Effect of starting composition on formation of $MoSi_2$–SiC nanocomposite powder via ball milling

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Abstract. $MoSi_2$–SiC nanocomposite powders were successfully synthesized by ball milling Mo, Si and graphite elemental powders. Effects of milling time and annealing temperature were also investigated. The composite formation and phase transformation were monitored by X-ray diffraction. The microstructure of milled powders was studied by SEM, TEM and XRD peak profile analysis. Formation of this composite was completed after 10 and 20 h of milling for 25%SiC and 50%SiC, respectively. High temperature polymorph (HTP) of $MoSi_2$ was obtained at the end of milling (20 h). On the other hand, annealing led to transformation of HTP to low temperature polymorph (LTP) of $MoSi_2$. Mo_5Si_3 was formed during annealing as a product of a reaction between $MoSi_2$ and excess graphite. Mean grain size <50 nm was obtained for 20 h milled sample on the basis of peak profile analysis and TEM images.

Keywords. Milling; nanocomposite; $MoSi_2$–SiC.

1. Introduction

$MoSi_2$ is a borderline ceramic–intermetallic compound with both covalent and metallic atomic bonds. $MoSi_2$ is a dimorph phase: the tetragonal C11b-type α-$MoSi_2$ phase is stable up to 2173 K; above this temperature, α-$MoSi_2$ is transformed into the hexagonal C40-type β-$MoSi_2$ phase. This high temperature phase melts in a congruent form at 2293 K. Besides traditional use as heating elements, materials based on $MoSi_2$ appear to be promising candidates for a wide variety of high-temperature structural applications, because of its high melting point, 2030 °C, excellent oxidation and corrosion resistance, thermodynamic stability, high-temperature ductility above the brittle–to–ductile transition temperature close to 1000 °C, good electrical conductivity, machinability and relatively low cost as well (Stoloff 1999; Mitra 2006; Kim *et al* 2007).

The main disadvantage of $MoSi_2$ is its low fracture toughness and strength at lower temperatures below 1000 °C, and low creep resistance at high temperatures. Several performance improvements have been developed by reinforcing with SiC, and ZrO_2 particulates (Bhattacharya and Petrovic 1992; Jayashankar and Kaufman 1992; Soboyejo *et al* 1995; Yamada *et al* 1995). Another possible mechanism is to prepare these materials in nanostructure. $MoSi_2$–SiC nanocomposite can be obtained easily by direct mixing, but resulting heterogeneous microstructure and high cost of starting materials are two important setbacks of this method (Hvizdos *et al* 2001). Alternatively, nanostructure $MoSi_2$–SiC powders can be obtained through high-energy reactive milling of Mo, Si and graphite elemental powders. Mechanical alloying is basically a dry and high energy ball milling process which has been used to synthesize oxide dispersion strengthened alloys, amorphous alloys and various intermetallic compounds (Murty 1993; Koch 2001; Suryanarayana 2001). There is no report on synthesizing of this composite by mechanical alloying. But other $MoSi_2$ composites were synthesized by Al_2O_3 and $CrSi_2$ by this method (Zakeri *et al* 2006; Yazdani-rad *et al* 2010, 2011). Zakeri *et al* also reported that high temperature polymorph of $MoSi_2$ begins to form after 50 h of milling and completes after 70 h of milling. $MoSi_2$–$CrSi_2$ composite powder was also prepared with a combination of short milling time (5 h) and low temperature annealing (850 °C).

In the present paper, $MoSi_2$–SiC composite powder is synthesized by ball milling Mo, Si and graphite elemental powder at room temperature. Effect of milling time, composition and annealing temperature were investigated on formation of this composite and phase transformation of $MoSi_2$.

2. Materials and methods

Mechanical alloying (MA) was performed in a planetary ball mill at nominal 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 wt.%), Si (99 wt.%) and graphite (99·3 wt.%) were mixed to give desired $MoSi_2$–(25 and 50% wt.) SiC compositions. Starting powders had a narrow size distribution with mean particles sizes of 50, 45 and 30 µm, respectively. The ball to powder weight ratio was 15:1 for both compositions. A distribution of 20, 15 and 10 mm balls (seven balls for each

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diameter) was used in MA experiments. For prevention of excess agglomeration 1 wt.% stearic acid was used as a process controlling agent. Mixture of powders with steel balls was charged into a steel cup (250 mL) in Ar atmosphere. Samples for analysis were removed in a glove box under argon atmosphere by interrupting milling at various intervals. Temperature and pressure of cups were measured during milling for determination of beginning and mechanism of reactions.

XRD profiles were recorded on a Siemens diffractometer (30 kV and 25 mA) with Cu Kα_1 radiation (l·5404 Å). All XRD experiments were carried out with a step size of 0·02° and time per step of 1 s. Recorded XRD patterns were used for calculation of crystallite size and strain. Before calculations, the background was automatically removed and the Kα_2 radiation was stripped (stripping ratio, Kα_2/ Kα1 = 0·5) from the scans using computer software X-pert High Score developed by PANalytical BV Company (Almelo, The Netherlands). Iron contents of milled powders were measured by inductively coupled plasma (ICP) method. Structural observations of milled powder were carried out with a Philips EM208 TEM operating at 200 kV. Ultrasonic method was used for dispersing of powder in methanol suspension. One drop of this suspension on a copper grid was used for TEM observation. The morphology and particle size of mechanically alloyed powders were examined by a Philips SEM operating at 25 kV. Heat treatment of as milled powders was conducted in a tube furnace in Ar atmosphere (2 L.min^{-1}). Annealing was performed with a heating rate of 10 k.min^{-1} and holding time at a maximum temperature of 1 h.

3. Results and discussion

Possibility of synthesis of MoSi$_2$–SiC nanocomposite powder was investigated by ball milling Mo, Si and graphite elemental powders. Two series of starting materials on the basis of 25 and 50% SiC (MS25 and MS50) were prepared. Figure 1 shows XRD patterns of these mixtures before
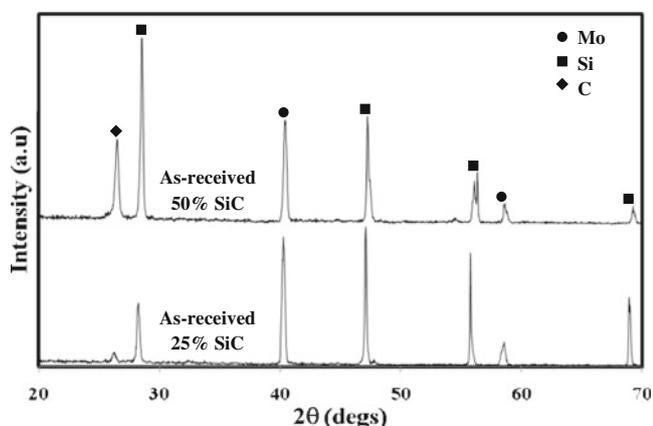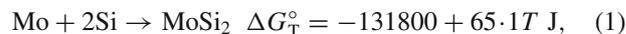
milling (just blended). Intensity of Si reflections in MS50 is bigger than MS25 due to its higher Si content. Effects of milling on these mixtures are shown in figure 2. Both LTP and HTP of MoSi$_2$ and SiC were synthesized after 10 h of milling in MS25 and MS50. Some Mo remained in MS50 due to incomplete reaction. With increasing milling time, starting materials reflections disappeared in MS50. The final products of MS50 are HTP of MoSi$_2$ with SiC, however in MS25, both LTP and HTP of MoSi$_2$ can be seen after 20 h of milling.

Formation of MoSi$_2$ and SiC are on the basis of following reactions:

$$\text{Mo} + 2\text{Si} \rightarrow \text{MoSi}_2 \quad \Delta G_\text{T}^\circ = -131800 + 65\cdot1T \text{ J}, \quad (1)$$

$$\text{Si} + \text{C} \rightarrow \text{SiC} \quad \Delta G_\text{T}^\circ = -53429\cdot7 + 6\cdot9T \text{ J}. \quad (2)$$

These reactions have the Gibbs free energy of -151200 and -51400 J at room temperature, respectively (Kubaschewski 1993). The negative ΔG shows that these reactions can be performed during ball milling at room temperature. It is very difficult to distinguish sequence of these reactions. Chemical affinity (A) definition is the negative partial derivative of Gibbs energy (G) with respect to the extent of reaction (ε) at constant pressure and temperature (Smith 2004):

$$A = -\left(\frac{\delta G}{\delta \varepsilon}\right)_{\text{P,T}}. \quad (3)$$

On the basis of this equation, both reactions (1) and (2) have positive chemical affinity, but in the same extent of reaction (ε), reaction (1) has higher chemical affinity due to its larger ΔG. Whatever, heat release of first reaction leads to the initiation of second reaction. Therefore, it can be concluded that these reactions approximately take place simultaneously.
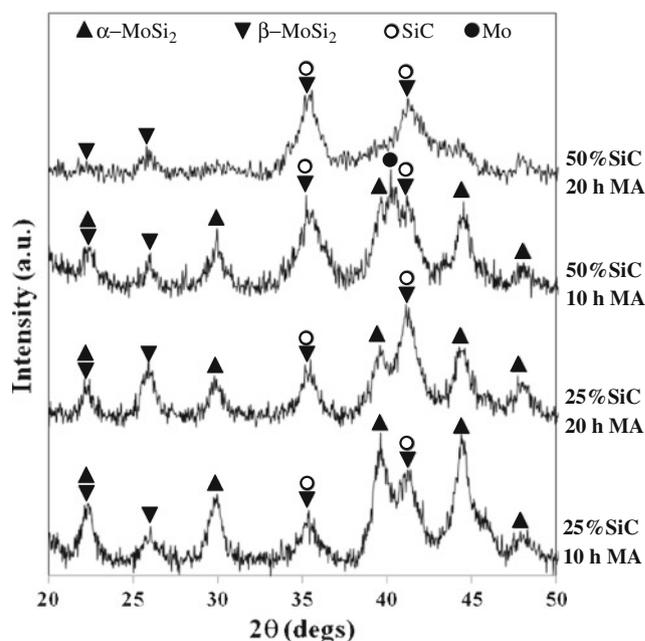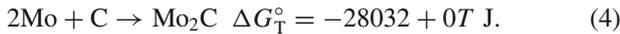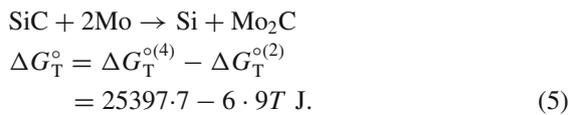

Figure 1. XRD patterns of starting materials.

Figure 2. XRD patterns of milled powders.

A question may be raised in the mind that why Mo_2C was not formed instead of SiC during milling by following reaction (Kubaschewski 1993):

$$2Mo + C \rightarrow Mo_2C \quad \Delta G_T^\circ = -28032 + 0T \text{ J.} \qquad (4)$$

It can be answered by chemical affinities of reactions (2) and (4). As discussed before, chemical affinity of reaction (2) is more than reaction (4) due to its larger ΔG. Therefore, reaction (2) took place before reaction 4 and whole graphite powders were consumed by reaction (2). Graphite content in staring composition is on the basis of reaction (2) for production of 25 and 50 wt.% SiC. There is another answer to this question on the basis of Ellingham–Richardson diagram of these carbides (figure 3). Variation of Gibbs free energy vs temperature was drawn in Ellingham–Richardson diagram for SiC and Mo_2C formation (reactions 2 and 4). On the basis of this diagram, every line that is lower, product of its reaction is more stable than other. As can be seen in figure 3 the line of SiC formation is lower and then SiC is more stable than Mo_2C. This theory can be explained as reaction (4) − reaction (2):

$$SiC + 2Mo \rightarrow Si + Mo_2C$$
$$\Delta G_T^\circ = \Delta G_T^{\circ(4)} - \Delta G_T^{\circ(2)}$$
$$= 25397 \cdot 7 - 6 \cdot 9T \text{ J.} \qquad (5)$$

The positive ΔG of this reaction (23341·5 J) indicates that it cannot be performed during ball milling (Kubaschewski 1993). It means that Mo cannot attract the carbon of SiC on the basis of the above reaction. On the other hand, Si can attract carbon of Mo_2C to form SiC on the basis of opposite route of above reaction.

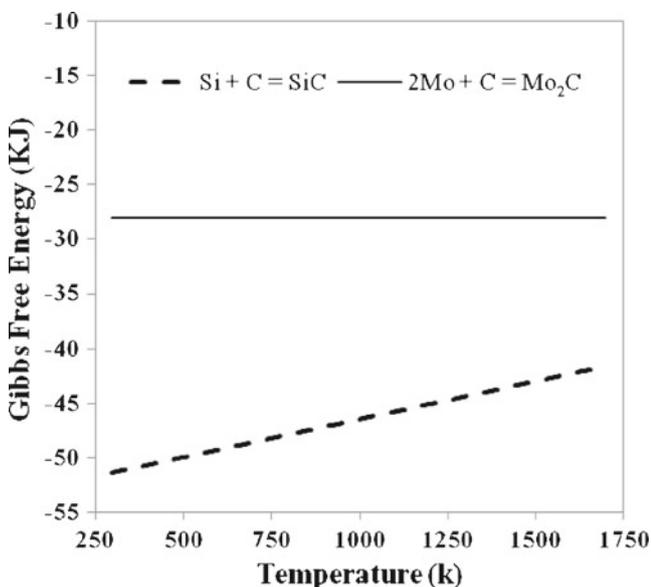Typically, $\Delta H/C > 2000$ K is required for propagation of a mechanically induced self-sustaining reaction (MSR)

(Sannia *et al* 2003). This ratio for $MoSi_2$ and SiC is 2050 and 1245 K, respectively. Consequently, the combustion propagation of a reaction in different parts of the powder may be possible depending on local composition, heat transfer and degree of mixing and activation. Exact propagating mechanism can be determined by measurement of temperature during milling. Temperature and pressure of milling cups were simultaneously measured. As seen in figure 4, there is no spontaneous change in temperature and pressure curves. It means that reactions (1) and (2) propagate gradually during milling. It seems to be correct because adiabatic temperature of reaction (1) is very close to the required limit for MSR mode and reaction (2) does not have this condition. If reaction (1) initiates in MSR mode, released heat of this reaction will be absorbed by components of reaction (2). It means that propagation of reaction (1) will be continued in gradual mechanism. This effect is very significant in MS50 that propagation of reaction (1) was completely stopped. So, Mo reflection can be seen in the pattern of 10 h milled
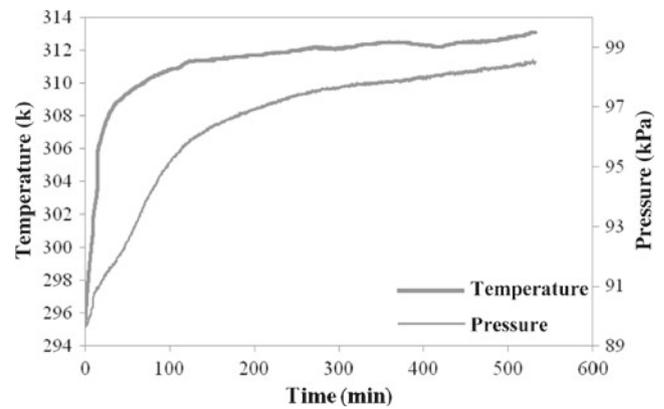

Figure 4. Results of temperature and pressure measurements during milling.

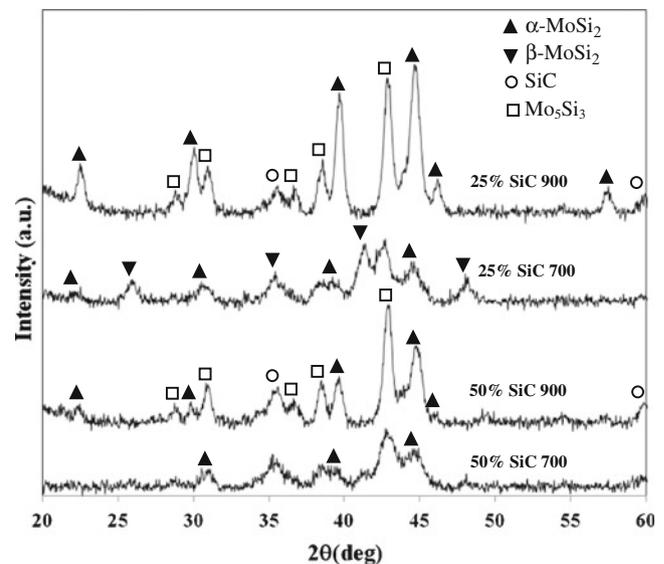**Figure 3.** Ellingham diagram of SiC and Mo_2C (Kubaschewski 1993).

Figure 5. XRD patterns of annealed powders.

MS50 sample that confirms above discussion. Temperature has a minor increase in the first stage (0–1 h) of milling and reaches approximately a constant value of 40 °C at the second stage (1–10 h) of milling. Mechanical energy of ball-ball and ball-wall impacts lead to this minor increased temperature. Temperature increase in the first stage of milling led to the pressure increase due to the fixed volume of the vials.

β-MoSi$_2$ is HTP that is stable above 1900 °C on the basis of Mo–Si binary phase diagram (Zakeri *et al* 2007). Formation of HTP of MoSi$_2$ at room temperature during milling can be explained as follows; it is now well recognized that the structure and constitution of advanced materials can be better controlled by processing them under non-equilibrium (or far-from-equilibrium) conditions. The central underlying technique is to synthesize materials in a non-equilibrium state by energizing and quenching. The energization involves bringing the material into a highly non-equilibrium (meta-stable) state by some external dynamical forcing, such as mechanical energy (Suryanarayana 1999). On the basis of above discussion, the non-equilibrium condition of milling leads to the formation of HTP of MoSi$_2$ that is unstable at room temperature. Longer milling time up to 20 induces more energy and leads to more departure from equilibrium. This is confirmed by the transformation of LTP to HTP of MoSi$_2$ at longer milling times. This transformation was completely performed in MS50, but in MS25, there is some minor amount of LTP after 20 h of milling. It indicates that MS50 has more departure from equilibrium than MS25. Full heat releasing of reaction (1) in MS25 led to decrease in departure from equilibrium and forming more stable phase (LTP).

Figure 5 shows effect of annealing on the structure of 10 h milled powders. Annealing at 700 °C had no considerable effect in MS25. But in MS50, no Mo peak can be seen in its pattern that indicates completion of reaction (1). With
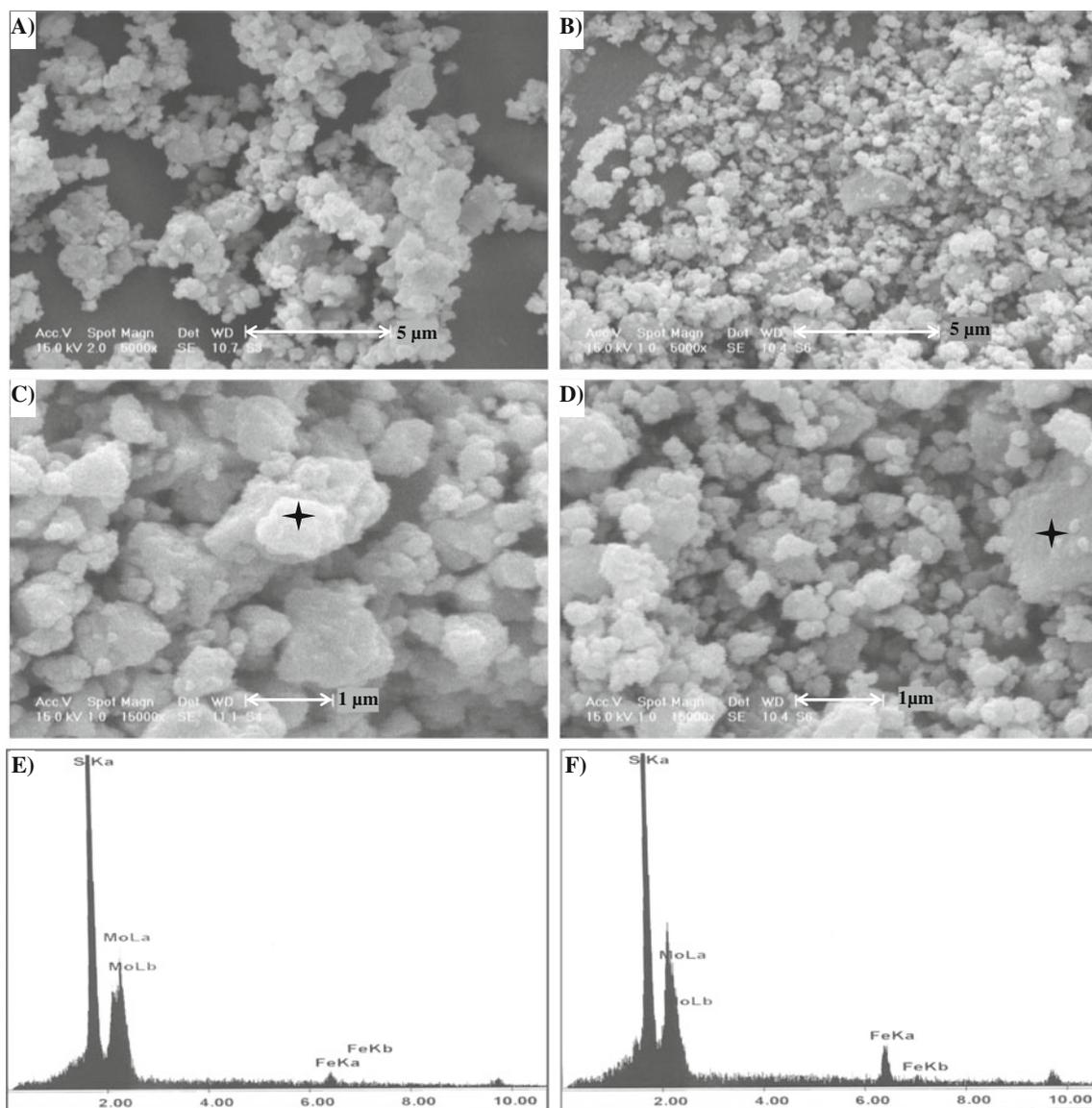

Figure 6. SEM images of 20 h milled samples: (**A**) MS25, (**B**) MS50, (**C**) MS25 and (**D**) MS50 (at higher magnification, (**E**) EDS analysis of image C and (**F**) EDS analysis of image D.

increasing temperature, whole HTP of $MoSi_2$ transformed to LTP. As seen, there is only LTP reflection in the patterns of annealed powders at 900 °C. It means that annealing leads to decreasing of departure from equilibrium that is suitable for LTP of $MoSi_2$. Final products in the annealed powders at 900 °C in both MS25 and MS50 are $MoSi_2$, Mo_5Si_3 and SiC. Formation of Mo_5Si_3 can be explained on the basis of following reaction:

$$5MoSi_2 + 2C \rightarrow Mo_5Si_3 + 7SiC \quad \Delta G_{298}^{\circ} = -116900 \text{ J.} \tag{6}$$
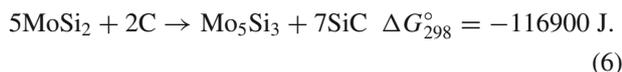
The negative ΔG shows that this reaction can take place in room temperature during milling. But it needs some excess graphite to perform during annealing. Graphite in the as-received materials was on the basis of 25 and 50 wt.% SiC that 1 wt.% excess graphite was added to compensate its oxidation during processing. It seems that this free graphite did not oxidize during processing. On the other hand, it attracts Si of $MoSi_2$ to form SiC on the basis of reaction (6). As seen in figure 5, Mo_5Si_3 reflections intensity in MS50 is larger than MS25. It means that more Mo_5Si_3 was formed in MS50 because of its more graphite content.

SEM images of 20 h milled powders are shown in figure 6. Milling led to the adhering and agglomeration of primary particles. The mean size and amount of these agglomerates in MS25 are higher than MS50. These particles and agglomerates are shown at higher magnification in figures 6C and 6D. These figures show details about particles size and agglomeration process. As seen, mean particles size of MS25 is bigger than MS50. Energy dispersive spectroscopy (EDS) analysis was performed on the marked particle. Figure 6E and 6F show that Mo, Si and Fe exist in these particles. C cannot be detected by this method. Fe is an impurity that was introduced to milled powders because of steel ball and cup wearing. SiC is a hard ceramic that can easily scratch steel cup and ball. Measurement of Fe impurity by ICP method showed that there is some minor Fe in milled powders (table 1). Fe content in the 20 h milled powder with 25% SiC is 0·9 wt.%, wherever it is about 1·4% in the 20 h milled powder with 50% SiC.

Table 1. Fe impurity of milled powders by ICP method.

Sample	Milling time (h)	Fe content (wt%)
MS25	10	0·7
25% SiC	20	0·9
MS50	10	0·8
50% SiC	20	1·4

Table 2. Mean grain size and strain calculated by Williamson–Hall method.

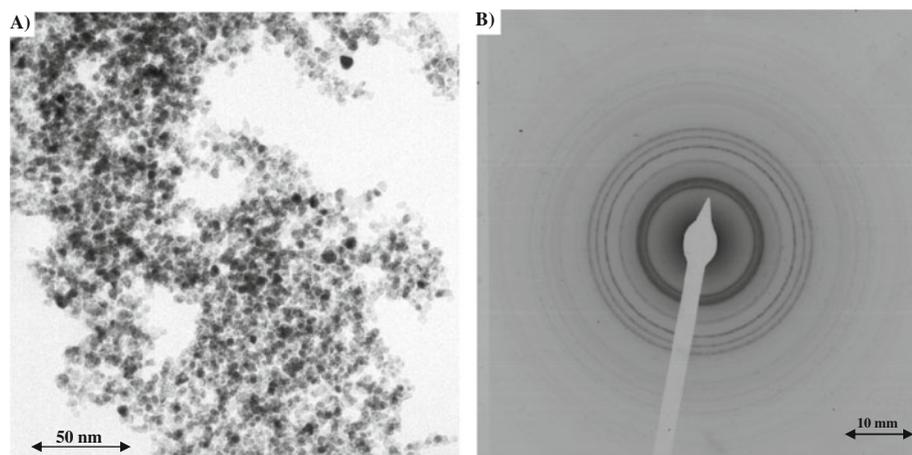| % SiC	Milling time (h)	Phase	Mean grain size (nm)	R^2	Microstrain (%)
25	0	Mo	400·7	1	0·18
	10	α-MoSi₂ (right zone)	44·7±7·6	0·98	0·95±0·05
	20	α-MoSi₂ (right zone)	31·8±1·9	0·99	1·19±0·04
	20 h–700 °C	β-MoSi₂ (left zone)	49±1·4	0·99	0·44±0·06
50	10	β-MoSi₂ (full zone)	20·7±0·6	0·96	0·56±0·11
	20 h–900 °C	α-MoSi₂ (left zone)	41·5±7·4	0·81	0·26±0·02

Figure 7. (**A**) Bright field TEM image and (**B**) selected area diffraction pattern of 20 h milled sample (MS25).

Microstructures of the milled and annealed powders were studied by peak profile analysis. After removing instrumental broadening, peak shape was fitted with pseudo Voigt function. After the measurement of peak width at half maximum, mean grain size and strain were calculated by Williamson–Hall method (Klug and Alexander 1974). Table 2 shows mean grain size and strain of milled and annealed powders. As seen, Mo in the as-received materials has very large grain size (400·7 nm). Milling led to the formation of $MoSi_2$ with very smaller size (44·7 nm). Decreasing of mean grain size progresses with a lower rate, so it reaches to 31·8 nm in 20 h milled powder. In other words, milling led to spontaneous rise in the strain of the 10 h milled powder and it grows up with a lower rate at further milling time and reached to 1·19% in 20 h milled powder. Annealing of 20 h milled powder at 700 °C led to minor grain growth and considerable strain release. Mean grain size and strain of $MoSi_2$ in this sample are 49 nm and 0·44 %, respectively. The calculated mean grain size of 10 h milled sample in MS50 is smaller than MS25. In spite of higher annealing temperature (900 °C), mean grain size of $MoSi_2$ in MS50 is smaller than MS25. On the other hand, strain releasing of $MoSi_2$ in MS50 is much more than MS25 after annealing.

For confirming of peak profile analysis, microstructure of 20 h milled sample (MS25) was studied by TEM. Figure 7 shows bright field image and selected area diffraction pattern of this sample. As seen in figure 7A, all of the grains are smaller than 50 nm that is in conformity with Williamson–Hall results. Selected area diffraction pattern of this microstructure was shown in figure 7B. There are some sharp rings in this image that is related to the very small grain size of the sample.

4. Conclusions

Possibility of synthesis of $MoSi_2$–SiC nanocomposite powder was investigated by mechano-chemical method. Formation of this composite was completed after 10 h of milling with 25% SiC. Required milling time for complete reaction was increased to 20 h at higher SiC content (50%). Both LTP and HTP of $MoSi_2$ were obtained at first stage of milling.

Longer milling time led to transformation of LTP to HTP. On the other hand, an inverse HTP to LTP phase transformation took place during annealing. A reaction between excess graphite and $MoSi_2$ led to the formation of Mo_5Si_3 during annealing at 900 °C. Mean grain size of 31·8 nm and strain of 1·19 % were procured for 20 h milled sample that is in conformity with TEM images.

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