrograph images of the Mo source powder (a), α-$MoSi_2$ powder (b), and β-$MoSi_2$ powder (c).

in the Na–Si melt at the solid–liquid interface as the intermetallic phases, followed by diffusion of Si across the formed $MoSi_2$ layer.

The as-sprayed samples prepared by plasma spraying were mixture of α-, β-$MoSi_2$, and Mo_5Si_3. [15,16]. Thermal annealing the sample powders above 973 K resulted in an irreversible transformation from β-$MoSi_2$ to α-$MoSi_2$ [16]. The exothermic irreversible transition from β- to α-$MoSi_2$ has been observed for the mixture at around 1110 K [15]. In the present study, the highest temperature at which β-$MoSi_2$ was contained in the samples was 973 K, which is in accordance with the irreversible transition temperatures of the previous reports.

The SEM micrographs of the Mo powder used for the starting material and the single phase α-$MoSi_2$ and β-$MoSi_2$ powders prepared at 1073 and 873 K are shown in Fig. 4. The grain size of the source Mo powder was 5–20 µm. The morphology of the α-$MoSi_2$ and β-$MoSi_2$ grains was irregular and angular. The grain sizes of these powders were less than 2 µm, and smaller than that of the Mo source powder. It suggests that the Mo grains were fractured due to the stress induced by the volume expansion from Mo to $MoSi_2$.

To our knowledge, single phase of β-$MoSi_2$ powders has not been obtained and the property has not been characterized in the previous studies. Preparation of bulk β-$MoSi_2$ is in progress for the characterization.

4. Conclusions

We have synthesized α- and β-$MoSi_2$ powders by heating a mixture of Mo and Si powders with Na. The XRD, SEM, and EDX results showed that α- and β-$MoSi_2$ powders, which were of angular and irregular morphology with a grain size of less than 2 µm, were obtained at 923–1173 K and 873–973 K, respectively. The $MoSi_2$ powders had the 1:2 stoichiometric ratio and the Na contamination in the powders was less than 0.3 at.%.

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