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Mechanochemical synthesis of $MoSi_2$–SiC nanocomposite powder

M. Zakeri [a,*], M. Ahmadi [b]

[a] *Ceramic Department, Materials and Energy Research Center, P.O. Box: 31787/316, Tehran, Iran*
[b] *Department of Materials, Saveh Branch, Islamic Azad University, Saveh, Iran*

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Abstract

$MoSi_2$–25 wt.%SiC nanocomposite powder was successfully synthesized by ball milling Mo, Si and graphite powders. The effect of milling time and annealing temperature were investigated. Changes in the crystal structure and powder morphology were monitored by XRD and SEM, respectively. The microstructure of powders was further studied by peak profile analysis and TEM. $MoSi_2$ and SiC were synthesized after 10 h of milling. Both high and low temperature polymorphs (LTP and HTP) of $MoSi_2$ were observed at the short milling times. Further milling led to the transformation of LTP to HTP. On the other hands, an inverse HTP to LTP transformation took place during annealing of 20 h milled powder at 900 °C. Results of peak profile analysis showed that the mean grain size and strain of the 20 h milled powder are 31.8 nm and 1.19% that is in consistent with TEM image.

Keywords: Nanocomposite; $MoSi_2$–SiC; Mechanochemistry

1. Introduction

$MoSi_2$ is considered to be a promising high temperature structural material for next generation turbine components because of its high melting point, elevated temperature oxidation resistance, brittle to ductile transition temperature and high electrical and thermal conductivity [1]. The brittle to ductile transition temperature of $MoSi_2$ is about 1000 °C. The plastic deformation of $MoSi_2$ above this temperature can be delayed by reinforcing with SiC particulates [2]. Preparing this composite in nanostructure is another method for improving its mechanical properties such as room temperature toughness.

$MoSi_2$–SiC composites have been synthesized by many methods including powder metallurgy [3], self-propagating high temperature synthesis [4], spray processing, exothermic dispersion [5], and solid state displacement reaction [6]. Recently Kim et al. [7] reported the synthesis of nanostructure $MoSi_2$–SiC composites by a high-frequency induction heated combustion method. There are many reports on the synthesis of $MoSi_2$ and its composites by mechanical alloying (MA) [8–10]. In our previous work $MoSi_2$–Al_2O_3 and $MoSi_2$–$CrSi_2$ composites were synthesized by MA. In the former, a mechanically induced self sustaining reaction (MSR) took place in a mixture of MoO_3, SiO_2 and Al powders after 6 h of milling. The product of this reaction was β-$MoSi_2$–Al_2O_3 nanocomposite powder which longer milling time led to the transformation of β-$MoSi_2$ to α-$MoSi_2$ [11]. In the case of later, both silicides of Mo and Cr were synthesized by ball milling Mo, Cr and Si elemental powders, simultaneously [12]. In the present work, $MoSi_2$–SiC composite powder is synthesized by ball milling Mo, Si, and graphite elemental powder at room temperature. The effect of milling time and annealing temperature are investigated on the formation of this composite and phase transformation of $MoSi_2$.

2. Experimental procedures

MA was performed in a planetary ball mill at approximately room temperature and 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.%) and graphite (99.3 wt.%) were mixed to give the desired $MoSi_2$–25%wt.SiC composition. The used starting powders have a narrow size distribution with the mean particles sizes 50, 25 and 10 μm, respectively. The ball to powder weight ratio was 15:1. A distribution of 20, 15 and 10 mm stainless steel balls (seven

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* Corresponding author. Tel.: +98 261 6204131; fax: +98 261 6201888.
E-mail address: M_zakeri@merc.ac.ir (M. Zakeri).

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balls for each diameter) 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 (250 mL) in an Ar atmosphere. Samples were removed for analysis in a glove box under an Ar atmosphere by interrupting milling at various intervals. The temperature and pressure of the cups were measured during milling for determination of beginning and mechanism of reactions. There is a small thermocouple and pressure load cell on the door of cup that they measure the internal temperature and pressure of cup and transfer to the computer software by wireless method. Heat treatment was conducted in a tube furnace in an Ar atmosphere ($2\,\mathrm{l\,min^{-1}}$). Heating rate and holding time at maximum temperature were $10\,\mathrm{k\,min^{-1}}$ and 1 h, respectively.

XRD profiles were recorded on a Siemens diffractometer (30 kV and 25 mA) with Cu $K\alpha_1$ radiation (1.5404 Å). All XRD experiments were carried out with the step size of 0.02° and the 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 $K\alpha_2$ radiation was stripped (stripping ratio $K\alpha_2/K\alpha1 = 0.5$) from the scans using the computer software X-pert High Score developed by PANalytical BV Company (Almelo, the Netherlands). 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.

3. Results and discussions

The feasibility of synthesizing of $\mathrm{MoSi_2}$–SiC nanocomposite powder was investigated by ball milling Mo, Si and graphite elemental powders. The XRD pattern of the blended starting materials is shown in Fig. 1. Ball milling of this mixture for 10 h led to the disappearing of their reflections. It means that the starting materials completely reacted. As seen in Fig. 2, the products of these reactions are both HTP and LTP of $\mathrm{MoSi_2}$ and SiC phases. Further milling up to 20 h led to the decreasing of LTP phase. On the other hand, longer milling time led to the phase transformation of LTP to HTP of $\mathrm{MoSi_2}$. The existent of only the HTP of $\mathrm{MoSi_2}$ at the end of milling confirms this transformation.

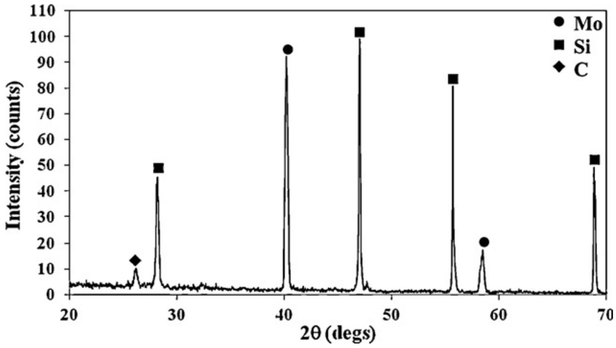

Fig. 1. XRD pattern of the as-received materials.

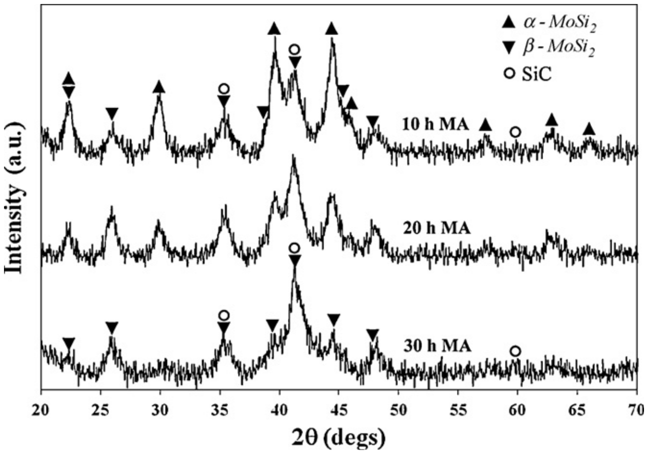

Fig. 2. XRD patterns of the milled powders.

Synthesizing of all possible products was studied on the basis of their Gibbs free energy for their attributed reactions. For this purpose, first the ΔH_{298}, ΔS_{298}, and C_p extracted for each phase from Ref. [13] and then the following equations were used for the calculation of ΔG_T:

$$\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} C_p\, dT \tag{1}$$

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^{T} \frac{C_p}{T}\, dT \tag{2}$$

$$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 \tag{3}$$

Formation of $\mathrm{MoSi_2}$ and SiC is on the basis of following reactions:

$$\mathrm{Mo} + 2\mathrm{Si} \rightarrow \mathrm{MoSi_2} \quad \Delta G_T^0 = -128003 - 55.4T + 8.52T\ln T\frac{\mathrm{j}}{\mathrm{mole}}\,298 < T < 1685\,\mathrm{K} \tag{4}$$

$$\mathrm{Si} + \mathrm{C} \rightarrow \mathrm{SiC} \quad \Delta G_T^0 = -74659.87 + 128.65T - 18.55T\ln T\frac{\mathrm{j}}{\mathrm{mole}}\,298 < T < 1100\,\mathrm{K} \tag{5}$$

These reactions have the negative Gibbs free energy $((\Delta G_{298}^{0(4)} = -130, \Delta G_{298}^{0(5)} = -67.83\,\mathrm{kj/mole}))$ at room temperature. The negative ΔG shows that these reactions can be performed during ball milling. It is very difficult to distinguish sequence of these reactions. But there are two approaches on the basis of formation heat (ΔH) and chemical affinity of the starting materials. The ΔH of these reactions at room temperature are -131.8 and $-66.9\,\mathrm{kj/mole}$, respectively [13]. Reaction (4) has more negative ΔH and ΔG in compare with reaction (5). Therefore it can be concluded that this reaction probably takes place before the reaction (5). Chemical affinity (A) definition is the negative partial derivative of Gibbs energy (G) with respect to extent of reaction ($\in$) at constant pressure and temperature [14] that is:

$$A = -\left(\frac{\delta G}{\delta \in}\right)_{P,T} \qquad (6)$$

On the basis of this equation, both reactions (4) and (5) have a positive chemical affinity, but in the same extent of reaction ($\in$), reaction (4) has higher chemical affinity due to its larger negative ΔG. Whatever, heat releasing of the first reaction leads to the initiating of second reaction. Therefore, it can be concluded that these reactions approximately take place simultaneously with some negligible delay.

A question may be raised in mind that why Mo_2C was not formed instead of SiC during milling by the following reaction [13]:

$$2\text{Mo} + \text{C} \rightarrow \text{Mo}_2\text{C} \quad \Delta G_T^0 = -54394.89 + 43.28T - 7.12T\ln T\,\frac{\text{j}}{\text{mole}}\,298 < T < 1100\,\text{K}. \qquad (7)$$

It can be answered by comparing reactions (5) and (7) chemical affinities. As discussed before, the chemical affinity of reaction (5) is more than reaction (7) due to its larger ΔG ($\Delta G_{298}^{0(5)} = -67.83, \Delta G_{298}^{0(7)} = -53.58\,\text{kj/mole}$). Therefore this reaction will be took place before the reaction (7) and all of the graphite powders will be consumed in the reaction (5). The graphite content in the staring composition was on the basis of reaction (5) for the production 25 wt.% SiC in the $MoSi_2$–SiC composite. There is another answer to this question on the basis of Ellingham diagram of these carbides (Fig. 3). Variation of ΔG versus temperature was drawn in Ellingham diagram for SiC and Mo_2C formation (reactions (5) and (7)). On the basis of this diagram, every line that is lower, the product of its reaction is more stable than other. As can be seen, in Fig. 3, line of SiC formation is lower and therefore SiC is more stable than Mo_2C. This thesis can be explained as:

Reaction (7)–Reaction (5):

$$\text{SiC} + 2\text{Mo} \rightarrow \text{Si} + \text{Mo}_2\text{C} \qquad \Delta G_T^0 = \Delta G_T^{0(4)} - \Delta G_T^{0(2)} = 20264.9 - 85.4T + 11.4T\ln T\,\frac{\text{j}}{\text{mole}}\,298 < T < 1500\,\text{K}. \qquad (8)$$

The positive ΔG of this reaction ($\Delta G_{298}^{0(3)} = +14.17\,\text{kj/mole}$) indicates that it cannot be performed during ball milling [13]. It means that Mo cannot attract the carbon of SiC on the basis of this displacement reaction. On the other hands, if in any condition, Mo_2C was synthesized, Si can attract its carbon and form SiC on the basis of above reaction.

The progress mechanism of a reaction during milling depends on its formation heat to the products heat capacity ratio ($\Delta H/C$) at room temperature. Typically, $\Delta H/C > 2000$ K is required for propagation of a mechanical induced self-sustaining reaction (MSR) [15]. This ratio for $MoSi_2$ and SiC is 2050 and 1570 K, respectively that was calculated on the basis of obtained data from Ref. [13]. Consequently, the combustion propagating of a reaction in different part of the powder may be possible depending on the local composition, heat transfer and the degree of mixing and activation. The exact propagating mechanism can be determined by measurement of temperature during milling. Temperature and pressure of milling cups were simultaneously measured. As can be seen in Fig. 4, there is no spontaneous change in the temperature and pressure curves. It means that reactions (4) and (5) propagate gradually during milling. It seems to be correct because the adiabatic temperature of reaction (4) is very close to the required limit for MSR mode and reaction (5) has not this condition. If the reaction (4) initiates in the MSR mode, its released heat will be absorbed by the components of reaction (5). It means that propagating of reaction (4) will be stopped and it will be continued in gradual mechanism. Temperature has a minor increase in the first stage (0–1 h) and reaches the approximately constant value of 312 K at the second stage of milling (1–10 h). Mechanical energy of ball-ball and ball-wall impacts lead to this minor increased temperature. This temperature rise in the first stage of milling led to the pressure increasing due to the fixed volume of the vials.

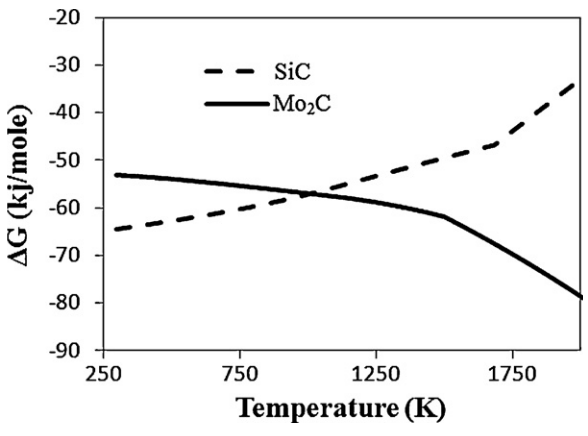

Fig. 3. Ellingham diagram of The SiC and Mo_2C [13].

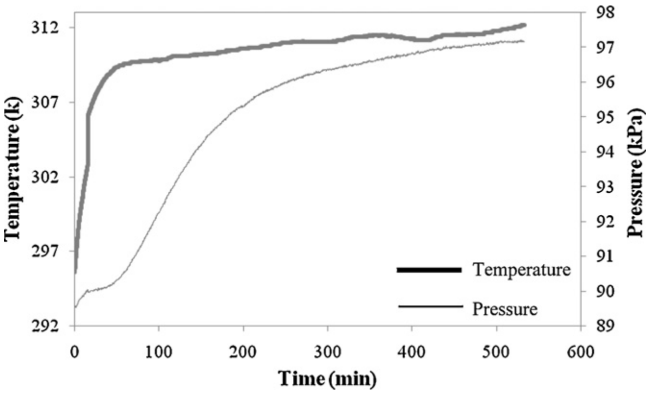

Fig. 4. Temperature and pressure measurement of the milling cups.

β-$MoSi_2$ is HTP of $MoSi_2$ that is stable above 1900 °C on the basis of Mo–Si binary phase diagram [9]. Formation of HTP of $MoSi_2$ can be explained as follow; 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 [16]. Amongst many processes, which are in commercial use, mechanical alloying has been receiving serious attention from researchers. 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 [16]. On the basis of above discussion, 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 and 30 h will induce more energy to the powders and leads to more departure from equilibrium. This is confirmed by the transformation of LTP to HTP of $MoSi_2$ at longer milling times (see Fig. 2, that there is only HTP of $MoSi_2$ at 30 h milled powder).

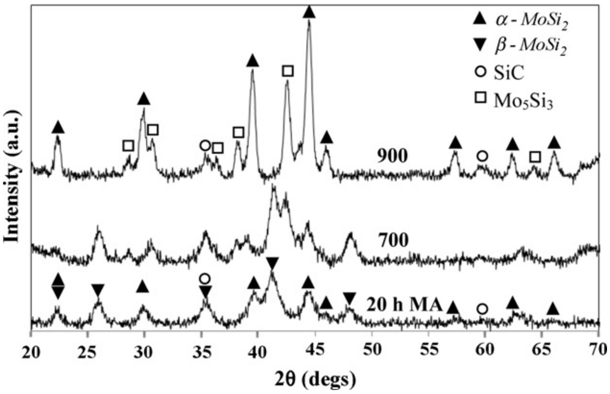

Fig. 5. XRD patterns of the 20 h milled powder that annealed at different temperatures.

HTP of $MoSi_2$ is a meta-stable phase at room temperature that can be transformed to LTP stable phase. But this transformation needs an activation energy that can be obtained by annealing. Fig. 5 shows the XRD patterns of the 20 h milled samples that annealed at different temperatures. This milled sample includes HTP and LTP in major and minor amounts, respectively. Annealing at 700 °C had no considerable effect on this transformation. On the other hands, annealing at 900 °C led to full transformation of HTP to LTP of $MoSi_2$. As seen in Fig. 5, all of the HTP's reflections were disappeared in the pattern of the annealed powder at 900 °C. This pattern includes LTP of $MoSi_2$, SiC and Mo_5Si_3. Formation of Mo_5Si_3 can be explained on the basis of following reaction:

$$5MoSi_2 + 7C \rightarrow Mo_5Si_3 + 7SiC$$
$$\Delta G^0_{298} = -119300 - 252.6T\,\text{J} \qquad (9)$$

The negative ΔG shows that this reaction can be took place. But it needs some excess graphite to perform during annealing. Graphite in the as-received materials was on the basis of 25 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 hands, it attracts the silicon of $MoSi_2$ to form SiC on the basis of reaction (9).

Effect of the milling on the morphology and particles size was investigated by SEM. Fig. 6A and B shows SEM images of

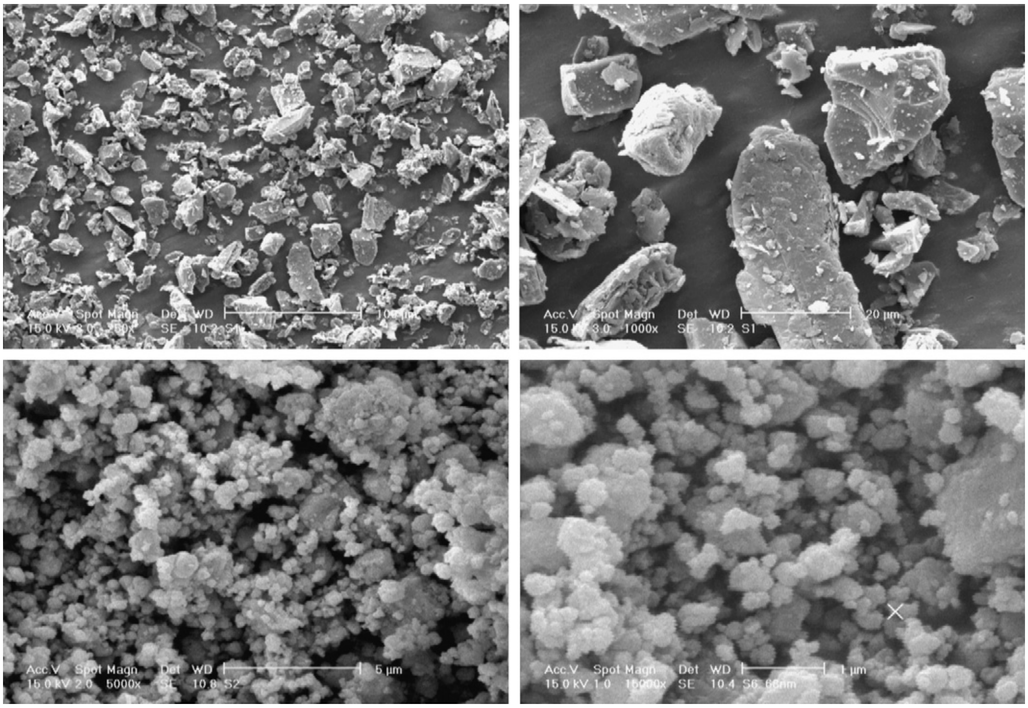

Fig. 6. Effect of milling on morphology and particles size; (a) as-received, (b) as-received at higher magnification, (c) 10 h milled and (d) 10 h milled at higher magnification.

Table 1
Mean grain size and strain of the milled and annealed powders with Williamson-Hall method.

Milling time (h)	Phase	Mean grain size (nm)	Micro strain (%)	R^2
0	Mo (full zone)	400.7	0.18	1
10	α-$MoSi_2$ (right zone)	44.7 ± 7.6	0.95 ± 0.05	0.98
20	α-$MoSi_2$ (right zone)	31.8 ± 1.9	1.19 ± 0.04	0.99
20 h–700 °C	β-$MoSi_2$ (left zone)	49 ± 1.4	0.44 ± 0.06	0.99

the as-received materials at two magnifications. As seen, there are three kinds of particles in these images. Large, average and small particles that are probably correspond to Mo, Si and graphite, respectively. Fig. 6C shows that milling of these staring materials led to considerable particle size decreasing to submicron. These particles were agglomerated due to heavy impacts of ball-ball and ball-wall during milling. Fig. 6D shows agglomeration at higher magnification. As seen, there are many small submicron particles that adhered together and formed this agglomerate. These particles have very small sizes that are less than 100 nm (Size of the marked particle in Fig. 6D is 86 nm).

The mean grain size and micro-strain of the milled and annealed powders were measured by Williamson-Hall method. This method works on the basis of peak profile analysis [17]. Each XRD profile shape is affected by microstructure of sample and instrumental parameters. Therefore, the first step is to separate instrumental from microstructural effects. It is usually performed by a standard material that has very large grain size with a minimum strain. In this investigation, pure $MoSi_2$ that annealed at 1300 °C was used as standard material. After the removing of instrumental effect, $K\alpha_2$ stripping and background modifying, the peak profile was fitted by the Pseudo-Voigt function. Due to the asymmetry, the left or right zone of profiles was used in some samples. In the final step, de-convulsion of mean grain size and strain was performed by Williamson-Hall method. More details about this procedure were presented in our previous papers [18,19]. Table 1 shows the results of these calculations. 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 progress with a lower rate, so it reaches to 31.8 nm in 20 h milled powder. On the other words, milling led to the 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 the 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. Heavy mechanical impacts and plastic deformation during milling lead to increasing of lattice defects such as dislocations. These dislocations form low angle grain boundaries (LAGB) with their arrangements. With fracturing of particles, LAGBs transforms to high angle grain boundaries (HAGB). This process take place frequently and leads to the decreasing of mean grain size and increasing of lattice strain. During annealing some recovery process leads to the decreasing of lattice defects.

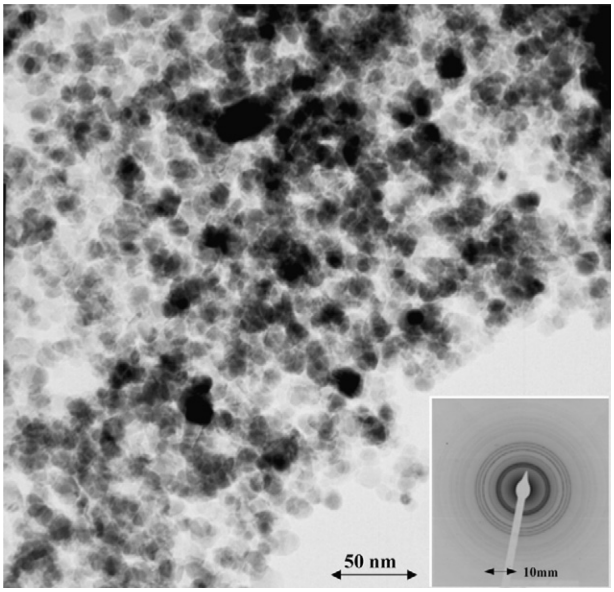

Fig. 7. Bright field TEM image of 20 h milled sample.

For confirmation of calculated grain size results, microstructure of 20 h milled sample was taken by TEM. As seen in Fig. 7, all of the grains are smaller than 50 nm that is in consistent with Williamson-Hall results. Selected area diffraction pattern of this microstructure was shown in bottom-right corner of this image. There are some sharp rings in this image that is related to the very small grain size of the sample.

4. Conclusion

The feasibility of synthesizing of $MoSi_2$–SiC nanocomposite was investigated by mechano-chemistry method. Ball milling of Mo, Si and graphite elemental powders led to the formation of $MoSi_2$–25 wt.%SiC after 10 h of milling. Non-equilibrium nature of ball milling led to formation of HTP of $MoSi_2$ at the end of milling (30 h). In the other words, LTP of $MoSi_2$ was synthesized after annealing of 20 h milled powder at 900 °C due to the equilibrium nature of annealing. The reaction between $MoSi_2$ and excess graphite led to the formation of Mo_5Si_3 during annealing. Results of peak profile analysis showed that the mean grain size and strain of the 20 h milled powder are 31.8 nm and 1.19% that is in consistent with TEM image.

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