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A novel process to prepare $MoSi_2$ by reaction between MoS_2 and Si

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ABSTRACT

In this study, a thermodynamic analysis of the reaction between MoS_2 and Si was performed, which indicated that when the molar ratio of MoS_2 to Si is 1:4, the final products were composed of SiS and $MoSi_2$, without other solid phases, in the temperatures range of 0 °C–1700 °C. The reaction between MoS_2 and Si powders with a MoS_2/Si molar ratio of 1:4 was investigated in the range of 800 °C–1600 °C. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the phase composition and microstructure of the products, respectively. The content of sulfur in $MoSi_2$ product was measured using an infrared carbon-sulfur analyzer. It was found that pure $MoSi_2$ can be successfully synthesized in the temperature range of 1100 °C–1600 °C after reacting for 2 h with very little sulfur residual. Meanwhile, gaseous SiS was also generated and escaped from the $MoSi_2$. It was also found that the reaction rate between MoS_2 and Si was very slow at 800 °C and 900 °C. The microstructural analyses indicated that grain size of the $MoSi_2$ product increased with increasing temperature.

1. Introduction

$MoSi_2$ has received considerable attention as a high-temperature structural material due to its promising properties, such as: high melting point (2030 °C), high electrical conductivity, rather low density (about 6.24 g/cm^3), high thermal and electrical resistance, as well as outstanding oxidation resistance in air or in a combustion gas environment at high temperature, because of the formation of a thin coherent, adherent, and protective silica layer above 1200 °C. Because of these outstanding properties, $MoSi_2$ and its composites are applied in a wide range of fields in the industrial, aerospace and automotive arenas, such as heating elements for furnaces, coating, turbine airfoils, combustion chamber components in oxidizing environments, missile nozzles, molten metal lances, industrial gas burners, diesel engine glow plugs, and materials for glass processing [1–8].

$MoSi_2$ can be synthesized using different techniques, including Self-propagating High-temperature Synthesis (SHS), mechanical alloying (MA), hot pressing, reaction bonding, and sintering. Synthesis of $MoSi_2$ via these methods was attempted in a number of investigations [9–14]. Angelescu [11] synthesized $MoSi_2$ using Mo and Si powders with a Si/Mo atomic ratio of 2 using the sintering method at 1100 °C–1550 °C. It was found that $MoSi_2$ formation was initiated in the range of 1100 °C–1300 °C, but in the range of 1300 °C–1400 °C, impurities of Mo_5Si_3 and $MoSi_{0.65}$ were found to exist in the final product. It was concluded that $MoSi_2$ should be synthesized at over 1500 °C for several hours. However, the main raw materials used in these methods are usually pure Mo and Si powders, and Mo powder is expensive due to its long manufacturing process. Molybdenite concentrate is an essential ore mineral of the molybdenum industry for the production of molybdenum [15]. Firstly, molybdenite concentrate is oxidation roasted to commercial molybdenum oxides. Secondly, the commercial molybdenum oxides are prepared to be ammonium molybdate via ammonia leaching. Thirdly, the ammonium molybdate is oxidation roasted to generate pure MoO_3. Finally, pure MoO_3 is reduced to MoO_2 and then to Mo by H_2 [15–20]. As discussed above, the preparation of Mo is complicated and involves high-energy consumption, resulting in a relatively high cost. On the contrary, the cost of pure MoS_2 powder, which can be prepared from molybdenite concentrate after acid leaching, is much lower than that of pure Mo powder. Therefore, it will be both energy and cost saving if MoS_2 can be directly used as the molybdenum source to prepare $MoSi_2$. In this paper, $MoSi_2$ was synthesized by roasting a mixture of MoS_2 and Si powder in the temperature range of 800 °C–1600 °C. The phase compositions, sulfur content, and microstructure of the products were studied by X-ray diffraction (XRD), an infrared carbon-sulfur analyzer and scanning electron microscope (SEM), respectively.

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2. Experimental procedure

The raw materials powders used in the present study were Molybdenum disulfide (MoS_2) with a purity of 98%, manufactured by Sinopharm Chemical Reagent Co., Ltd., and silicon (Si) with a purity of 99.99%, manufactured by China New Metal Materials Technology Co., Ltd. The mixture of Si and MoS_2 powders were prepared with a MoS_2/Si molar ratio of 1:4. Fig. 1 shows the X-ray diffraction patterns and the SEM micrographs of the mixture. In order to obtain a product with homogeneous composition, the powders were thoroughly mixed in agate mortar in a slurry state by adding alcohol. After thorough mixing, the slurry was dried. Then as-mixed powders were pressed into a stainless steel die with a uniaxial charge of about 192 MPa to be cold-pressed into cylindrical compacts, approximately 18 mm in diameter, and 7.5 mm in height. The weight of each sample disk was about 5 g.

Fig. 2 shows the schematic diagram of the apparatus. Alumina crucibles 30 mm in diameter and 25 mm in height were used. In each experimental run, a sample was weighed and put into the alumina crucible. When the crucible with a sample was placed in the furnace, argon was introduced into the system to drive air out. The furnace was heated from room temperature to the desired temperature at a heating rate of 5 °C/min, under an argon atmosphere. After reacting for certain time at the specified temperature, the furnace was cooled to room temperature in an argon atmosphere. At room temperature, the obtained samples in the crucibles were weighed again. The gas product was cooled to solid phase and collected in a glass bottle.

The binary phase diagram of the Si-MoS_2 system and the changes of Gibbs free energy for reaction (1) and reaction (2) were calculated using the commercial software Factsage 6.4. The mass of the samples was measured using an electronic balance with a sensitivity of ±1 mg. The content of sulfur in the product was measured using the infrared carbon-sulfur analyzer (CS-2008, NCS). The products were characterized via XRD (Model TTRIII, Japan) and SEM (Zeiss Supra 55), respectively.

3. Results and discussion

3.1. Thermodynamic analyses

Fig. 3 shows the binary phase diagram of the Si-MoS_2 system calculated by Factsage 6.4. It can be seen from Fig. 3 that the reaction between Si and MoS_2 can result in the formation of two silicide compounds, $MoSi_2$ and Mo_5Si_3, and only one sulfide compound, SiS, in the temperatures range of 0 °C–1700 °C. It is apparent that Mo_5Si_3 with lower silicon content is a thermodynamically stable phase while at a higher silicon addition the Mo_5Si_3 phase disappears. In the presence of excess silicon, Mo_5Si_3 converts to $MoSi_2$ [21]. From Fig. 3, it can also be concluded that only when the molar ratio of MoS_2 to Si is 1:4 the composition of the product will be only SiS and $MoSi_2$ without any other solid phases. When the temperature reaches 1363 °C solid SiS sublimates directly to the gas phase and escapes from the product, which provides the foundation for the separation of $MoSi_2$ and SiS to produce pure $MoSi_2$.

The phase diagram suggests that the formation of $MoSi_2$ and SiS with a molar ratio of MoS_2 to Si of 1:4 is based on the following

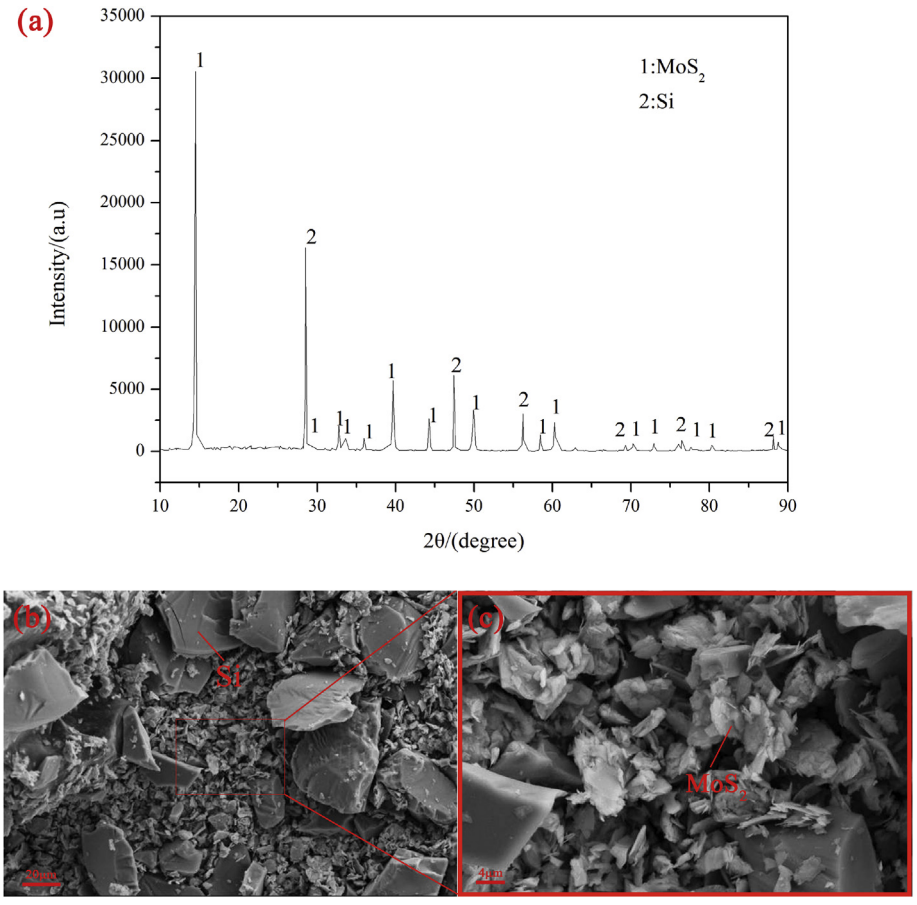

Fig. 1. XRD patterns and SEM micrographs of raw 4Si + MoS_2 mixture: (a) XRD patterns, and (b)–(c) SEM micrographs.