# PREPARATION OF AMORPHOUS $Mo_5Si_3$ BY MECHANICAL ALLOYING AND THE CRYSTALLIZATION①

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**ABSTRACT** Considerable interest and efforts are being directed to the synthesis of amorphous materials by mechanical alloying (MA). $Mo_5Si_3$ amorphous alloy was obtained by using MA of elemental Mo and Si powders. $Mo_5Si_3$ intermetallic compound was also gotten by vacuum annealing at high temperature. The structural change during the MA procedure was examined by XRD, SEM, and TEM and the crystallization process was monitored by DTA.

**Key words** amorphous alloy mechanical alloying $Mo_5Si_3$ crystallization

## 1 INTRODUCTION

Recently, an increasing amount of experimental work has been carried out on amorphization induced by mechanical alloying (MA). Starting from elemental crystalline powders, a large number of alloy systems, for example Ni-Nb[1,2], Ni-Ti[2,3], Ti-Al[4], Cu-Ta[5], Nb-Al[6], Nb-Be[7], Al-Ta[8], and several transition metal-Zr systems[9], have been investigated.

Compared with the conventional method for preparing amorphous alloys, i. e., rapid quenching from the melt, MA technique exhibits some specific advantages, including the potential to produce bulk amorphous alloys, the ease of preparing amorphous alloys containing both high and low melting point constituents[8], and the possibility of extending the glass forming range of some systems[10]. All of these make MA a particularly promising method for the manufacture of homogeneous amorphous alloy powders.

In this paper, we present the preliminary results about mechanical alloying of 5Mo+3Si powder mixtures.

## 2 EXPERIMENTAL PROCEDURE

Pure elemental powders of Mo(2～5 μm, purity 99.95%) and Si ( 1～3 μm, purity 99.9%) were mixed with an atomic ratio of 5:3. The powder mixture (100 g) and tungsten carbide balls (10 mm in diameter) were introduced in a cylindrical stainless steel vial (500 ml) with a ball-to-powder weight ratio of 10:1. Mechanical alloying was carried out in a laboratory planetary ball mill with a rotation rate of 225 r/min. The loaded vial was always sealed under a protective argon atmosphere during milling.

After selected times, the milling process was interrupted and a small quantity of milled powder was removed and examined using X-ray diffraction (XRD) with Cu$K_\alpha$ radiation in a SIEMENS D500 diffractometer to follow the structural evolution. The morphological characteristics of final as-milled powders were observed by scanning electron microscopy (SEM) in a JEOL JSM-35C microscope and by transmission electron microscopy (TEM) in a H-800 microscope. For preparing the specimen for TEM observation, we put some

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powders in alcohol and dropped this blended liquid onto a carbon film in order to scatter the powder particles. Differential thermal analysis (DTA) was made using a Rigaku instrument.

The longest mechanically alloyed powders were also annealed under vacuum.

## 3 RESULTS AND DISCUSSION

The XRD patterns for the as-mixed 5Mo + 3Si powder mixtures and after MA for 5 h are presented in Fig. 1. It can be seen that during the early stage of milling, there is a significant decrease in the intensity of Bragg peaks and an increase in width, indicating a reduction in the size of the crystallites. After milling for 5 h, the diffraction peaks associated with Si disappear first while the Mo peaks remain high, suggesting complete dissloution of Si in the Mo lattice at this stage. According to the Mo-Si binary phase diagram[11], the solubility of silicon in molybdenum is very limited under equilibrium conditions. At 150 C, about the MA temperature, this solubility is negligible. Thus, it is believed that a Mo(Si) supersaturated solid solution is formed after only 5 h of MA. This manifests that MA can be an effective way to produce powdered materials with extended solid solubility.

The XRD patterns for the 5Mo+3Si powder mixtures after MA for 10, 30, 50, and 70 h are presented in Fig. 2. There is a further peak broadening with a simultaneous peak height decrease. It is noted in the spectra, beginning from 10 h, that several peaks other than those from Mo and Si have appeared. These extra peaks belong to WC (001), (100) and (101), respectively. Their intensities grow as the milling time increases, showing considerable contamination originating from the WC balls. The contamination should be attributed to the intense collisions among the balls, caused by relatively small volume fraction of the powder sample in vial. The same phenomenon is reported in Nb-Be binary system using a Spex 8000 Mixer/Mill[7]. In the spectrum after 30h MA, a trace of amorphous phase is clearly identified. Amorphization tendency is more apparent as the MA time increases. The peaks of Mo(Si) solid solution eventually extinguish in the XRD pattern after 70 h MA, only two broad amorphous humps (at about $2\theta = 40°$ and 70°) and WC peaks are left, suggesting that the 5Mo + 3Si powder mixtures have transformed into an almost completely amorphous powder. The amorphous humps in this spectrum are relatively small due to the insufficient quantity

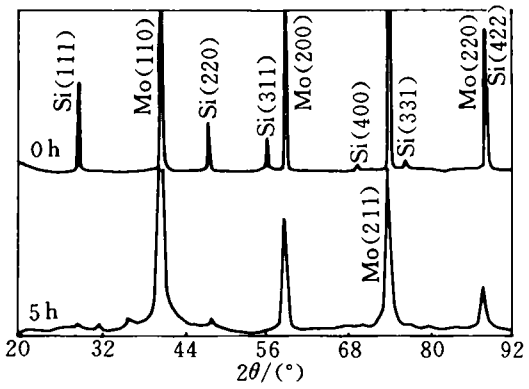


**Fig. 1 XRD patterns of the 5Mo+3Si powder mixtures after milling for 0 h and 5 h**

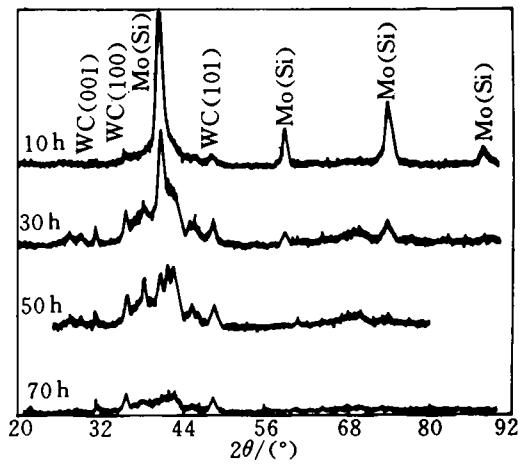


**Fig. 2 XRD patterns of the 5Mo+3Si powder mixtures after milling for 10, 30, 50 and 70 h**

of the specimen subjected to XRD examination.

Fig. 3 shows a SEM micrograph of the powder after 70 h of MA. Loose agglomerates of the particles is clearly observed in the figure.

TEM image of the powders milled for 70 h is shown in Fig. 4. The particles are spheroid and most of them have a size of about 100 nm, demonstrating that the product of the MA process is a homogeneous and fine powder.

The result of DTA of the 70 h milled powder is shown in Fig. 5. There appear three sharp exothermic peaks on the DTA curve. This shows intense crystallization processes have happened at different temperatures due to the formation of several stable phases.

Vacuum annealing of the powder at 1 100 C for 1 h results in complete crystallization of the amorphous material, as shown in Fig. 6. Most of the diffraction peaks correspond to $Mo_5Si_3$ phase and a small amount of $MoSi_2$ and Mo also exists. There are several peaks which cannot be identified. They should be some intermediate phases of Mo-Si system. Paradoxically, the WC peaks disappear after annealing. Perhaps WC has dissolved in other phases. So, we can know that annealing amorphous MA-processed materials beyond the crystallization temperatures is a practical

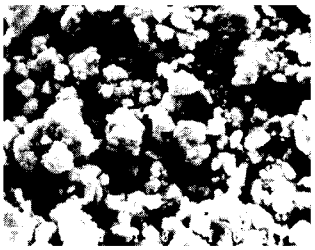

**Fig. 3 SEM micrograph of the 5Mo+3Si powders milled for 70 h, ×4 000**

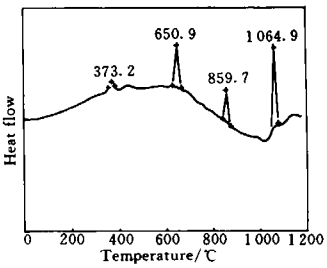


**Fig. 5 DTA of the amorphous $Mo_5Si_3$ under flowing Ar at a heating rate of 10 C/min**

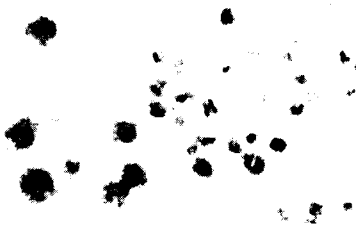

**Fig. 4 TEM image of the 5Mo+3Si powders milled for 70 h, ×10 000**

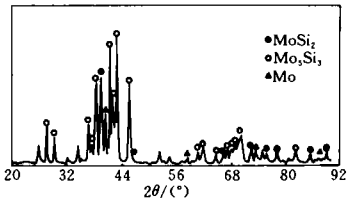


**Fig. 6 XRD pattern of the 5Mo +3Si powders milled for 70 h and annealed at 1 100 C for 1 h**

method to prepare intermetallic alloys which cannot be synthesized directly by MA. Nanocrystalline material can also be achieved by this means.

During the MA procedure, continuous milling of the powders leads to a great reduction in grain size, which is manifested by the continuous broadening of the diffraction peaks in XRD patterns. When the "effective crystallite size" is reduced to a nanometer level, and at a fine enough stage, an amorphous phase can form directly, as suggested in ref. [12]. In a former experiment, we have succeeded in synthesizing $MoSi_2$ intermetallic compound form a Mo+2Si powder mixture only after 4 h MA under the same conditions as in the present work. Hence, it seems that the composition corresponding to $Mo_5Si_3$ facilitates the formation of an amorphous phase in Mo-Si system. This perhaps relates to the self-sustained nature of $MoSi_2$ formation during ball milling of elemental powders[13].

## 4 CONCLUSIONS

Mechanical alloying of mixed 5Mo + 3Si powders leads directly to the formation of a Mo (Si) supersaturated solid solution and a nearly completely amorphous phase after 5 h and 70 h milling, respectively. Annealed at high temperature (1 100 C), this amorphous phase turns into $Mo_5Si_3$ crystalline phase although some other phases also exist. During the MA procedure, the degree of amorphization increases with the increasing of the MA time.

## REFERENCES

1 Koch C C, Cavin O B, McKamey C G, Scarbrough J O. Appl Phys Lett, 1983, 43: 1017.
2 Schwarz R B, Koch C C. Appl Phys Lett, 1986, 49: 146.
3 Schwarz R B, Petrich R R, Saw C K. J Non-Cryst Solids, 1985, 76: 281.
4 Bonetti E, Valdre G, Enzo S, Cocco G. J Alloys Compds, 1993, 194: 331.
5 Lee C H, Fukunaga T, Yamada Y, Mizutani U. J Phase Equilib, 1993, 14: 167.
6 Hellstern E, Schultz L, Bormann R, Lee D. Appl Phys Lett, 1988, 53: 1399.
7 Chou T C, Nieh T G, Wadsworth J. Scripta Metall Mater, 1992, 27: 881.
8 Sherif El-Eskandarany M, Itoh F, Aoki K, Suzuki K. J Non-Cryst Solids, 1990, 117/118: 729.
9 Hellstern E, Schultz L. Appl Phys Lett, 1986, 48: 124.
10 Weeber A W, Bakker H. J Phys F: Met Phys, 1988, 18: 1359.
11 Lyman T *et al*. Metals Handbook, 8th Edition, Vol 8, Ohio: ASM, 1973: 321.
12 Weeber A W, Bakker H. Physica B, 1988, 153B: 93.
13 Ma E, Pagan J, Cranford G, Atzmon M. J Mater Res, 1993, 8: 1836.

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