Journal of Alloys and Compounds 509 (2011) 2617–2620

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Structural characterization of $MoSi_2$ synthesized by high-energy mechanical milling followed by annealing heat treatment

A. Toghian Chaharsoughi [a], Gh. Borhani [b], R. Tahmasebi [a,*]

[a] Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
[b] Department of Materials Engineering, Malek Ashtar University of Technology, Shahin Shahr, Iran

ARTICLE INFO

Article history:
Received 26 July 2010
Received in revised form
22 November 2010
Accepted 23 November 2010
Available online 30 November 2010

Keywords:
Molybdenum disilicide
Annealing
X-ray diffraction
Mechanical milling

ABSTRACT

In this research $MoSi_2$ intermetallic compound was synthesized from the elemental powders using an attritor mill in extended milling times (up to 30 h) followed by an annealing heat treatment. In order to study the structural evolution of the products, X-ray diffraction and scanning electron microscopy were employed. Since no solid solution and phase transformation was detected by X-ray diffraction pattern analysis, therefore annealing of the milled powders was carried out by using an atmosphere controlled conventional furnace. The heat treatment process resulted in the formation of dual $MoSi_2$ and Mo_5Si_3 phases above 1000 °C and single Mo_5Si_3 phase below 1000 °C.

1. Introduction

Intermetallic molybdenum disilicide ($MoSi_2$) demonstrates unique properties such as low density (6.24 g/cm^3), high melting point (2030 °C), excellent oxidation resistance and high temperature strength. Therefore, it can be an attractive candidate for high temperature applications, especially in the aerospace industry [1,2]. Its oxidation resistance originates primarily from the formation of self-heating SiO_2 coating under an oxidizing atmosphere at temperatures above 1200 °C. $MoSi_2$ compound is dimorphous, the tetragonal α-phase ($C11_b$ type) is a stable phase up to 1900 °C, above which is transformed to the hexagonal β-phase (C40 type) [3]. Casting, conventional arc melting or powder metallurgy including sintering, hot pressing and self-sustaining (SHS) combustion are among the various methods that are being used to synthesize $MoSi_2$. However, the high melting point and line compound phase always limit the fabrication of $MoSi_2$ by these conventional methods [4,5].

Mechanical alloying (MA) is a promising method for producing these kinds of intermetallics. This method is basically a solid state process involving repeated welding, fracturing and rewelding of powder particles in a high energy ball mill. MA has been extensively used to produce a variety of non-equilibrium phases or alloys such as amorphous phases, supersaturated solid solutions, meta-stable crystalline and quasi-crystalline intermediate phases as well as nanostructured materials [6–10]. In the present work, $MoSi_2$ has been synthesized using Mo–Si binary mixture by means of mechanical milling followed by annealing heat treatment. In addition, morphology and structural changes have been investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses of the milled samples. Additionally, solid state reactions occurring in annealing process have been investigated by means of X-ray diffraction method.

2. Experimental

In this investigation a stoichiometric composition of pure molybdenum and pure silicon with an average diameter of 4 and 45 μm, respectively, was used for the milling process. The mechanical milling was performed using an attritor mill with stainless steel vial and balls (10 mm in diameter). The rotational speed was 360 rpm and the ball-to-powder mass ratio was set to be 20:1. The powder sample and milling balls were loaded into the vial and 0.5 wt% stearic acid was used as the process control agent (PCA) (also referred to as lubricant or surfactant) in order to minimize the cold welding between powder particles. Milling was performed in an Ar atmosphere. Water circulation kept the temperature of vial at room temperature during the milling process. A Philips XPert X-ray diffractometer using CuK_α radiation was employed to investigate structural evolution of the powder samples during the milling process. In order to study the microstructure and morphology of the as-milled samples, a scanning electron microscope was used. It was also used for measuring the particle size. Heat treatment of as-milled powders was carried out with a constant heating rate of 10°/min in Ar atmosphere. The holding time at the selected temperatures (900–1200 °C) was 1 h.

* Corresponding author. Current address: Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7. Tel.: +1 905 525 9140x27249/26586; fax: +1 905 528 9295.
E-mail addresses: am.toghian@ma.iut.ac.ir (A.T. Chaharsoughi), ra_tahmasebi@ma.iut.ac.ir, tahmasr@mcmaster.ca (R. Tahmasebi).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.11.142

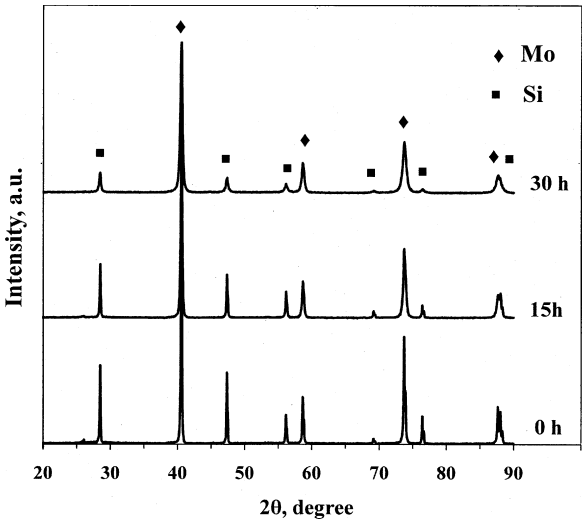

Fig. 1. XRD pattern of powders milled for different times.

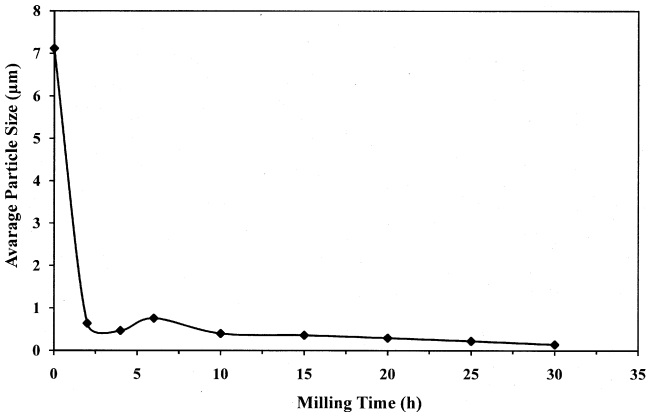

Fig. 2. Changes in average particle size during the milling process.

3. Results and discussion

Fig. 1 shows the XRD pattern of the mechanically milled powders for 0, 15 and 30 h. It can be seen that milling not only decreases peaks intensities but also peak broadening takes place. It is especially well pronounced for the case of Si peaks. This is due to the fact that the reduction in peak intensity stems from Mo high X-ray absorption coefficient [11]. The metallic radius of Mo and Si is 0.1363 and 0.132 nm, respectively. So when Si atoms dissolve in the Mo lattice, the Mo reflection peaks will shift to larger angles [12]. Since no major shift in the Mo peak positions was observed, it can be concluded that no reciprocal solid solution has occurred. Because mechanism and amount of $MoSi_2$ produced during mechanical milling is largely affected by the milling energy [10,13], it can be

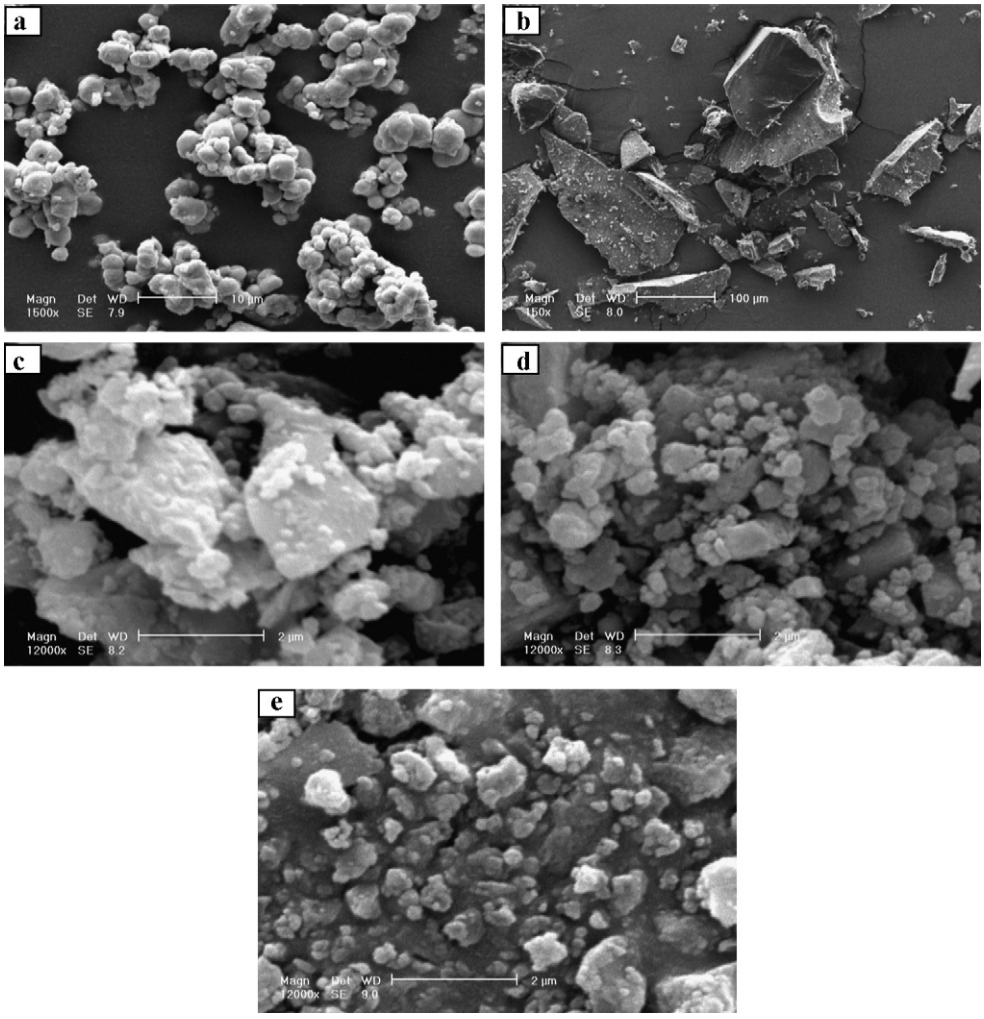

Fig. 3. Changes in the morphology of powders, prior to milling (a) pure Mo, (b) pure Si and Mo–Si stoichiometric mixture milled for (c) 2 h, (d) 6 h and (e) 20 h.

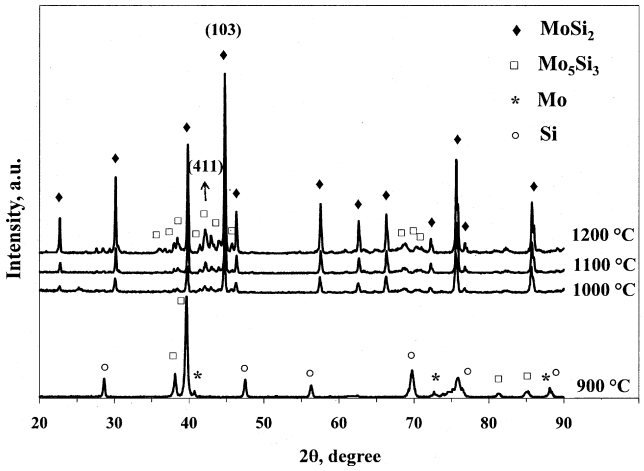

Fig. 4. XRD patterns of samples milled for 30 h right after annealing.

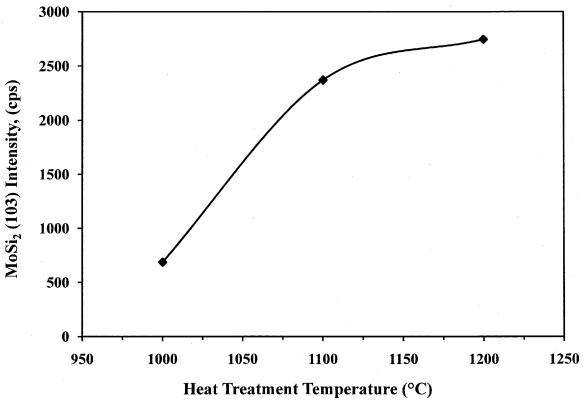

Fig. 5. Variations in the $MoSi_2$ (1 0 3) peak intensity vs. heat treatment temperature.

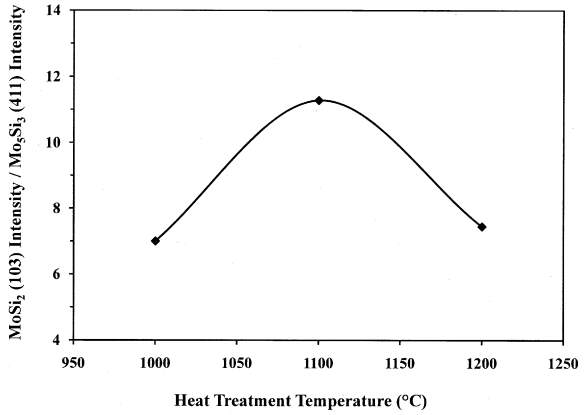

Fig. 6. Variations in the ratio of the intensities of the sharpest peaks of $MoSi_2$ and Mo_5Si_3 vs. heat treatment temperature.

deduced that the input energy in this system has not been enough to produce $MoSi_2$. Therefore, it can be said that as-milled powders are well-mixed and highly activated only.

Fig. 2 shows the variation in average particle size during the milling process. In the initial stages of milling, large decrease in average particle size is a result of grinding of Si coarse powder particles. Since Mo particles are subjected to compressive impact forces and undergo plastic deformation, therefore metal powder particles get flattened but welding of soft powder particles has not occurred [14]. In extended milling times however new surfaces in Mo powder particles created and the rate of welding between powder particles increased. When the welding occurs, the average particle size slightly increases. But in further milling, work hardening happens and consequently due to an increased brittleness of powders, particle size continuously decreases. This decrease can happen mostly in the first 15 h of the milling process. Using SEM it was found that the average particle size of the samples milled for 30 h was approximately 140 nm. Fig. 3 shows the changes in morphology of powders.

In order to investigate the effect of heat treatment on the formation of $MoSi_2$ phase, annealing in Ar atmosphere was carried out at different temperatures from 900 °C to 1200 °C on the powder samples milled for 30 h. Fig. 4 shows the XRD patterns of 30 h milled samples right after the annealing heat treatment. As can be seen in the XRD pattern of the sample heated at 900 °C, diffraction peaks were identified as elemental Mo and Si powders and just a small trace of Mo_5Si_3 was detected which could be the result of solid state diffusion of Si in Mo [5,15]. In contrast, it is seen in the XRD patterns of the samples heated at 1000 °C and above that Mo and Si can form $MoSi_2$. The increase in heat treatment temperature clearly leads to an increase in $MoSi_2$ (1 0 3) peak intensity.

Fig. 5 shows changes in $MoSi_2$ (1 0 3) peak intensity at different heat treatment temperatures. The effect of annealing is stress relieving and grain growth, which leads to decrease in the peak width and increase in sharpness of the peaks [11]. It is seen in Fig. 4 that peak width reduces and $MoSi_2$ peaks are much sharper in higher temperatures. Fig. 6 shows the variations in the ratio of the intensities of the sharpest peaks of $MoSi_2$ and Mo_5Si_3 at different heat treatment temperatures. Since it is seen in Fig. 5 that intensity of $MoSi_2$ peaks are continuously increasing as temperature increases, it can be concluded from the decline in the ratio of the intensity of the sharpest peaks of $MoSi_2$ and Mo_5Si_3 in Fig. 6 that the amount of Mo_5Si_3 phase has actually considerably increased at 1200 °C. It has been justified in the literature that this increase is related to the following reaction [5]:

$$3MoSi_2 + 7Mo = 2Mo_5Si_3$$

By increasing the heat treatment time, the amount of Mo_5Si_3 can be reduced again though [5].

4. Conclusion

1 By performing mechanical milling on pure Mo and Si powders only grinding, mixing and mechanical activation happens and no reciprocal solid solution was observed.
2 The average particle size of the powder samples milled for 30 h was about 140 nm. Decrease in average particle size mainly happens in the initial 15 h of the milling process.
3 To produce $MoSi_2$ from activated powders, heat treatment of samples milled for sufficient amount of time at temperatures above 1000 °C is required. In addition, the amount of intermetallics produced increases by increasing the heat treatment temperature.

Acknowledgements

Authors are very grateful to Dr. M. Salehi for his support and helpful discussions throughout this research.

References

[1] A.K. Vasudevan, J.J. Petrovic, Mater. Sci. Eng. A 155 (1992) 1–17.
[2] Y. Liu, G. Shao, P. Tsakiropoulos, Intermetallics 8 (2000) 953–962.
[3] B.k. Yen, T. Aizawa, J. Kihara, J. Am. Ceram. Soc. 79 (8) (1996) 2221–2225.
[4] Y.L. Jeng, E.J. Lavernia, J. Mater. Sci. 29 (1994) 2557–2571.

[5] P. Kang, Z. Yin, Mater. Lett. 57 (2003) 4412–4417.
[6] B.K. Yen, T. Aizawa, J. Kihara, Mater. Sci. Eng. A 220 (1996) 8–14.
[7] M. Sannia, R. Orru, J.E. Garay, G. Cao, Z.A. Munir, Mater. Sci. Eng. A 345 (2003) 270–277.
[8] L. Takacs, V. Soika, P. Balaz, Solid State Ionics 141–142 (2001) 641–647.
[9] L. Liu, F. Padella, W. Guo, N. Magini, Acta Metall. Mater. 43 (10) (1995) 3755–3761.
[10] L. Liu, K. Cui, J. Mater. Process. Technol. 138 (2003) 394–398.
[11] M. Zakeri, R. Yazdani-Rad, M.H. Enayati, M.R. Rahimipour, J. Alloys Compd. 403 (2005) 258–261.
[12] K. Zuo, S. Xi, J. Zhou, Mater. Sci. Eng. A 445–446 (2007) 48–53.
[13] H. Zhang, X. Liu, Int. J. Refract. Met. Hard Mater. 19 (2001) 203–208.
[14] C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1–184.
[15] H.S. Park, K.S. Shin, J. Mater. Res. 16 (2001) 3060–3068.