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NaF-assisted combustion synthesis of $MoSi_2$ nanoparticles and their densification behavior

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ABSTRACT

The exothermic reduction of oxides mixture (MoO_3+2SiO_2) by magnesium in NaF melt enables the synthesis of nanocrystalline $MoSi_2$ powders in near-quantitative yields. The combustion wave with temperature of about 1000–1200 °C was recorded in highly diluted by NaF starting mixtures. The by-products of combustion reaction (NaF and MgO) were subsequently removed by leaching with acid and washing with water. The as-prepared $MoSi_2$ nanopowder composed of spherical and dendritic shape particles was consolidated using the spark plasma sintering method at 1200–1500 °C and 50 MPa for 10 min. The result was dense compacts (98.6% theoretical density) possessing submicron grains and exhibiting hardness of 8.74–12.92 GPa.

1. Introduction

Because $MoSi_2$ has attractive properties such as a high melting point, low electrical resistance, superior high-temperature stability and strength, and low density, it has already been used as a heating element and high-temperature protective coating, and has been studied for applications not only as high-temperature structural material, but also as gate electrodes, interconnects, and diffusion barriers in microelectronic devices [1–6].

The commercial processes for producing $MoSi_2$ powders are arc melting or siliciding of molybdenum powders [7,8]. Mechanical alloying of Mo-Si mixtures by energized ball-mill system [9–15] and combustion synthesis [16–21] can be considered alternative methods for $MoSi_2$ synthesis. Like for other intermetallics, the refinement of the grain size of $MoSi_2$ to nanometer dimensions is predicted [22,23] to improve ductility, fracture toughness, and strength by inducing fundamental changes in the strengthening and deformation mechanisms. Therefore, $MoSi_2$ nanopowder is needed first as a precursor, for preparation of compact materials of fine grain size.

Before the present work, $MoSi_2$ nanopowder was prepared using the sonochemical synthesis method [24]. With this method co-reduction of $MoCl_5$ and $SiCl_4$ with NaK alloys in hexane was carried out using 600 W of irradiation at 20 kHz. The precipitate was annealed at 900 °C, and 16–31 nm size $MoSi_2$ nanoparticles was obtained. Preparation of nanocrystalline $MoSi_2$ using a chlorine-transfer reaction between $MoCl_3$ and Si at 500 °C has been reported to be useful for fabrication of dense compact with 95 wt% theoretical density [25]. A known route to preparation of nanocrystalline $MoSi_2$ powder is the mechanical alloying of silicon and molybdenum [26,27]. In this technique α-$MoSi_2$ nanoparticles were obtained after more than 30 h of milling time. Each synthesis approach for nanocrystalline $MoSi_2$ synthesis is scientifically attractive, and each of them has particular advantages and disadvantages. Even do with a large variety of existing approaches, the development of a process that can produce good sinterability $MoSi_2$ nanopowders in a simple manner and a low-cost would be always welcomed.

Recently we reported the synthesis of $MoSi_2$ fine powders using a combustion synthesis approach [28]. We investigated the synthesis of $MoSi_2$ powders from a MoO_3+SiO_2+Mg system diluted with NaCl. The $MoSi_2$ particle size produced by the combustion reaction was 100–500 nm, and the specific surface area was 25–30 m^2/g. A very similar investigation was performed by Vershinnikov et al. [29,30] who suggested basic principles for fabrication of fine $MoSi_2$ powders by SHS process with a reduction stage. Also investigated was the influence

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of green composition, stoichiometric ratio, inert NaCl additive, and synthesis conditions on the structure/properties of thus-fabricated $MoSi_2$ powders. With increasing NaCl, the mean size of the $MoSi_2$ crystallites was found to decrease. The fabricated $MoSi_2$ powders represented agglomerates formed by crowds of smaller (200 nm) and larger (up to 1–3 μm) particles. The powders were characterized using SEM, XRD, and chemical analysis.

This article is a continuation of our previous report which pinpointed the synthesis of nanocrystalline $MoSi_2$ using NaCl diluent. Here, a new development in the synthesis and characterization of $MoSi_2$ nanocrystallites in molten NaF medium is made. Moreover, we investigated the consolidation behavior of nanopowders in the temperature range 1200–1500 °C, using the spark plasma sintering (SPS) method. The densities and Vickers hardness for the consolidated specimens were also determined and discussed within the context of data from the literature.

The choice of NaF as a flux compared to earlier used NaCl, was conditioned by the following circumstances:

1. NaF has a higher melting point (991 °C) than NaCl (810 °C) and this temperature difference may affect not only on the combustion characteristics, but also on the depth of combustion reaction. As reported in [28] $MoSi_2$ powder synthesized with NaCl flux contain a visible portion of Mo_5Si_3 phase in all diapason of NaCl concentration. We believe that the presence of Mo_5Si_3 in the final product was related to the low melting point of NaCl, i.e. the melting of NaCl in the early stages of combustion reaction limits the reactivity of the reaction species leaving behind secondary phases in the final product. Therefore, the substitution of NaCl by NaF may contribute to the compositional improvement of the final product.
2. The $MoSi_2$ powders synthesized with NaF and NaCl salts can differ essentially in the shape and size and this difference may reflect on its densification behavior. Such a phenomenon was described in our early reports [31] devoted on the synthesis of WC nanopowders.

2. Experimental

2.1. Materials

The chemicals used were: MoO_3 (purity 99.5%, particle size 0.2–0.3 μm, Daejung Chemicals, Korea), SiO_2 powder (purity 98.5%, particle size: 0.5–1.0 μm, Samchun Chemicals, Korea), Mg powder (purity 99%, particle size: 50–200 μm, Samchun Chemicals, Korea), and NaF powder (purity 97%, particle size: 50–100 μm, Samchun Chemicals, Korea).

2.2. Sample preparation and synthesis procedure

In a typical experiment, 28.8 g MoO_3, 36 g SiO_2, 48.2 g Mg, and 73.6–134.4 g NaF (k=12–16) were hand mixed in a ceramic mortar for about 10–15 min and compacted by hand into a paper cup (diameter: 4.0 cm, height: 8–9 cm). During compaction, two Λ-shaped tungsten-rhenium thermocouples (W*R*-26/W*R*-5), 100 μm in diameter, were placed inside the sample near its center. The individual thermocouples were coated with a thin layer of Al_2O_3 (~5–10 μm) to increase their resistance to oxidation and to avoid possible interactions between the thermocouples and the powder bed at elevated temperatures. Approximately 2–3 g of Ti +0.9 C (black soot) +0.1$[(C_2F_4)_n]$ was placed on top of the reaction sample as an ignition agent. The cup containing the reaction mixture and thermocouples was subsequently placed under a nickel/chromium coil in a combustion chamber (Fig. 1, (1)). The reactor was tightly closed and the air was pumped out using a vacuum pump, after which it was filled with argon to a pressure of 2.0 MPa (Fig. 1, (2)). Local ignition of the reaction sample was achieved within 1–2 s using a nickel-chromium filament electrically heated to 900–1000 °C (Fig. 1, (3)). A computer-assisted data logger (GL100A, Graphtec Co., Japan) continuously recorded the temperature–time history of the process at a rate of 10 Hz (Fig. 1, (4)).

The surface layer of the combusted sample was mechanically removed, and the remaining sample was ground by hand and put into a 500-mL beaker for acid leaching. The reaction by-products (MgO and NaF) were dissolved in diluted HCl (pH ≤2.0) at room temperature for 5–10 min. Then, the acid-leached powder was washed with distilled water, rinsed with ethanol, and dried at 80–100 °C.

2.3. Characterization of the $MoSi_2$ powders

The crystal structures and morphologies of the final powders were characterized using an X-ray diffractometer with Cu Kα radiation (X′Pert PRO, Panalytical), a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F), and transmission electron microscope (JEOL JEM-2100, Japan) with an accelerating voltage of 200 kV. Raman scattering spectra were obtained at room temperature using a Horiba Jobin Yvon LABRAM-HR800 laser micro-Raman spectrometer with a 514-nm laser.

2.4. Spark plasma Sintering (SPS)

$MoSi_2$ samples 10 mm in diameter were sintered using the Spark-Plasma Sintering (SPS) technique at 1200–1500 °C with 50 MPa of applied pressure, without sintering additive. The rate of temperature increase was 100 °C/min, and the dwell time, 10 min

2.5. Metallographic and mechanical characterization of $MoSi_2$ compacts

$MoSi_2$ samples mounted in epoxy-resin were subjected to a standard metallographic procedure, which included polishing with 200, 400, 800, 1200, 1500, 2000, 3000, and 4000 SiC papers; after which samples were polished with diamond suspensions of 9, 3, and 1 μm particle sizes. The samples were next etched with Kroll's reagent (10 mL of HF, 30 mL of HNO_3, and 50 mL of water, ASTM E407) for 5–10 s. Hardness testing of the material was carried out using a Vickers hardness tester (JP/FM-7) on the xy-plane with a load of 1000 gf and a dwell time of 10 s. The densities of SPS sintered samples were determined from the measured masses and the known volume of the pycnometer.

3. Results and discussion

3.1. Adiabatic temperatures and equilibrium phases

Thermodynamic simulation of the MoO_3+2SiO_2+7Mg+kNaF system was performed using the program Thermo [32] which predicted 2557 °C for the undiluted system (k=0) (Fig. 2a). The addition of NaF decreased the combustion temperature. For instance, T_{ad} can be decreased from 2557 to 1000 °C by using 16 mol of NaF. When, less than 5 mol of NaF was applied, the T_{ad} remained over 2000 °C and a number of secondary phases, such as Na (gas), Mg (gas), SiO (gas), Mo_5Si_3 (liquid) and Mg_2SiO_4 (liquid) could be detected along with the main reaction phases ($MoSi_2$, MgO, and NaF). Hence, the use of the range 0–5 mol for k is not preferable for the experiments. The most favorable temperature region for producing $MoSi_2$ nanocrystals is 1000–1500 °C, and this can be reached when k is > 10 mol. The range of k was further refined for performing the combustion experiments. Also, the calculation result indicates that within the specified interval of k, T_{ad} is always higher than the melting point of NaF (993 °C); hence, all chemical reactions are expected to be done within molten NaF medium.