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Synthesis of $MoSi_2$–TiC nanocomposite powder via mechanical alloying and subsequent annealing

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Abstract

$MoSi_2$–30 wt.% TiC nanocomposite powder was successfully synthesized by ball milling and following heat treatment. Effect of milling time and annealing temperature were investigated. The products synthesis and reactions progress were characterized by XRD. Morphology and microstructure of milled powders were monitored by SEM and TEM, respectively. Results showed that the synthesis of this composite begins after 10 h of milling and progresses gradually up to 30 h of milling. $MoSi_2$–TiC composite was completely synthesized after annealing of 30 h milled powder at 900 °C. On the basis of Reitveld refinement method, the mean grain size and microstrain of 13.2 nm and 0.44% were obtained, respectively for 30 h milled powder that is in consistent with TEM image. In the spite of grain growth and strain release, this nanocomposite powder maintained its nanostructure after annealing.

Keywords: Nanocomposite; Mechanical alloying; $MoSi_2$

1. Introduction

$MoSi_2$ is a very promising intermetallic compound as a high-temperature structural material because of its much higher melting point of 2030 °C. At present, it is mainly used as a heating element of furnaces operating in air at temperatures as high as 1750 °C, but many studies indicated that materials based on $MoSi_2$ had a wide variety of high-temperature structural applications such as high-temperature heat exchanger, turbine aircraft engine hot-section components like blades, vanes, combustors and nozzles, automotive turbocharger rotors and valves [1–4]. Its oxidation resistance at high temperatures is excellent, clearly the best of the silicides and nearly as good as silicon carbide SiC due to the formation of protective silicon dioxide SiO_2 layers.

However, $MoSi_2$ has the intrinsic disadvantages such as low fracture toughness at room temperature and poor tensile creep resistance at high temperature. Therefore, it is imperative to increase the room temperature fracture toughness and high-temperature tensile creep resistance of monolithic $MoSi_2$ by means of proper strengthening and toughening [5]. Fortunately, it is feasible to improve the high-temperature mechanical properties of monolithic $MoSi_2$ by the introduction of a suitable second phase such as SiC, Al_2O_3, Si_3N_4, $CrSi_2$, and TiC [6–14].

Another possible mechanism to improve mechanical properties is to prepare these materials in nanostructure. $MoSi_2$–TiC nanocomposite can be produced easily by direct mixing of its components [15–19]. But the resulting heterogeneous microstructure and high cost of the starting materials are two important setbacks of this method. Alternatively, $MoSi_2$–TiC nanocomposite powder can be synthesized through high-energy reactive milling of mixtures of Mo, Si, Ti and C powders. Mechanical alloying (MA) has been used for preparing thermally stable metallic glasses and amorphous alloys, nanocrystalline and nanocomposite materials, and refractory hard materials, carbides, and hydrides [20].

The aim of this work is in situ synthesis of $MoSi_2$–TiC nanocomposite powder by mechanical milling of its elemental powders. Formation of this composite will be studied by thermodynamic discussions and its microstructure will be investigated by Reitveld refinement method.

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2. Experimental procedures

Mechanical alloying (MA) was performed in a planetary ball mill at approximately room temperature and vial rotation speeds (cup speed) 750 rpm. The four cup planetary ball mill of Retch Company was used for MA experiments. Pure Merck Mo (99.7 wt.%), Si (99.8 wt.%), Ti (99.0 wt.%) and graphite (99.3 wt.%) were mixed to give the desired $MoSi_2$–30 wt.% TiC composition. The used starting powders have a narrow size distribution with the mean particles sizes of 50, 25, 30 and 10 μm, respectively. The ball to powder weight ratio was 5:1. A distribution of 20, 15 and 10 mm stainless steel balls was used in MA experiments. In order to prevent agglomeration, 1 wt.% stearic acid was added. The powders and balls were charged into a steel cup (25 mL) in an Ar atmosphere. Samples were removed for analysis in a glove box under an Ar atmosphere by interrupting milling at various intervals. Heat treatment was conducted in a tube furnace in an Ar atmosphere (2 l min^{-1}). Heating rate and holding time at maximum temperature were 10 k min^{-1} and 1 h, respectively.

XRD profiles were recorded on a Siemens diffractometer (30 kV and 25 mA) with Cu $K\alpha_1$ radiation (l.5404 Å). Recorded XRD patterns were used for calculation of crystallite size and strain. Mean grain size and microstrain were calculated on the basis of Reitveld refinement method by using of X'Pert high score plus software (developed by PANalytical BV Company, Almelo, the Netherlands, and version 2.0). In this method, peak profile fitting, size broadening and strain broadening were calculated on the basis of following equations [21]:

$$G_{ik} = \gamma \frac{C_0^{1/2}}{H_k \pi} [1 + c_o X_{ik}^2]^{-1} + (1-\gamma) \frac{c_1^{1/2}}{H_k \pi^{1/2}} \exp[-C_1 x_{ik}^2] \quad (1)$$

$$D_i = \left(\frac{180}{\pi}\right) \frac{\lambda}{(W_i - W_{std})^{0.5}} \quad (2)$$

$$\eta_i = \frac{[(U_i - U_{std}) - (W_i - W_{std})]^{0.5}}{(1/100)[180/\pi]4(2\ln 2)^{0.5}} \quad (3)$$

where G_{ik} is pseudo-Voigt function, $C_0 = 2$, $C_1 = 4 \ln 2$, H_k is full with at half maximum of the K_{th} brag reflection, γ is shape parameter, $X_{ik} = (2\theta_i - 2\theta_k)/H_k$. D_i, η_i, λ, U and W are grain size function, strain function, wavelength, strain parameter and size parameter of peak profile, respectively. In the size and strain functions, *i* and *std* are referred to analyzed and standard samples, correspondingly. In this project a pure $MoSi_2$ that annealed at 1500 °C for 10 h, was used as standard material for deconvolution of instrumental broadening.

Structural observations of milled powders were carried out with a Philips EM208 TEM operating at 200 kV. The powders were ultrasonically dispersed in a methanol. One drop of this suspension was placed on a copper grid for TEM observation. The morphology and particle size of samples were examined using a Philips (XL30) SEM operating at 30 kV. Energy dispersive X-ray (EDX) analysis was used for composition characterization. Iron contamination of milled powder was measured by inductive coupled plasma (ICP) method.

3. Results and discussion

3.1. Milling and annealing

Synthesis possibility of $MoSi_2$–TiC composite powder was studied by mechanical alloying of Mo, Si, Ti and graphite elemental powders on the basis of following reactions [23]:

$$Mo + 2Si \rightarrow MoSi_2 \quad \Delta G_T^\circ = -131,800 + 65.1T\,(J/mol) \quad (4)$$

$$Ti + C \rightarrow TiC \quad \Delta G_T^\circ = -183,050 + 10.1T\,(J/mol) \quad (5)$$

The starting powders were mixed to give the desired composition of $MoSi_2$–30 wt.% TiC. Fig. 1A shows the XRD pattern of this mixture before milling. Intensity decreasing, peak broadening and disappearing of some peaks are the effects of 10 h milling. It seems that the process of intimate mixing in the early stages of milling is responsible, to a large extent, for the decrease in the intensity of Si and graphite reflections. In fact, the graphite and Si reflections were approximately disappeared due to the high mass absorption coefficients of Mo and Ti (Table 1). With increasing milling time to 20 h, some small peaks of β-$MoSi_2$ and TiC were appeared in its pattern (Fig. 1B). In other words, reactions (1) and (2) were partially performed at this stage of milling. There is a sharp Mo peak in

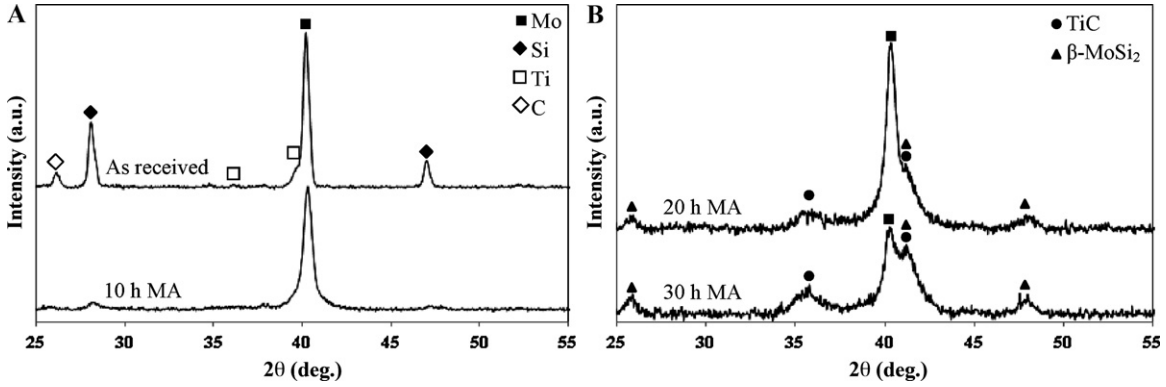

Fig. 1. XRD patterns of the (A) as received, 10 h milled and (B) 20 h and 30 h milled powders.

Table 1
Mass absorption coefficients of the as received and product materials [22].

Phase	Mo	Ti	Si	C	$MoSi_2$	TiC
Mass absorption coefficient ($cm^2\ g^{-1}$)	158.45	196.14	62.07	4.3	122.86	157.68

the 20 h milled sample that with further milling up to 30, its intensity significantly decreased. It means that the above reactions progress gradually and were not completed at this stage of milling (20–30 h). There are two approaches for completing of these reactions. The first one is continuing milling time and another one is annealing of milled powders. At this study, the 10 h and 30 h milled powders were annealed at different temperatures.

The Gibbs free energy of the reactions (4) and (5) are −112,400 and −180,040 J/mol at room temperature, respectively [23]. The negative ΔG indicates that these reactions can take place during milling at room temperatures that is in consistent with the above results. But there are two important questions, which is why SiC and Mo_2C was not synthesized instead of TiC? This question can be explained on the basis of Ellingham diagram of these phases (Fig. 2). Ellingham diagram shows the variation of Gibbs free energy formation versus temperature. There is a concept in this diagram, every line which is lower; its final phase is more stable. It means that every phase which has the lower free energy; it is more stable thermodynamically. TiC formation line has the minimum free energy that means it is more stable in comparison with other phases. It can be concluded that if kinetical condition will be provided during milling, this phase will be formed before others. Experimental results show that this phase is favorable thermodynamically and kinetically (Fig. 1). On the basis of Fig. 2, $TiSi_2$ stability is more than $MoSi_2$. It means that $TiSi_2$ must be formed during milling before $MoSi_2$. But it must be noted that with the formation of TiC and consumption of Ti in reaction (5), there is no possibility for the formation of $TiSi_2$. Therefore $MoSi_2$ is the next favorite phase for the formation during milling that is in consistent with experimental results (Fig. 1).

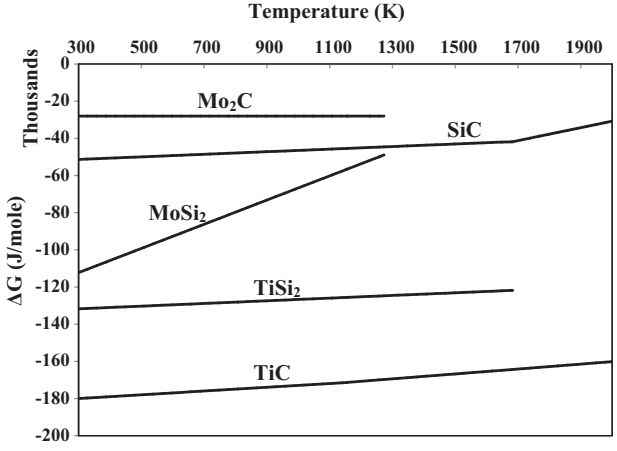

Fig. 2. Gibbs free energy calculation results of some phases at different temperatures [23].

An annealing was performed at 900 °C on the 10 h milled powder. This sample includes starting materials and only activated during milling. Annealing led to the partial reaction between the starting materials. As seen in Fig. 3, α-$MoSi_2$, Mo_5Si_3 and TiC phases were formed after annealing. For complete reaction, more energy must be given by thermal or mechanical method. For this purpose, at first, more mechanical energy was given to the sample by 30 h milling. Further milling in this sample led to the partial reaction between the starting materials. At second stage, more thermal energy was given by annealing at different temperatures (Fig. 4). As seen in this figure, the intensity of Mo peak decreases dramatically due to the $MoSi_2$ formation after annealing at 700 °C and completely disappears at 900 °C. At this temperature $MoSi_2$–TiC composite powder was successfully synthesized. This sample includes both polymorphs of $MoSi_2$ due to the partially phase

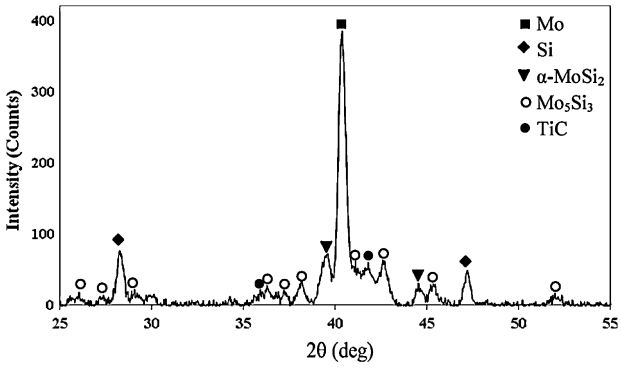

Fig. 3. XRD pattern of the 10 h milled powder after annealing at 900 °C.

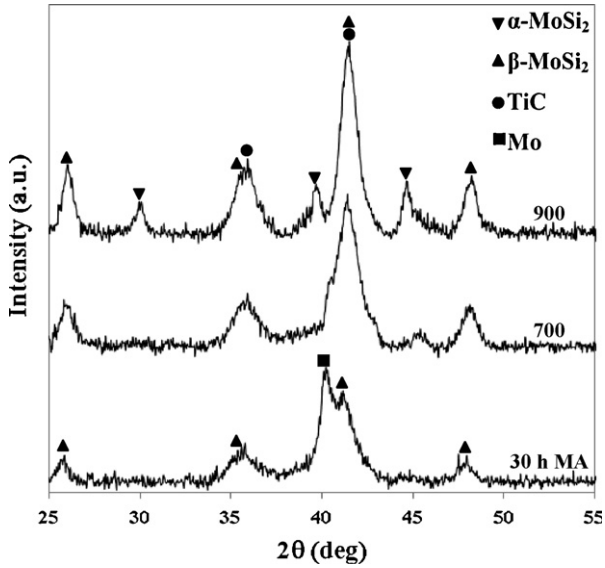

Fig. 4. Complete reaction of 30 h milled powder after annealing at different temperatures.

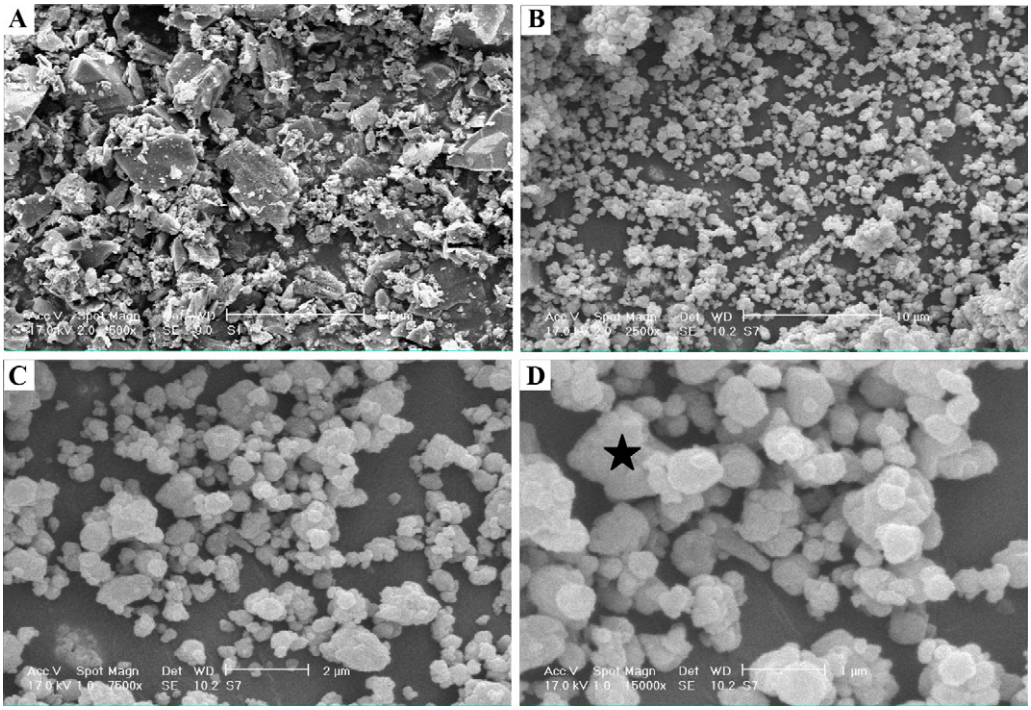

Fig. 5. Morphology and particle size distribution of: (A) as received and (B–D) 30 h milled powders at different magnifications.

transformation of β-$MoSi_2$ to α-$MoSi_2$. β-$MoSi_2$ is high temperature polymorph of $MoSi_2$ that is a meta-stable phase at room temperature. Mechanical alloying is a non-equilibrium process that led to the formation of meta-stable phases at room temperature. On the other hand, annealing led to the formation of equilibrium phase after cooling to room temperature. α-$MoSi_2$ is low temperature polymorph of $MoSi_2$ that is stale at room temperature.

3.2. Morphology and microstructure

Morphology and particle size of milled powder were investigated by SEM. As seen in Fig. 5A, the mixture of starting materials before milling has a very wide particles size distribution with very different and irregular shapes. There are four kind powders of Mo, Si, Ti and graphite in this mixture that everyone has its mean particle size and distribution. Milling of this mixture for 30 h led to the formation of very fine particles that partially agglomerated (Fig. 5B). The mean particle size of this mixture decreases dramatically after 30 h of milling (Fig. 5C). These primary particles were clearly shown in Fig. 5D at higher magnification. As seen, there are very fine submicron particles in the 30 h milled powder. Energy dispersive X-ray (EDX) was performed on the marked particle in Fig. 5D. The result of this analysis was shown in Fig. 6. There are the Mo, Si and Ti reflections in this figure that confirm the composition of milled powder ($MoSi_2$–TiC). Carbon reflections cannot be analyzed by this method. There is a very small Fe peak which introduced from the milling media. ICP analysis showed that the Fe contamination is very low about 0.23 wt.% after 30 h of milling that can easily be removed by leaching in HCl.

The mean grain size and microstrain of milled and annealed powders were calculated by Reitveld refinement method. A seen in Table 2, a nanostructure powder was obtained after 10 h of milling. Further milling led to the decreasing of mean grain size and increasing of microstrain. The minimum mean grain

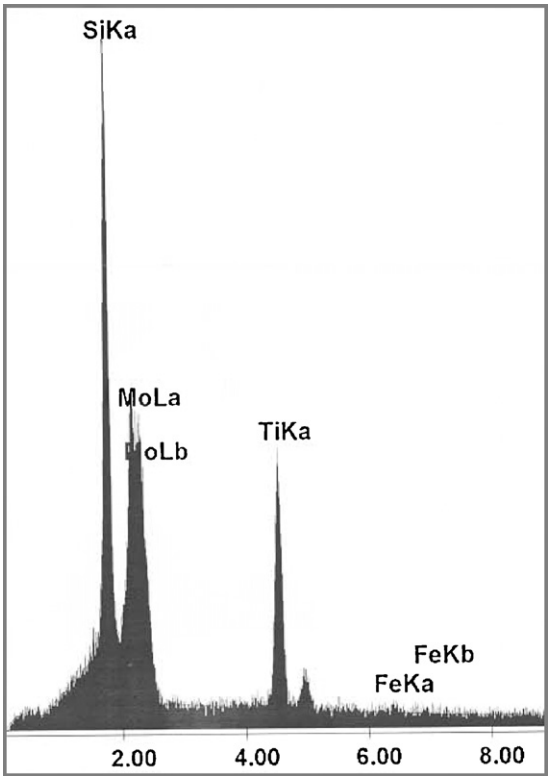

Fig. 6. EDX analysis of 30 h milled powder.

Table 2
The mean grain size and microstrain of milled and annealed powders that calculated by Reitveld refinement method.

Milling time (h)	10		20	30		
Annealing temperature (°C)	As milled	900	As milled	As milled	700	900
Phase	Mo	Mo	Mo	$MoSi_2$	$MoSi_2$	$MoSi_2$
Mean grain size (nm)	22.3	23.3	14.6	13.2	15.2	21.5
Micro strain (%)	0.28	0.14	0.36	0.44	0.38	0.29

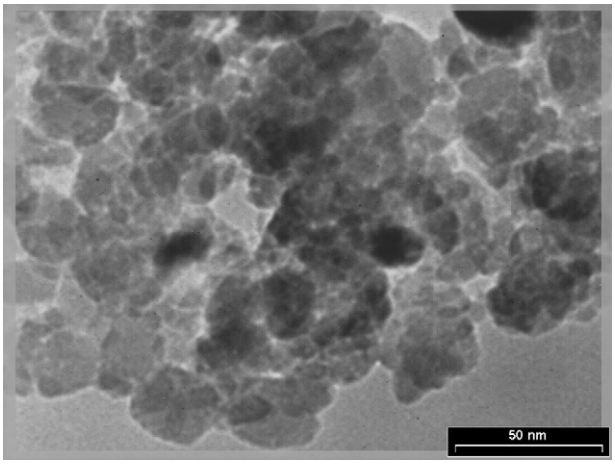

Fig. 7. Bright field image of 30 h milled powder.

size of 13.2 nm was obtained for 30 h milled powder. Grain growth and strain release were the results of annealing. The mean grain size and microstrain of 30 h milled powder after annealing at 900 °C were 21.5 nm and 0.29%, respectively. The microstructure of 30 h milled powder was shown in Fig. 7. There are very fine grains less than 30 nm in this figure that is in consistent with Reitveld analysis results.

4. Conclusion

Effect of milling time and annealing temperature were investigated on the synthesis of $MoSi_2$–TiC nanocomposite from its elemental powders. Results showed that this composite was incompletely synthesized after 30 h of milling. On the other hands, this composite was successfully synthesized after annealing of 30 h milled powder at 900 °C. SEM images showed that a very fine and submicron particles with spherical morphology were obtained after 30 h of milling. On the basis of Reitveld refinement method, the minimum mean grain size and maximum microstrain of 13.2 nm and 0.44% were obtained, respectively for 30 h milled powder that is in consistent with TEM image. Annealing of milled powders led to the significant grain growth and strain release, but the synthesized phases maintained their nanostructure after annealing.

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