STRUCTURAL AND MORPHOLOGICAL EVALUATION OF NANO-SIZED MoSi₂ POWDER PRODUCED BY MECHANICAL MILLING

MAHMOOD SAMEEZADEH ^a

msamee@ut.ac.ir

HASSAN FARHANGI ^b

hfarhangi@ut.ac.ir

MASOUD EMAMY ^c

emamy@ut.ac.ir

^{a,b,c} *School of Metallurgy and Materials Engineering, University of Tehran
Tehran, Iran*

Nano-sized intermetallic powders have received great attention owing to their property advantages over conventional micro-sized counterparts. In the present study nano-sized MoSi₂ powder has been produced successfully from commercially available MoSi₂ (3 μm) by a mechanical milling process carried out for a period of 100 hours. The effects of milling time on size and morphology of the powders were studied by SEM and TEM and image analyzing system. The results indicate that the as-received micrometric powder with a wide size distribution of irregular shaped morphology changes to a narrow size distribution of nearly equiaxed particles with the progress of attrition milling up to 100 h, reaching an average particle size of 71 nm. Structural evolution of milled samples was characterized by XRD to determine the crystallite size and lattice microstrain using Williamson-Hall method. According to the results, the crystallite size of the powders decreases continuously down to 23 nm with increasing milling time up to 100 h and this size refinement is more rapid at the early stages of the milling process. On the other hand, the lattice strain increases considerably with milling up to 65 h and further milling causes no significant changes of lattice strain.

Keywords: Nano-sized MoSi₂; structural evaluation; mechanical milling.

1. Introduction

Molybdenum disilicide (MoSi₂) is one of the intermetallic compounds with a potential for being used as advanced high temperature structural materials because of its high melting point (2030 °C), high thermal conductivity and elevated oxidation resistance, low electrical resistance and excellent diffusion-barrier characteristics.^{1,2} Some current potential applications of MoSi₂-based materials include turbine airfoils, combustion chamber components, industrial gas burners, electrical conductors, intermetallic reinforcement for aluminum matrix composites and specially furnace heating elements.

Molybdenum disilicide heating element is a resistance generate-heating component which is used in high temperature up to 1800 °C under the oxidizing atmosphere. It looks like glass in its surface and form a light SiO_2 glass film which can protect the element not to be oxidized, so this kind of element has unique effect for resisting oxidation in the high temperature. In addition MoSi_2 elements support high power densities on their surface and can be used in rapid cycle and continuous furnace applications. These elements also offer the longest inherent life of all electric heating elements.¹⁻⁶

MoSi_2 (Tetragonal) is one of the three intermetallic phases present in the Mo-Si system (Fig. 1) along with Mo_5Si_3 (Tetragonal) and Mo_3Si (Cubic).^{1,7-8}

Fig. 1. Mo-Si phase diagram.⁸

Nano-sized ceramics and intermetallics (<100 nm) have several advantages in comparison with conventional micrometric particles. For example the mechanical properties of nano-metric dispersion strengthened metal matrix composites (MMCs) are far superior to those of micrometric dispersion strengthened MMCs with a similar volume composition of particles.⁹ Also, one can deduce from Ref. 3 that because of the small grain size of nano particles, the volume fraction of atoms present at the grain boundaries is much higher and this can lead to interesting properties such as high diffusivity and sinterability and improved strength and hardness.

Currently, several techniques are available to produce nano-sized intermetallics and ceramics; some examples are plasma arcing, chemical vapor deposition, sol-gel synthesis, reactive arcing and high intensity mechanical milling. Among these methods, mechanical

milling is an available and simple technique which has been used widely to produce nano-sized particles such as TiO_2 ¹⁰, SiO_2 ¹¹, Al_2O_3 ¹², CeO_2 ¹³ and Fe_3O_4 ¹⁴.

Because of the above special attributes, the main purpose of this work is production of nano-sized MoSi_2 powder by mechanical milling and evaluation of structure and morphology of the nano powder.

2. Experimental Procedure

In current investigation, MoSi_2 powder (> 99% purity, 3 μm) was mechanically milled in an attrition ball mill. The attrition mill vial and shaft were made of stainless steel (AISI 316) and was case hardened through gas nitriding process. Hardened chromium steel balls (6 and 10 mm diameter) were used for wet milling in ethanol. The ball to powder weight ratio (BPR) and shaft rotational speed were chosen 12:1 and 270 rpm, respectively. The powder in the vial was protected with high purity argon gas and the milling tank was cooled with cold water. The mechanical milling process was performed up to 100 hours and samples for analysis were removed by interrupting the ball mill at various intervals.

The effects of milling time on the morphology of powders were characterized by scanning electron microscopy (SEM, Oxford CamScan MV2300) and Transmission electron microscopy (TEM, ZEISS EM1013). An image analyzing software was used to quantify the average particle size and size distribution of powders by measuring the dimensions of particles in several micrographs for each milled samples.

Structural evolution of the as-milled powders was characterized by X-ray diffraction (XRD, Philips X' Pert). XRD was conducted using $\text{Co-K}\alpha_1$ (1.78897 $^\circ\text{A}$) radiation at 40 kV and 30 mA setting. The crystallite size (size of the coherently diffracting domains) and lattice microstrain of the samples were determined using Williamson-Hall method.¹⁵

3. Results and Discussion

3.1. Electron microscopy evaluation

Figure 2 shows the SEM micrographs of the as-received and up to 80 hour-mechanically milled MoSi_2 powders. Figure 3 exhibits the TEM micrograph of 100 h milled MoSi_2 that confirms the production of nano-sized particles. The average particle size and its distribution versus milling time for all samples are shown in Fig. 4(a). Also, Fig. 4(b) displays the particle size histogram of the 100 h milled MoSi_2 measured from several TEM micrographs. The results indicate that the as-received micrometric powder, with a wide size distribution of irregular shaped morphology, changes to a narrow size distribution of nearly equiaxed particles with the progress of attrition milling time up to 100 h, reaching an average particle size of 71 nm. Furthermore, according to the results a sharp decrease in the average particle size has occurred at initial stages of milling (up to 50 h) but this rate gradually decreases in the final stages of the process.

Fig. 2. SEM micrographs of as-received and milled MoSi_2 powders.

These results are consistent with previous investigations regarding milling of hard particles.¹⁶ During mechanical milling of metal powders; the morphology and structure of the particles undergo changes. Plastic deformation, welding and fracture of the particles are dominant mechanisms which influence the characteristics of milled powders.¹⁷ Figure 4(a) indicates that while fracture is the dominant mechanism at early stages of the milling and it leads to the powder size refinement, for final stages of milling a balance between fracture and welding mechanisms is gradually established which prevents significant changes of the powder particles size. After milling for a certain length of time, steady state equilibrium is attained when a balance is achieved between the rate of welding and the rate of fracturing. Also the particle size distribution at this stage is narrow, because particles larger than average are reduced in size at the same rate that fragments smaller than average grow through agglomeration of smaller particles.¹⁷

Fig. 3. Typical TEM micrograph of MoSi₂ nano-particles after 100 h milling time.

Fig. 4. (a) Average particle size and its distribution for milled powders versus milling time, (b) particle size histogram of 100 h milled powder.

3.2. X-Ray diffraction evaluation

Figure 5 shows the X-ray diffraction patterns of as-received and milled MoSi₂ powders. These spectra which clearly show the presence of the α -MoSi₂ phase (PDF card #41-0612) with a body-centered tetragonal structure are very similar to each other except for minor differences in the intensities and width of the diffraction peaks. After milling up to 100 h, the crystalline phase was preserved but intensity and width of the characteristic X-ray diffraction peaks gradually decreased and broadened, respectively.

Peak broadening at half height intensity of the XRD patterns is induced by a reduction in crystalline size, faulting and microstrains within the diffracting domains. In the mechanical milling, the powder particles are subjected to plastic microforging. Dislocations and other defects are generated resulting in an increase in internal energy. At the same time dislocation arrays such as all angle boundaries which subdivide the original grains into small coherent domains or crystallites, are produced. The dislocations and their associated stress fields produce microstrains within the coherently diffracting domains. The microstrains associated with the domains maybe conceived as strain dislocations about dislocations and dislocation networks which have an isotropic stress distribution.¹⁸

Fig. 5. X-ray diffraction patterns of as-received and milled MoSi₂ powders.

In order to determine crystallite size and lattice microstrain in the milled samples, the full width at half maximum (FWHM) of each characteristic peak is usually considered.¹⁹ In this study the analysis of the XRD peaks was performed via the Williamson-Hall method according to the following equation:^{15,20}

$$\beta_s \cos \theta = K\lambda/d + 2\varepsilon \sin \theta. \quad (1)$$

where β_s is the sample broadening in radians, 2θ is the position of peak maximum, K is Scherrer constant ($K = 0.9$)²¹, λ is the X-ray wavelength ($\lambda_{\text{CoK}\alpha_1} = 0.178897$ nm), d is so-called crystallite size and ε is an approximate upper limit of the lattice distortion.²⁰ The instrumental broadening (β_i) was removed according to Gaussian-Gaussian relationship by using an annealed MoSi₂ powder:²⁰

$$\beta_s^2 = \beta_e^2 - \beta_i^2. \quad (2)$$

where β_e is the FWHM of the measured XRD peak.²⁰ When $\beta_s \cos \theta$ is plotted versus $\sin \theta$, a straight line is obtained with the slope of 2ε and the intercept of $K\lambda/d$. From this plot and Eq. (1), the crystallite size (d) and lattice strain (ε) can be calculated.

The variation of the calculated crystallite size of the MoSi₂ powders as a function of milling time is shown in Fig. 6(a). According to the results, the crystallite size of the powders decreases continuously down to 23 nm with increasing milling time up to 100 h and this size refinement is more rapid at the early stages (up to 50 h) of milling. The lattice strain is plotted versus milling time in Fig. 6(b). It can be seen that the strain increases considerably with milling up to 65 h and further milling causes no significant changes of lattice strain. Finally a steady state is obtained at a strain of about 0.56 %.

The nearly unchanged structure characteristics of the powder at final stages of milling has been attributed to a balance between the plastic deformation via dislocation motion and the dynamic recovery and recrystallization behavior of the material during mechanical milling process.¹⁷

Fig. 6. XRD results: (a) mean crystallite size and (b) the lattice strain, of milled powders versus milling time

The nanostructure and nano-sized MoSi₂ particles which were produced in this work, are expected not only to have good inherent physical and mechanical properties but also to be an important material for using in metal matrix composites as intermetallic reinforcement, regarding to the some investigations⁴⁻⁶ which reported that MoSi₂ micrometric particles cause significant improvement to the tensile and wear properties of aluminum matrix composites.

4. Conclusion

The main results of this research are:

- (1) Nano-sized MoSi₂ powder (71 nm) is produced successfully from commercially available MoSi₂ (3 μm) by an attrition milling process carried out for a period of 100 hours.
- (2) The as-received micrometric powder with a wide size distribution of irregular shaped morphology changes to a narrow size distribution of nearly equiaxed particles with the progress of mechanical milling.
- (3) The crystallite size of the powders decreases continuously down to 23 nm with increasing milling time up to 100 h and this size refinement is more rapid at the early stages of the milling process.
- (4) The lattice strain increases considerably with milling up to 65 h and further milling causes no significant changes of lattice strain.

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