

Rare earth activated sintering of MoSi₂ and its electric conductivity^①

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[Abstract] The effects of rare earth on activation sintering of MoSi₂ and electric conductivity of the matrix were analyzed on the basis of a method proposed by German and Munir. The results show that the addition of rare earth could refine the powder size and obviously reduce sintering activation energy of MoSi₂ which, for rare earth/MoSi₂ system, is 83.1 kJ/mol at 1200~1400 °C, about half of that of pure MoSi₂. This decreases the sintering temperature of MoSi₂ by about 200 °C at least, and decreases the resistivity of the matrix as well. The mechanism of rare earth activated sintering of MoSi₂ is an integrated process mostly ruled by grain boundary diffusion. When the density of materials is identical, the rare earth addition is found to have no noticeable effect on the electric conductivity of MoSi₂.

[Key words] activated sintering; rare earth; MoSi₂; electric conductivity

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1 INTRODUCTION

Intermetallic MoSi₂ holds considerable promise for a wide variety of elevated temperature structural applications at temperatures above 1000 °C^[1]. Since Maxwell first put forward the hypothesis that MoSi₂ could be a potential structural material in the early 1950s, material scientists have done much work to improve its room temperature properties by means of more synthesis methods such as mechanical alloying (MA), self-propagating high-temperature synthesis (SHS)^[2], and material design by adding SiC, Nb, TiC, ZrO₂ and Al₂O₃.

There is no report about the use of rare earth (RE) as an addition but Y₂O₃ as coating of MoSi₂^[3]. The author has preliminarily studied the effects of rare earth added in MoSi₂, and demonstrated that with the addition of RE, the theoretical density of sinters increased from 91.5% to 96.4%, with attendant increase in room temperature strength and toughness^[4,5]. Some investigations^[6~9] concerned the activated sintering of refractory metals. However, no study of the activated sintering of MoSi₂ was reported. In general, MoSi₂ itself is good electric conductor, but the effect of second-phase on the electric conductivity was rarely studied. Here we study RE activation effects during sintering of MoSi₂ and their influence on electric conductivity on the basis of a German and Munir's method to better understand the

behavior of RE in MoSi₂.

2 EXPERIMENTAL

MoSi₂ and 1.0% RE/MoSi₂ prepared by MA were shaped under pressure of 100 MPa for 2 min. Then they were sintered in a tungsten wire furnace under reduction atmosphere, at temperatures of 1200 °C, 1300 °C, 1400 °C, 1500 °C and 1600 °C for 0.5, 1, 1.5, 2 and 2.5 h, respectively. The radial sizes of pressed and sintered compacts were measured by micrometer calipers, each data is the average of 10 measurements, in order to calculate the radial linear shrinkage of compacts. Their density and resistivity were measured by drainage and double electric bridge, respectively. Their microstructures and morphology were observed by JSMT-200 scanning electron microscopy.

3 RESULTS

3.1 Density of sintered compact

Fig. 1 shows that the density of the RE/MoSi₂ is obviously higher than that of pure MoSi₂ when sintered at a temperature of 1200~1400 °C. Their maximum density was obtained through sintering at 1400 °C. Because the hot-pressing temperature for MoSi₂ matrix composites is often above 1600 °C^[2], so the addition of RE decreases the sintering tempera-

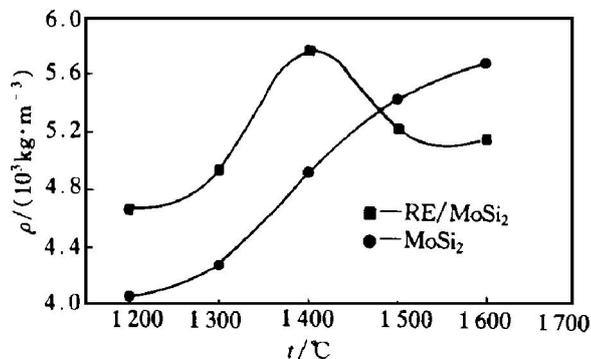


Fig. 1 Density of compacts sintered at different temperatures

ture of MoSi₂ by about 200 °C at least.

3.2 Electric conductivity of sintered compacts

The relations of resistivity of MoSi₂ or RE/MoSi₂ to sintering temperature are shown in Fig. 2. When the two kinds of materials are sintered at 1200 ~ 1400 °C, the resistivity of RE/MoSi₂ is lower than that of MoSi₂, but higher at 1600 °C. When the density of materials is similar, for example when sintered at 1470 °C, their resistivity values are close to each other too. This indicates that in this case the addition of RE has no noticeable effects on the electric conductivity of the matrix.

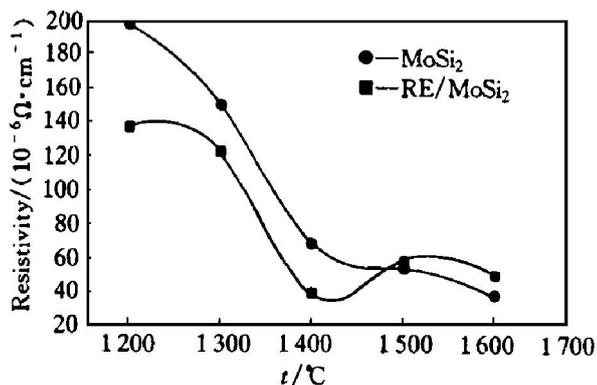


Fig. 2 Resistivity of compacts sintered at different temperatures

4 DISCUSSION

4.1 Sintering apparent activation energy and sintering mechanism

Fig. 3 and Fig. 4 describe the relation of sintering radial linear shrinkage to time and temperature respectively. Sintering linear shrinkage can be approximately expressed as^[10]

$$\left[\frac{\Delta l}{l_0} \right]^n = \left[\frac{\delta}{a} \right]^m \frac{grD_0 t \cdot \exp\left(\frac{Q}{RT}\right)}{kT} \quad (1)$$

It can be simplified to

$$\lg \frac{\Delta l}{l_0} = \frac{1}{n} \lg t + k \quad (2)$$

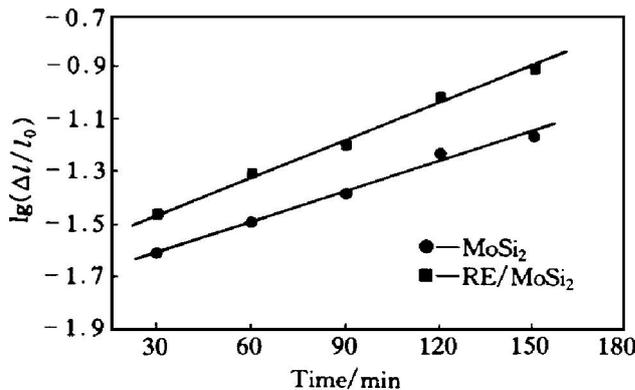


Fig. 3 Relation between sintering radial linear shrinkage and time

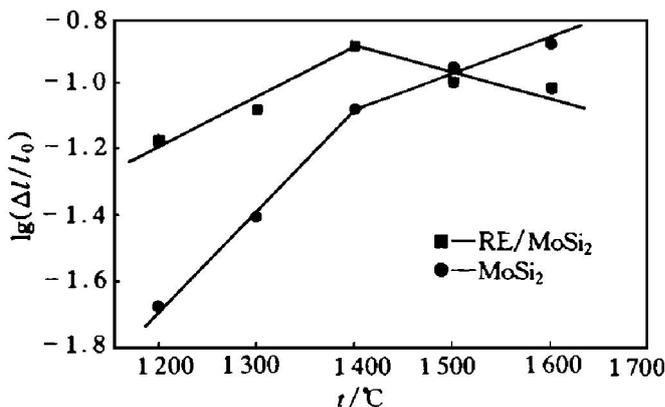


Fig. 4 Relation between sintering radial linear shrinkage and temperature

$$\lg \frac{\Delta l}{l_0} = \frac{-Q}{2.303Rn} \cdot \frac{1}{T} + b \quad (3)$$

$$Q = -2.303RnA \quad (4)$$

where $\Delta l/l_0$ is the sintering linear shrinkage, R is the gas constant, T is the absolute temperature, t is the sintering time, n is the characteristic exponent for the dominant shrinkage producing mechanism, Q is the sintering apparent activation energy, k and b are the constants and A is the linear slope.

From Figs. 3 and 4, the values n , A and Q of MoSi₂ sintered at 1200~1400 °C are determined to be 1.45, -0.549 and 152.4 kJ/mol, respectively. The Q value is close to 130 kJ/mol reported by Petrovic and Vasudevan^[11]. But for RE/MoSi₂ these values are 1.18, -0.360 and 81.3 kJ/mol respectively. Thus, adding RE decreases the sintering activation energy of MoSi₂ by 50%, suggesting that RE accelerates sintering of MoSi₂ and reduces sintering temperature. From Fig. 5, adding RE particles obviously refines the powder size and increases powder contiguity area in the early stage of sintering, which benefits that material transport process such as gas volatilization and diffusion. In spherical process of close pore and elimination stage, recrystallization firstly occurs at particle interface, which increases the density of

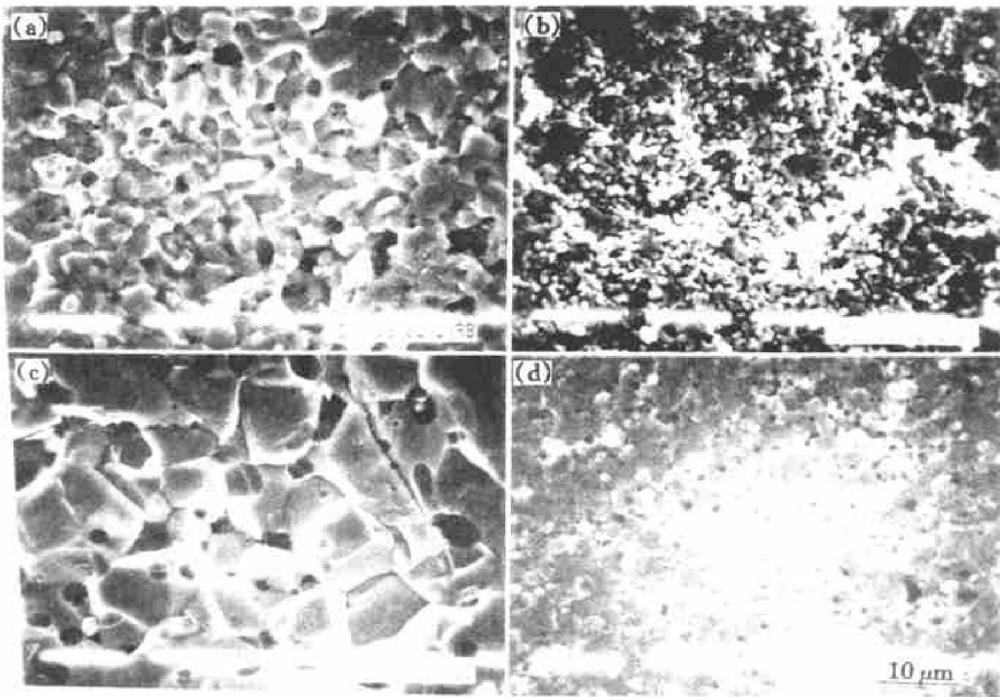


Fig. 5 Microstructures of sintering at different temperatures
 (a) $-\text{MoSi}_2$ 1200 °C; (b) $-\text{RE}/\text{MoSi}_2$ 1200 °C; (c) $-\text{MoSi}_2$ 1600 °C; (d) $-\text{RE}/\text{MoSi}_2$ 1400 °C

compacts. Crystal grains were refined because of pinning effect on the motion of the grain boundary by RE particles^[12]. Consequently, in the RE activated sintering process, RE addition not only causes chemical effect resulted from decreasing activation energy but also causes physical effects resulted from grain refinement and second phase particles.

There is an obvious change in sintering effects at 1400 °C as shown in Fig. 4. It is shown in Fig. 1 that the sintering neck growing stage and the spherical process of close pore and its elimination stage during sintering of MoSi₂ occurred when temperature is lower or higher than 1400 °C, respectively, but for RE/MoSi₂, the spherical process of close pore and its elimination stage and the crystal grains coalesce stage occurred respectively. As we know, sintering is a complex process and there exist different viewpoints on the mechanism of activated sintering. In this experiment, according to the results of calculation, the sintering apparent activation energy of RE/MoSi₂ is 83.1 kJ/mol at 1200~1400 °C, which is approximately half of that of pure MoSi₂. It supports the argument that grain boundary diffusion activation energy is half of volume diffusion activation energy. Furthermore, the absolute value of A is 0.46~0.50 in volume diffusion model and 0.3 in grain boundary diffusion^[13], which respectively corresponds to A value of MoSi₂ and RE/MoSi₂ in this experiment. So the authors consider the mechanism of RE activated sintering of MoSi₂ as an integrated action process mostly ruled by grain boundary diffusion, together with the influence of volume diffusion and second phase particles^[12].

4.2 Effect of RE on electric conductivity of MoSi₂^[12]

Generally, the conductivity of powder sintering materials is closely related to porosity and conductivity of the second phase. In this experiment, comparison of Fig. 3 and Fig. 4 shows that the resistivity of the materials strongly depended on their density. In other words, it is mainly controlled by porosity. The effect is described as

$$\lambda = \lambda_0(1 - 1.5\theta) \quad (5)$$

where λ is the conductivity of hole materials, λ_0 is the conductivity of corresponding imperforate materials, and θ is porosity (volume fraction).

Based on the above analysis, it is known that the addition of RE increases the density of MoSi₂ sintered at temperature lower than 1400 °C, which means θ is reduced. Thus λ is raised so that its resistivity is lower than that of pure MoSi₂, as shown in Fig. 2. This is also why the resistivity of the two materials is similar when their density is equal at sintering temperature of 1470 °C. The improvement of resistivity of RE/MoSi₂, sintered at temperature higher than 1400 °C, may be attributed to grain coalesce and hole growing.

5 CONCLUSIONS

1) Adding rare earth can obviously reduce sintering activation energy of MoSi₂, which is 83.1 kJ/mol at 1200~1400 °C, about half of that of pure MoSi₂, and accelerates the sintering process of MoSi₂. It decreases the sintering temperature of MoSi₂ by about

200 °C at least.

2) The mechanism of RE activated sintering MoSi₂ is an integrated action process mostly ruled by grain boundary diffusion. It not only includes chemical effect resulted from decreasing activation energy but also physical effects resulted from grain refinement and second phase particles.

3) The addition of rare earth element reduces the resistivity of MoSi₂ sintered at 1 200~ 1 400 °C and improves its electric conductivity. When the density of materials is identical, the rare earth element has no noticeable effects on the electric conductivity of MoSi₂.

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