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Formation of nanocrystalline $MoSi_2$ compound subjected to mechanical alloying

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Molybdenum disilicide has been recognized as an attractive candidate material for high temperature structural applications. In this study, we have used mechanical alloying by a high-energy ball milling process to produce alloy powders of α-$MoSi_2$ starting from mixtures of elemental molybdenum and silicon powders at room temperature. The α-$MoSi_2$ plus Mo phases have been obtained by ball milling of a $Mo_{33}Si_{67}$ mixture of the pure elements for 100 hours, which was transformed to a single α-$MoSi_2$ phase by subsequent heat treatment up to 725 °C. The grain size of the α-$MoSi_2$ powders thus obtained was 19 nm, being approximately four times smaller than that of commercial alloy powders. It was also seen that the α-$MoSi_2$ phase once formed begins to transform to the high-temperature β-$MoSi_2$ phase when the total milling time exceeds 160 hours.

Key words: Mechanical alloying (MA), Nanocrystalline α-$MoSi_2$ compound, High-temperature structural material, Hall plot, Differential scanning calorimetry (DSC).

Introduction

Molybdenum disilicide has come to be recognized as the ideal matrix for high temperature intermetallic matrix composites. The combination of a high melting point (2020 °C), low density (6.24 g/cm^3), and extremely high resistance to oxidation and corrosion makes $MoSi_2$ an attractive candidate material for high temperature structural applications. The increasing use of $MoSi_2$ as a heating element in furnaces that operate in air at temperatures up to 1700 °C is a clear demonstration of its excellent high-temperature properties [1-7].

$MoSi_2$ compound has been synthesized by various techniques such as conventional arc-melting and casting, powder pressing and sintering, reaction synthesis and hot pressing [2, 3]. However, the conventional melting method is hampered by the high melting point of $MoSi_2$. Furthermore, in all these synthesis methods, oxygen is invariably incorporated in the material during the process. Oxygen reacts with silicone to form a glassy SiO_2 second phase in the $MoSi_2$ matrix [2, 4, 5].

Mechanical alloying (MA) based on a solid state reaction through severe plastic deformation at room temperature has been recognized as one of the noble techniques in synthesizing ultra-fine and nano-structured powder materials [8-13]. All the alloying reactions during the process occur in the solid state. This technique is thus well suited for synthesizing high melting-point materials such as $MoSi_2$ compound. The product of the MA process is a highly homogeneous and fine-grained powder. Therefore, in order to get $MoSi_2$ compound with a fine microstructure, the MA process is believed to be very effective in grain refinement [9, 12].

In the present study, we have applied mechanical alloying, a high energy ball-milling process, to prepare nanocrystalline α-$MoSi_2$ compound starting from mixtures of the pure elements. Optimal ball milling and heat treatment conditions to obtain a single α-$MoSi_2$ phase with a fine microstructure were investigated by the structural and thermal analysis of MA powders. This study will help in the understanding of the solid-state reaction mechanism by MA in the Mo-Si alloy system and will lead to stimulate industrial use of nano-structured α-$MoSi_2$ compound for new applications.

Experimental Details

The mechanical alloying was carried out at room temperature in an argon gas atmosphere, using pure Mo (99.9%, 150 μm in average size) and Si (99.999%, 50 μm in average size) powders with an atomic ratio 33 : 67. A planetary-type ball mill (Fritsch Pulverisette 5) was used with its rpm of 200. The vial and balls are made of a hardened steel (SKD11) and tungsten carbide (WC), respectively. The total mass of powders was about 15 g and the ratio of balls to powders was about 7 : 1.

The structural change for the samples after MA and heat treatment have been studied by differential scanning calorimetry (DSC) in combination with ordinary X-ray diffraction with Cu-Kα radiation. The average grain size of $MoSi_2$ powders was evaluated by the Hall plot method using a diffraction line-width [14, 15]. X-ray diffraction line-broadening from the equipment was calibrated with the standard Si powders. X-ray diffraction measurements were done in step scanning mode. More details are

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described in Ref. 15. The morphology of the MA powders was observed using a scanning electron microscope (SEM).

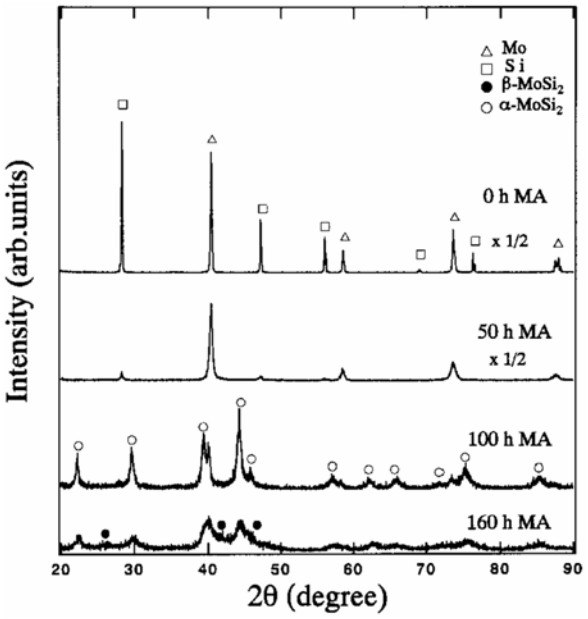
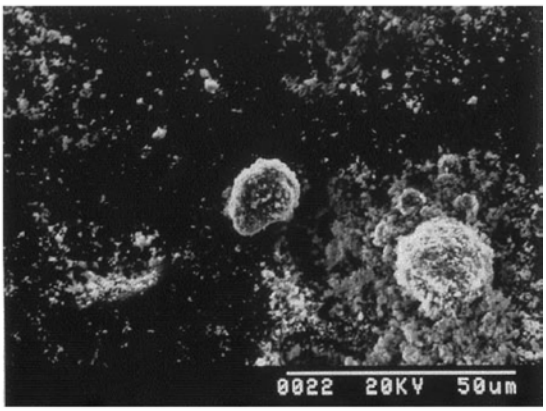
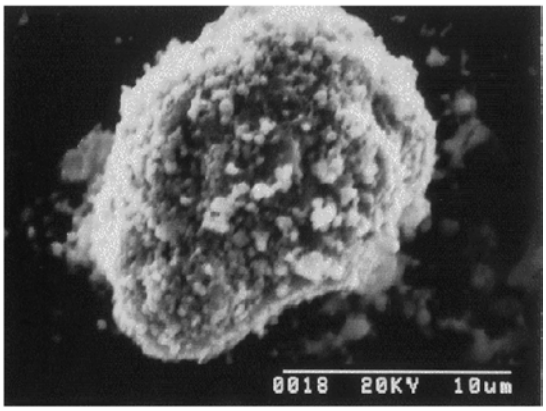


Fig. 1. X-ray diffraction patterns for $Mo_{33}Si_{67}$ powders as a function of total MA time.



(a)



(b)

Fig. 2. Scanning electron micrographs for $Mo_{33}Si_{67}$ powders mechanically alloyed for 100 hours.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns for a mixture of molybdenum and silicone powders with the composition of $Mo_{33}Si_{67}$ mechanically alloyed for various time intervals. It can be seen that the diffraction lines associated with silicone disappear drastically after 50 hours of MA without any evidence for the formation of $MoSi_2$ compound. The decrease in intensity and the broadening of diffraction lines are caused by the grain refinement and also by the accumulation of defects and strains [14, 15]. On the other hand, a mixture of α-$MoSi_2$ compound and pure molybdenum apparently form after 100 hours of MA. However, it is important to notice that a non-equilibrium β-$MoSi_2$ compound, which is high temperature phase stable above 1900 °C, begins to appear after 160 hours of MA [16].

Figure 2 shows the scanning electron micrographs for the $Mo_{33}Si_{67}$ powders treated by MA for 100 hours. Fig. 2(b) is an enlarged image by five times of Fig. 2(a). The figure shows individual particles and loose agglomerates of these particles. High magnification SEM reveals that the particles are about 0.5-1 μm in size.

To get a single α-$MoSi_2$ compound, we tried to determine the heat treatment condition for the formation of α-$MoSi_2$ compound in combination with ball milling by thermal analysis. Figure 3 shows DSC the spectrum of $Mo_{33}Si_{67}$ powders treated by MA for 100 hours. The DSC run was made up to 725 °C with a heating rate of 20 K $minute^{-1}$ in a copper cell. The DSC spectrum of 100 hours MA powders consists of only one exothermic peak at 630 °C. To investigate the phase formation related to the exothermic reaction, we analyzed structural changes after heat treatment in the DSC measurements and the results are shown in Fig. 4. It is found that the exothermic reaction of 100 hours MA powders can be identified as arising from the formation of the α-$MoSi_2$ compound, indicating that a single α-$MoSi_2$ phase can be obtained by MA of $Mo_{33}Si_{67}$ mixture of pure elements for 100 hours coupled with heat treatment up to 725 °C.

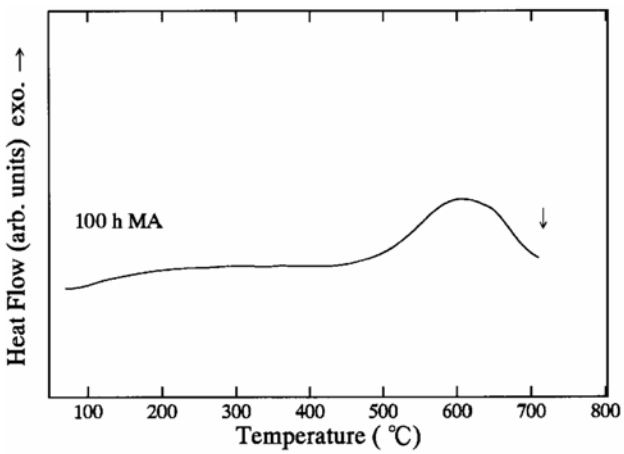


Fig. 3. DSC spectrum for $Mo_{33}Si_{67}$ powders mechanically alloyed for 100 hours.

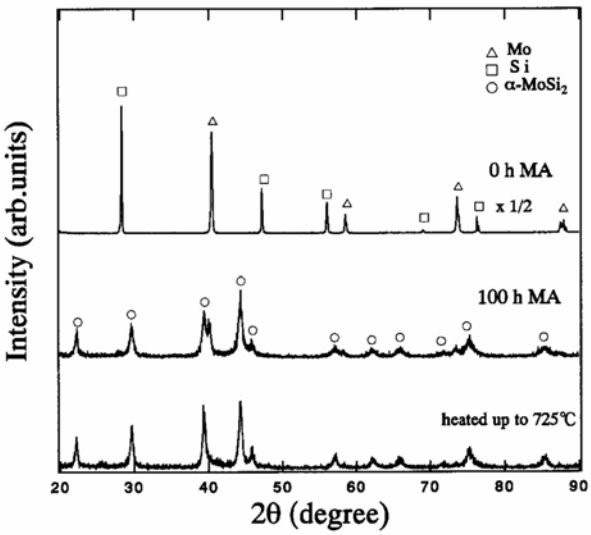


Fig. 4. Effect of heat treatment on the phase transformation for $Mo_{33}Si_{67}$ powders mechanically alloyed for 100 hours.

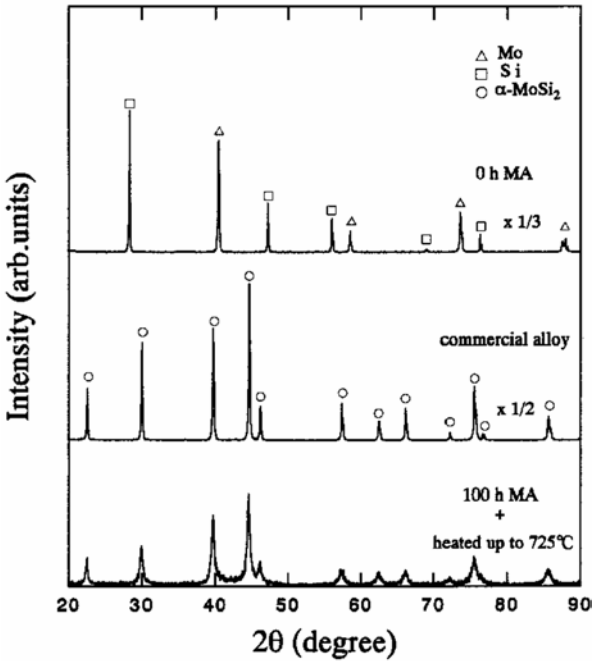


Fig. 5. X-ray diffraction patterns for the commercial $MoSi_2$ powders and 100 hours MA sample after heat treatment up to 725 °C.

Figure 5 shows the X-ray diffraction patterns of the α-$MoSi_2$ compound prepared by MA and heat treatment, along with the data of commercial α-$MoSi_2$ powders (99.9%, High purity chem. Japan). It can be seen that the diffraction lines of the α-$MoSi_2$ compound by MA are much broader than those of the commercial alloy powders, suggesting that the microstructure of MA powders is finer. An average grain size of α-$MoSi_2$ compound may be evaluated from the half-width of the diffraction lines in Fig. 5.

Figure 6 shows the so-called Hall plot for the α-$MoSi_2$ powders prepared by MA and heat treatment, along with commercial α-$MoSi_2$ powders [14, 15]. Here

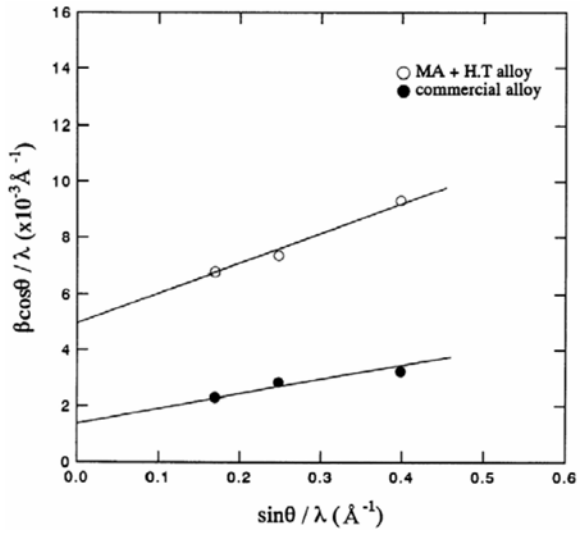


Fig. 6. Hall plot for the samples shown in Fig. 5.

Table 1. Average grain and particle sizes for the mechanically alloyed α-$MoSi_2$ and commercial alloy powders

Alloy Designation	Grain size (nm)	Particle size(μm)
100 h MA sample	14	0.5-1
100 h MA + HT (725 °C)	19	1
100 h MA + HT (1000 °C)	25	2
Commercial alloy powders	75	5-10

the half-width β of the diffraction line is expressed as:

$$\beta\cos\theta/\lambda = (2\eta\sin\theta/\lambda) + (1/\varepsilon) \quad (1)$$

where θ is the Bragg angle, λ is the X-ray wavelength, η is the internal strain and ε is an average grain size. As is clear from Fig. 6, the data can be fitted to a straight line with average grain sizes being deduced from the intercepts. Table 1 shows average grain sizes for α-$MoSi_2$ powders, along with particle sizes characterized by SEM observation. It is seen that the grain size of the α-$MoSi_2$ powders by MA and heat treatment up to 725 °C is 19 nm, being approximately four times smaller than that of the commercial alloy powders. It is also worth noting that the grain size of α-$MoSi_2$ compound remains 25 nm even after being heated up to 1000 °C in DTA measurements [14, 15]. This result indicates that nanometre-sized α-$MoSi_2$ compound by MA has a very strong resistance to grain growth and a very high thermal stability [11, 17]. Further study is underway to examine in more detail the microstructure by means of a transmission electron microscope.

Conclusions

We have revealed that the α-$MoSi_2$ and Mo phases form by mechanical alloying of a $Mo_{33}Si_{67}$ mixture of pure elements for 100 hours, which is transformed to a single α-$MoSi_2$ phase by subsequent heat treatment up

to 725 °C. Interestingly, the α-$MoSi_2$ phase once formed begins to transform to the high-temperature β-$MoSi_2$ phase when the total milling time exceeds 160 hours. The grain size of the α-$MoSi_2$ powders by mechanical alloying is 19 nm, being approximately four times smaller than that of the commercial alloy powders.

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