

## The influence of starting powder characteristics on the performance of MoSi<sub>2</sub>-based heating elements

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The influence of starting powder characteristics, involving purity and particle size, on the properties and performance of MoSi<sub>2</sub>-based heating elements was investigated in this study. Compared to a fine powder, densification of the green rods with a coarse powder should be carried out at a higher temperature. This creates a Mo<sub>5</sub>Si<sub>3</sub> layer with a poor capability of a protective SiO<sub>2</sub> film formation on the surface. Another negative impact of the high densification temperature is that the rods cannot be bent to a U-shape due to the coarse crystal size. The critical damage temperature of a heating element is significantly influenced by the purity of the starting powder. Impurities will deteriorate the performance of a heating element by decreasing the critical damage temperature.

**Key words:** Purity, Particle size, Film formation, Hot bending, Performance.

### Introduction

Molybdenum disilicide (MoSi<sub>2</sub>), a high-melting-point (2030 °C) material with moderate density (6.24 g/cm<sup>3</sup>), possesses a combination of properties of a metal and a ceramic [1-3]. It has been employed in heating elements since 1956 due to the good heat and electrical conductivity as well as excellent oxidation and corrosion resistance [4]. With an increasing interest in electric heating, MoSi<sub>2</sub>-based heating elements are widely used in steel, glass, ceramic and engineering industries in either controlled atmospheres or air. The recent Kanthal Super 1900 can operate at an element temperature of 1850 °C in an oxidizing atmosphere [5].

Metallurgical technology is the practical manufacturing method of MoSi<sub>2</sub>-based heating elements in industry. The starting MoSi<sub>2</sub> powder is mixed with a certain volume percentage of aluminosilicate to form a paste, which is then extruded into rods with various diameters for terminal and heating zone applications [6]. The MoSi<sub>2</sub> powder is synthesized by igniting Mo-Si mixture compacts - a method known as combustion synthesis or self-propagating high-temperature synthesis (SHS) [7]. Being the predominant component, the starting MoSi<sub>2</sub> powder characteristics certainly have an impact on the performance of the heating element.

In this study, MoSi<sub>2</sub>-based heating elements were prepared starting with various MoSi<sub>2</sub> powders: fine with a high purity (FH), coarse with a high purity (CH) and fine with a low purity (FL). A comparative

investigation was carried out to clarify the effect of the purity and grain size of the MoSi<sub>2</sub> powder on the performance of heating elements. Specifically, the performance involves the capability of forming a protective scale, the feasibility of hot-bend processing, and the critical damage temperature.

### Experimental Procedure

#### MoSi<sub>2</sub> powder synthesis

3N Si (99.9%, < 43 μm) and industrial Si (98.5%, < 43 μm) powder together with elemental Mo (99.5% pure, 2–4 μm) powder were used as starting materials for synthesizing high and low purity MoSi<sub>2</sub>, respectively. Mixtures at an atomic Mo : Si mole ratio of 1 : 2 were mixed in a ball mill for 2 hours. Cylinder-shaped pellets with diameter of Ø150 mm were pressed under a pressure of 100 MPa and then transferred into a sealed combustion chamber. Subsequently, hydrogen was continuously flowed into the chamber from the bottom and emitted from the top, followed by the combustion treatment. After hydrogen flowed for 5 minutes, the pellet was ignited by heating its top surface with an incandescent tungsten coil. Hydrogen introduction was not stopped until the chamber was cooled down to ambient temperature. The low purity product was crushed into 2 μm powder whereas the high purity product into 2 μm and 20 μm powders by ball-milling in acetone. Phase identification was carried out using a D/max 2500V X-ray Diffractometer (XRD) with CuK<sub>α</sub> radiation (Rigaku, Japan). The elemental composition was analyzed with a PW2404 X-ray fluorescent spectrometer (XRF) (Philips, Holland). The particle size distribution of the crushed powders was measured with a Cilas 1090 particle size analyser (Cilas, France).

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### Preparation of heating elements

To achieve a homogeneous distribution of the components, the MoSi<sub>2</sub> powders were blended with 5 wt.% aluminosilicate of Na-Montmorillonite powder from Kunimine (JP) in a twin-screw mixer for 2 hours. The compound was then kneaded together with deionized water to form a paste suitable for extrusion. Straight rods with diameters of Ø14.2 mm and Ø6.9 mm were prepared by extruding for applications of terminal sections and heating zones, respectively. Afterwards, the rods were processed by drying, sintering, filming, hot-bending and welding in turn to fabricate heating elements for evaluation.

### Performance evaluation

With deionized water as the immersion medium, the bulk density of the sintered rods was measured by means of the Archimedes method. The rods are qualified for fabricating heating elements only when the bulk density reaches 5.60 g/cm<sup>3</sup> at least. Microstructural observations on the mechanically-polished cross-sections of the rods were performed with an optical microscope (STM6, Olympus, JP) and SEM (JSM-6700F, JEOL, JP). The flexural strength of the sintered rods covered with SiO<sub>2</sub> scale was tested using a three-point bending method (Instron-5566 universal testing machine, UK) and the strength distribution was characterized with a Weibull modulus.

The as-prepared heating elements were installed into a box furnace to elevate the furnace up to a working temperature and maintain at that point for 600 minutes. The initial working temperature was set at 1600 °C, increasing by 10 °C each time until damage of the protective scale occurred. The critical damage temperature is defined as an indicator of the performance of the heating elements.

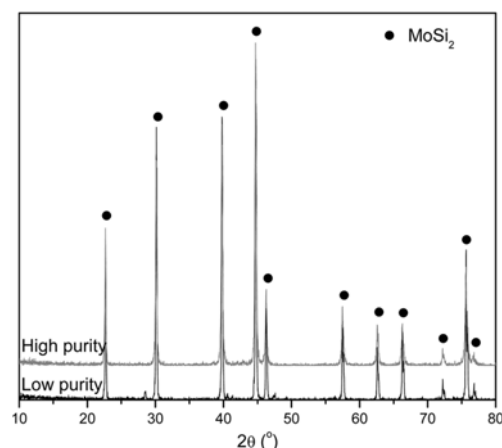
## Results and Discussion

The XRF analysis results of the synthesized MoSi<sub>2</sub> specimens are listed in Table 1. It can be seen that the main elemental impurities in low-purity MoSi<sub>2</sub> are Al and Fe. XRD patterns indicate the major phase is monolithic C11b MoSi<sub>2</sub> in both the high and low purity specimens, as exhibited in Fig. 1, where no obvious difference can be distinguished. The curves of the particle size distributions of the ground specimens are shown in Fig. 2. FH and FL are characterized by a small D50 around 1.5 µm and a narrow distribution, whereas CH by a D50 of 20 µm and a wide distribution.

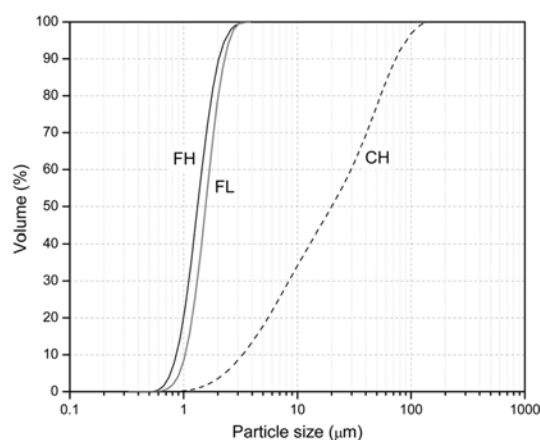
Sintering was carried out in a two-stage mode. Green rods were fired firstly at 1400 °C with holding for 4 hours in a vacuum furnace and then transferred to a carbon tube furnace with an atmosphere of a flowing nitrogen-hydrogen mixture, which was produced by decomposition of liquid ammonia. With holding for 10 minutes, calcining in a carbon tube furnace was

**Table 1.** XRF analysis results of high and low purity MoSi<sub>2</sub> specimens.

| Specimen    | Elemental composition (%) |      |      |      |      |      |      |      |
|-------------|---------------------------|------|------|------|------|------|------|------|
|             | Al                        | Si   | Ca   | Fe   | Mo   | Ni   | Ti   | Th   |
| High purity | 0.03                      | 39.8 | -    | -    | 59.9 | 0.03 | -    | -    |
| Low purity  | 0.19                      | 39.2 | 0.06 | 0.26 | 59.9 | 0.08 | 0.11 | 0.08 |



**Fig. 1.** XRD diffraction patterns of the high and low purity MoSi<sub>2</sub> specimens.



**Fig. 2.** Curves of particle size distributions of the ground powder specimens.

performed at temperatures of 1500 °C, 1600 °C and 1700 °C. The variation of the bulk density of the specimens with the calcining temperature is presented in Fig. 3. The density of all specimens increased with an elevation of the calcining temperature. The two specimens with fine powders reach a density level above 5.60 g/cm<sup>3</sup> at 1600 °C whereas the specimen with a coarse powder at 1700 °C. Evidently, coarse MoSi<sub>2</sub> powder is difficult to densify compared to fine powder.

The rods with a density above 5.60 g/cm<sup>3</sup> were heated to 1550 °C by passing a current through them. After holding for 5 minutes, an adhesive SiO<sub>2</sub> film layer formed on the surface of the rods sintered at

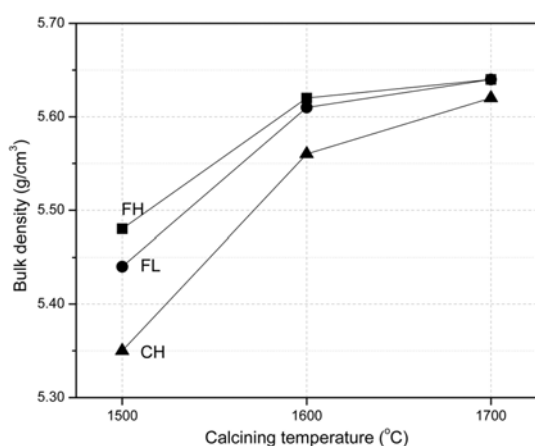


Fig. 3. Variation of the density of specimens with the calcining temperature.

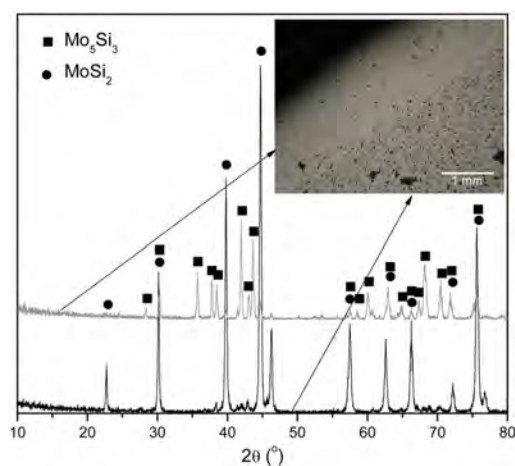


Fig. 4. XRD diffraction patterns of the surface and interior of the CH rod sintered at 1700 °C.

1600 °C. Regarding the rods sintered at 1700 °C, the surface only became a little dark but no continuous  $\text{SiO}_2$  film was formed. It is well known that the formation of a  $\text{SiO}_2$  film is the result of selective oxidation of Si [8]. Therefore, the poor capacity of film formation of the rods sintered at 1700 °C is attributed to the evaporation of elemental Si in the form of  $\text{SiO}$  (g) under a low oxygen partial pressure at high temperature [9]. This clearly corresponds to the result of microscopic observations, which indicates that the microstructure of the surface layer is obviously different from the interior. As shown in Fig. 4, XRD identifies the major phase of the surface layer as  $\text{Mo}_3\text{Si}_5$ .

After being processed by film formation, the flexural strength was measured with a three-point bending method. The Weibull plots of the rods are shown in Fig. 5. The strength of the FH and FL rods is much higher than that of the CH rods. This is attributed to the adhesive  $\text{SiO}_2$  film formed on the surface. Griffith theory reveals that the brittle fracture of a ceramic is caused by propagation of pre-existing surface defects induced by excessive stress concentration. For  $\text{MoSi}_2$

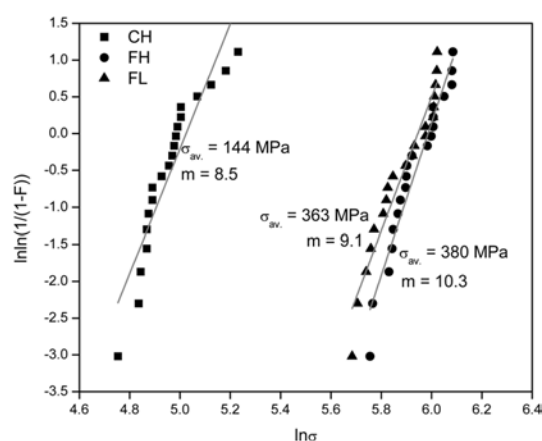


Fig. 5. Weibull plots of the flexural strength data.

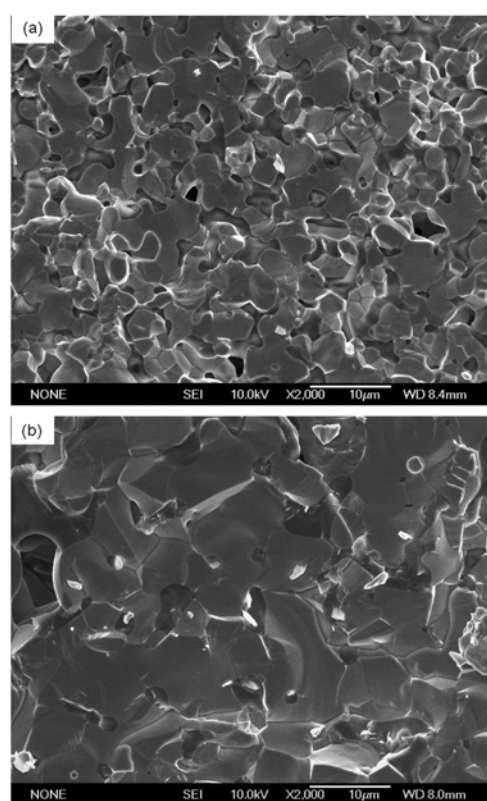


Fig. 6. SEM images of fracture surfaces of a FH rod sintered at 1600 °C (a) and a CH rod sintered at 1700 °C (b).

rods, a continuous  $\text{SiO}_2$  film can cover the surface defects and thus improve the flexural strength as well as its reliability, which is embodied in the value of the Weibull modulus. A high value of the Weibull modulus means a generally concentrated strength distribution, and therefore high reliability [10].

The filmed FH and FL rods sintered at 1600 °C and CH at 1700 °C were heated by an induction coil and meanwhile bent to a U-shape for hot zone applications. It was found that FH and FL rods can be bent easily above 1550 °C. However, CH rods fractured during bending even when heated up to 1700 °C and conducted under a very low bending speed. This is no

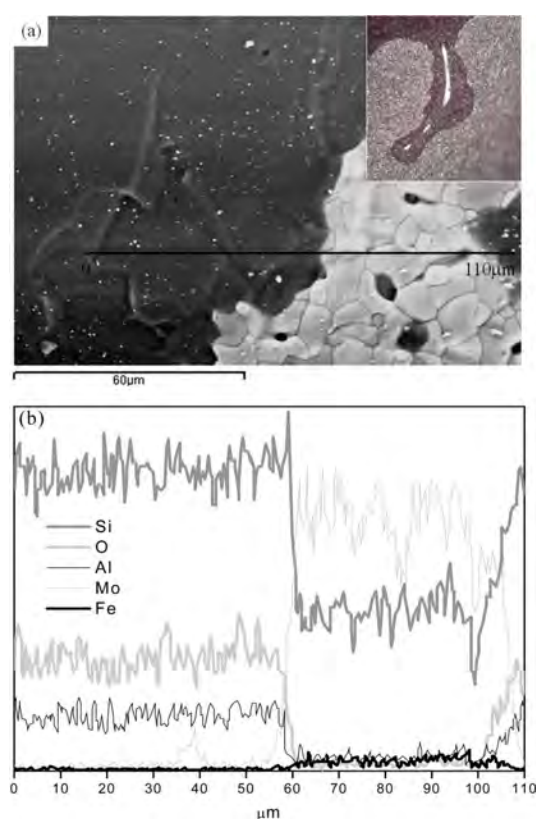


Fig. 7. SEM image of the cross section (a) and elemental distribution profile (b) of the damage area of a FL heating zone.

doubt related to the crystal size, as exhibited in Fig. 6 in a comparative view. A coarse crystal size undermines the movement of slip systems in the MoSi<sub>2</sub> lattice. Hence, the CH rods failed to be processed by hot bending.

Elements were fabricated by utilizing FH and FL rods sintered at 1600 °C as well as CH rods sintered at 1700 °C. After holding at 1600 °C for 600 minutes, the FH heating zone shows almost no change whereas the CH is covered with a continuous film. Damage occurs in the form of blisters due to the release of interior gas from sealed pores or volatilized components. Corresponding to FH, FL and CH heating zones, the critical damage temperatures are 1670 °C, 1610 °C and 1650 °C respectively. This indicates that the impurities from the starting silicon powders have a negative impact on the performance of MoSi<sub>2</sub>-based heating elements. The typical damage of a FL heating zone is embedded in a micrograph of cross section, as presented in Fig. 7(a). Determination of the elemental distribution profiled in Fig. 7(b) reveals that the film consists of elemental Si, O and Al, which is probably from the Montmorillonite component. The impurity of elemental Fe exists in the adjacent Mo<sub>5</sub>Si<sub>3</sub> belt predominantly rather than in the film. This means the impurities do not lower critical damage temperature of the FL heating zone through deteriorating the film. The exact mechanism is being investigated.

## Conclusion

In the current study, the influence of purity and particle size of starting MoSi<sub>2</sub> powders on the properties and performance of MoSi<sub>2</sub>-based heating elements was investigated. The following conclusions can be drawn based on the experimental results.

1. A higher calcining temperature is necessary for the densification of green rods of heating elements with a coarse starting MoSi<sub>2</sub> powder. It will take longer to form a protective film on the surface due to a relatively thick layer of the Mo<sub>5</sub>Si<sub>3</sub> phase. In addition, the densified rods cannot be bent to U-shape even at a very high temperature because of the coarse crystal size.
2. The purity of the starting powder has a significant impact on the performance of MoSi<sub>2</sub>-based heating elements. Impurities will result in damage to the protective film at a relatively low working temperature.
3. Both high purity and a fine particle size are the necessary requisites for MoSi<sub>2</sub> powder to fabricate high-performance heating elements.

## Acknowledgments

This work was supported by Program for New Century Excellent Talents in University (NCET-10-0323), “Shu Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (No.11SG34), Shanghai Rising-Star Program (No.12QH1400100), the Fundamental Research Funds for the Central Universities, and Shanghai Leading Academic Discipline Project (No.B603).

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