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Synthesis of $(Mo_{1-x}–Cr_x)Si_2$ nanostructured powders via mechanical alloying and following heat treatment

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ABSTRACT

$MoSi_2$–$CrSi_2$ nanocomposite powder was successfully synthesized by ball milling of Mo, Si and Cr elemental powders. Effects of the Cr content, milling time and annealing temperature were studied. X-ray diffraction (XRD) was used to characterize the milled and annealed powders. The morphological and microstructural evolutions were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). High temperature polymorph (HTP) 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 (50 h) and low temperature annealing (850 °C). Annealing led to the HTP to low temperature polymorph (LTP) transformation of $MoSi_2$. $MoSi_2$–$CrSi_2$ nanocomposite powder with the mean grain size less than 50 nm was obtained at the end of milling. This composite maintained its nanocrystalline nature after annealing. A spherical morphology was procured for 50 h milled powder with 0.25 mole Cr.

1. Introduction

Due to their attractive high temperature properties, silicides of various metals have been the focus of numerous investigations. In the case of molybdenum silicide ($MoSi_2$), the combination of a low density, a high melting point and a very good high temperature corrosion resistance leads to the consideration of this silicide for structural applications in a temperature range as high as 1523 K for turbine engines [1–4]. Some of the major disadvantages of $MoSi_2$ are its poor room temperature ductility and fracture toughness [5], sharp drop in high temperature creep [6] and yield strengths [7] at and above 1473 K, and the possibility of pest disintegration in the temperature range of 673–873 K [8]. Some of the methods with the potential of improving the room temperature fracture toughness and high temperature strength, as reported in the literature, have involved alloying and adding reinforcements [5–9]. SiC, Si_3N_4, Al_2O_3 and $CrSi_2$ can be used as reinforcements. Another possible mechanism to improve mechanical properties is to prepare these materials in nanostructure [10].

The added chromium in the form of $CrSi_2$ must be well dispersed in the matrix ($MoSi_2$) of composite. Mechanical alloying (MA) [11] has been considered as a powerful and practical process for fabrication of several advanced materials with unique properties [12], in particular, for those materials that are difficult to be obtained by the traditional way of liquid metallurgy. During ball milling, the diffusion couples were formed through a dynamic process of deforming, fracturing and cold-welding of the powders. After some time of milling, each powder consists of a large number of diffusion couples formed by sequential stacking of elemental nano-sized thin elemental layers or by agglomeration of equiaxed elemental particles, the reaction occurs at low temperature [13].

$MoSi_2$ [14,15] and $CrSi_2$ [16,17] were separately synthesized by MA, but there is no attempt to prepare $MoSi_2$–$CrSi_2$ nanocomposite powder by MA. The aim of this work is to synthesize $MoSi_2$–$CrSi_2$ nanocomposite powder by milling of Mo, Cr and Si elemental powders at nominal room temperature. Effect of the Cr content, milling time and annealing temperature were investigated.

2. Experimental

The MA was performed in a planetary ball mill at nominal room temperature and at a vial rotation speed (cup speed) of 540 rpm. Pure Merck Mo (99.7%, 40 μm), Si (99.0%, 150 μm) and Cr (99.3%, 40 μm) were mixed to give the desired $(Mo_{1-x}–Cr_x)Si_2$ composition with 0.15 and 0.25 mole Cr. The ball to powder weight ratio (BPR) was 10:1. One ball with 12 mm and three balls with 11 mm diameter were used in the MA experiments. For preventing of excess agglomeration 0.8% (weight percent) stearic acid was used as process controlling agent (PCA). The mixture of the powders with the stainless steel balls was charged into a stainless steel cup (250 ml) in argon atmosphere. Samples for analysis were removed in a glove box under argon atmosphere by interrupting the ball mill at various intervals.

X-ray diffraction profiles were recorded on a Philips diffractometer (30 kV and 25 mA) with Cu $K\alpha_1$ radiation (λ = 1.5404 Å). All XRD experiments were done with the step size of 0.02° and a time per step of 1 s. The recorded XRD patterns were

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used for the calculation of crystallite size and strain. Prior to calculations from the diffraction peaks, the background was automatically removed and the $K\alpha_2$ radiation was stripped (stripping ratio $K\alpha_2/K\alpha_1 = 0.51$) from the scans using the computer software X-pert High Score developed by PANalytical B. V. Company (Netherlands) [18].

Structural observations of the milled powder were carried out with a Philips EM208S transmission electron microscope (TEM) operating at 100 kV. Ultrasonic method was used for dispersing of the powder in the ethanol suspension. Two drop of this suspension on a copper grid was used for the TEM observation. The morphology and particle size of the mechanically alloyed powder samples were examined by a Cambridge scanning electron microscope (SEM) operating at 25 kV. Heat treatment of the as milled powders was conducted in a tube furnace in argon atmosphere (2.2 l/min). The heating rate was 10 °C/min and holding time at maximum temperature was 2 h.

3. Results and discussions

3.1. Structural evolutions

The feasibility of synthesizing of $MoSi_2$–$CrSi_2$ nanocomposite powder with 0.15 mole Cr was investigated. Fig. 1 shows the XRD patterns of the as received and milled powders. As received material includes Mo, Cr and Si elemental powders than can still be seen after 30 h of milling. Peak broadening and intensity decreasing are the results of milling in this stage. Lack of any shift in Mo peak position indicates that there is no reciprocal solid solution. With increasing milling time to 50 h, the β-$MoSi_2$ reflections appeared in the pattern on the basis of following reaction:

$$0.85Mo + 1.7Si = 0.85MoSi_2 (\Delta H^{\circ}_{298} = -111.4\,kJ \ldots\ldots \Delta G^{\circ}_{298} = -128.4\,kJ) \quad (1)$$

This reaction is thermodynamically favorable at room temperature during milling because of its negative Gibbs free energy [19]. Heavy plastic deformation of the starting materials leads to the higher lattice defects and smaller grain size. These phenomena increase the internal energy and decrease the diffusion distance in the milled powders that they are kinetically favorable parameters for the formation of $MoSi_2$ by reaction (1). Formation of β-$MoSi_2$ in the 50 h milled sample is due to its same crystal system with $CrSi_2$. These phases have hexagonal crystal system [20].

The exothermicity of a reaction is often characterized by the ratio of the heat of formation to the room temperature heat capacity ($\Delta H/C$). Typically, $\Delta H/C > 2000$ K is required for mechanically induced self-sustaining reaction (MSR) [21]. The reaction between Mo and Si is close to this limit, $\Delta H/C = 2060$ K. Consequently, the propagation of the reaction in different parts of the powder may be possible depending on the local composition, heat transfer and the degree of mixing and activation. But, the existence of Mo and Si reflections in the 50 h milled sample, and long period of milling during reaction (between 30 and 50 h) indicates that this reaction was performed in gradual mode. This reaction propagates gradually at longer milling times. On the other hand, all starting material reflections disappeared in the 70 h milled powder. As seen, some of the β-$MoSi_2$ transformed to α-$MoSi_2$ at this stage of milling. β-$MoSi_2$ is the high temperature polymorph (HTP) that cannot be stable at room temperature during milling. Further milling up to 100 h had no considerable change except peak broadening of the synthesized phased due to the microstructure refinement.

Effect of the Cr content on the formation of $MoSi_2$–$CrSi_2$ composite powder was investigated. Fig. 2 shows the XRD patterns of the as received and milled powders with 0.25 mole Cr. There is no difference in the results of this condition compared with previous Cr content (0.1 mole) up to 50 h of milling. No transformation of HTP (β) to (LTP) (α) was performed at longer milling times. As discussed before, the formation of HTP of $MoSi_2$ is because of its similar crystal system with $CrSi_2$. And higher Cr content (0.25 mole) prevents

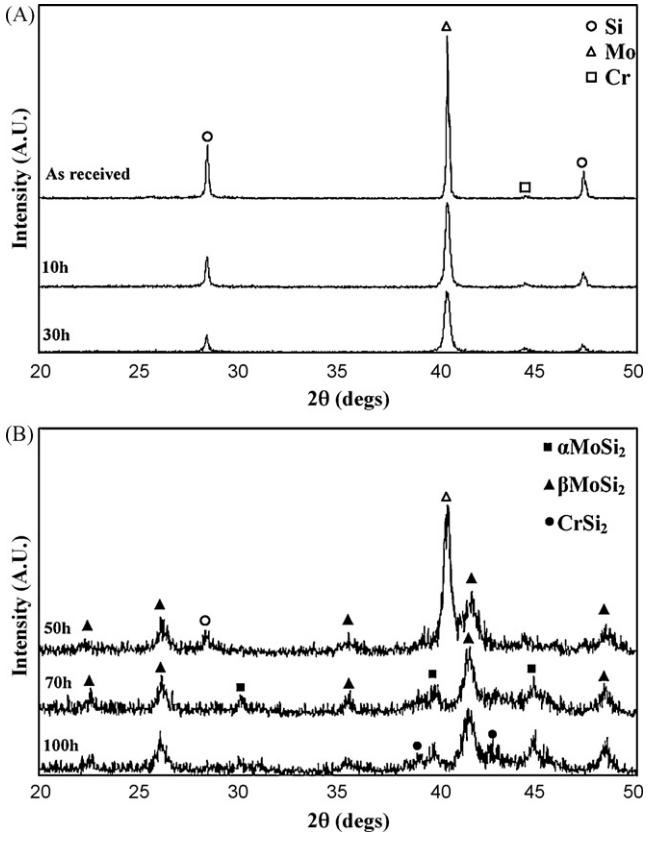

Fig. 1. XRD patterns of the as milled powders with 0.15 mole Cr at the cup speed of 540 rpm.

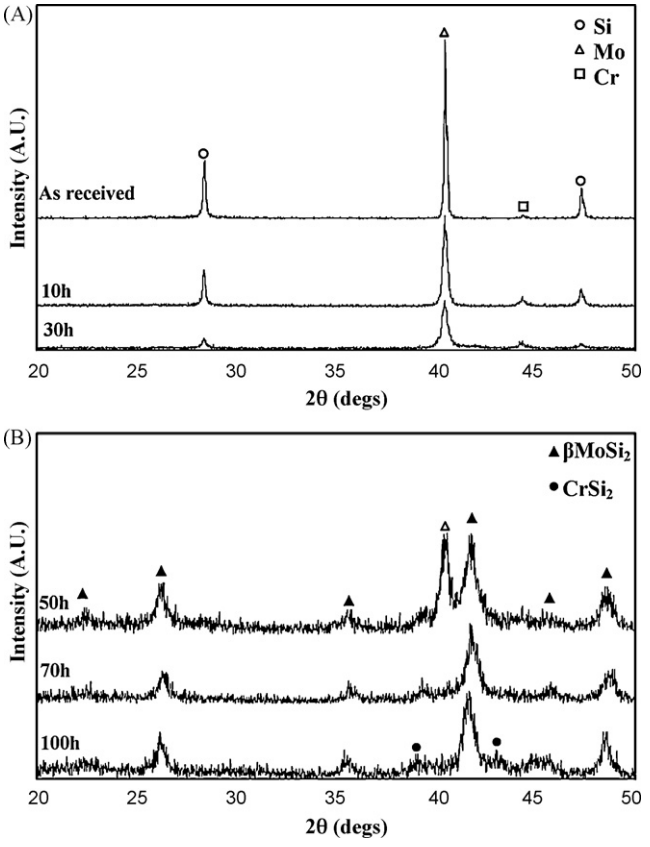

Fig. 2. XRD patterns of the as milled powders with 0.25 mole Cr at the cup speed of 540 rpm.

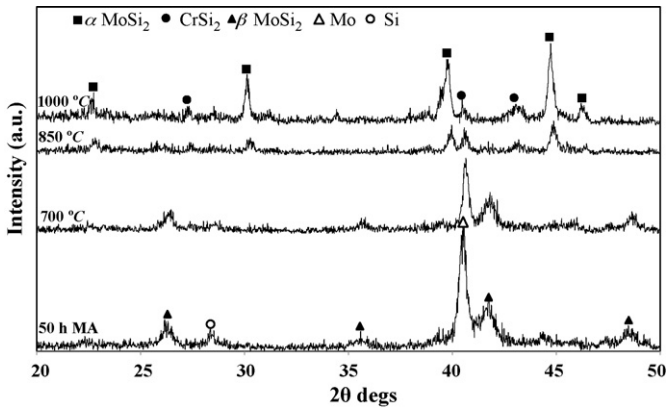

Fig. 3. XRD patterns of the annealed powders after 50 h of milling with 0.15 mole Cr at the cup speed of 540 rpm.

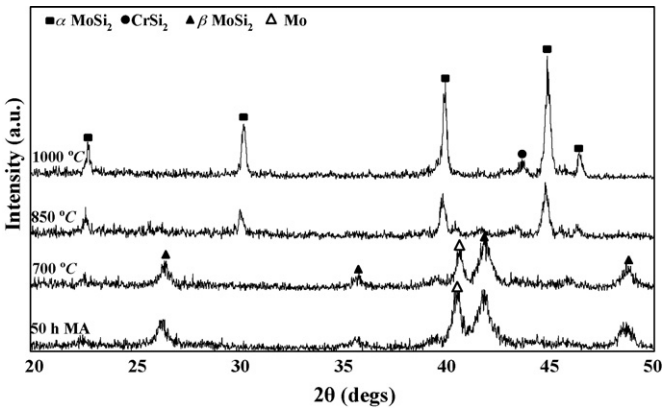

Fig. 4. XRD patterns of the annealed powders after 50 h of milling with 0.25 mole Cr at the cup speed of 540 rpm.

HTP to LTP phase transformation during milling at room temperature. As seen, there is only HTP of $MoSi_2$ and $CrSi_2$ reflections in the pattern of the 100 h milled powder.

Thermal stability and phase transformation of the synthesized phases after 50 h of milling were investigated during annealing at different temperatures. The XRD patterns of the as milled and annealed powders with 0.15 mole Cr are presented in Fig. 3. The as milled powder includes HTP of $MoSi_2$ and some remaining starting materials. Formation of $MoSi_2$ continues during annealing at 700 and 850 °C and completes at 1000 °C, i.e. all of the starting materials reflections disappeared in the pattern of the annealed powder at 1000 °C. HTP of $MoSi_2$ is stable during annealing at 700 °C, but it transforms to LTP of $MoSi_2$ at 850 °C. There in no considerable change at higher temperature (1000 °C) except for peak sharpening of the included phases because of microstructure refinement that will be discussed in next section. There is a same behavior in the annealing of the 50 h milled powder with 0.25 mole Cr. As seen in Fig. 4, the annealed powder at 1000 °C includes, the LTP of $MoSi_2$ and $CrSi_2$. It can be concluded that with combination of milling and annealing, the $MoSi_2$–$CrSi_2$ composite powders can be prepared in short time of milling as well as low temperature of annealing.

3.2. Microstructure and morphology

Mean grain size and lattice strain of the $MoSi_2$, Mo and Si were calculated by peak profile analysis. The reference powders were the Mo, Si and $MoSi_2$ powders that annealed at 1000, 800 and 1400 °C for 6 h, respectively. The well-known Williamson–Hall method was used for calculation of mean grain size and lattice strain [22]. The results of these calculations are presented in Table 1. Longer milling time led to the smaller grain size and larger lattice strain for all

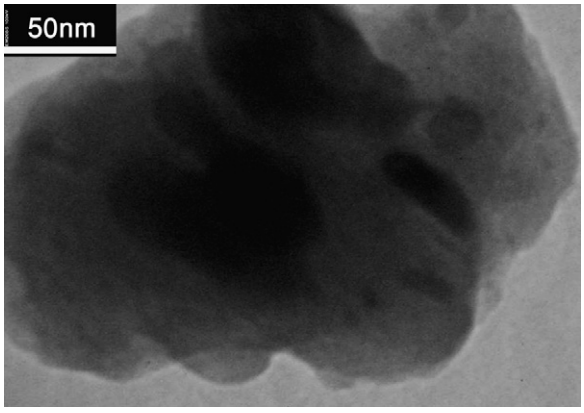

Fig. 5. Bright field image of the 100 milled powder with 0.15 mole Cr.

phases in both Cr contents. The mean grain size and lattice strain in the samples with higher Cr content at fixed milling time, are larger than the samples with lower Cr content. The mean grain size of 23 nm was obtained for α-$MoSi_2$ after 100 h of milling. The microstructure of this sample was presented in Fig. 5. Very small grains with the size less than 25 nm can be seen in this figure that is in consistent with the XRD results. There is a homogeneous distribution of two different phases (black and light) attributed to $MoSi_2$ and $CrSi_2$. In general, it can be concluded that $MoSi_2$–$CrSi_2$ nanocomposite powders with the grain size less than 50 nm were obtained at the end of milling in all compositions. High impact between ball–ball and ball–wall during milling leads to heavy plastic deformation of the powders and increasing of lattice defects such as dislocations. Fracturing and rearrangement of the dislocations leads to the microstructure refinement as well as grain size

Table 1
Mean grain size and micro-strain of the milled powders with different Cr content at the vial speed of 540 rpm.

Phases		Mo		Si		β-$MoSi_2$	
X_{Cr} mole fraction	Milling time (h)	G.S. (nm)	Strain%	G.S. (nm)	Strain%	G.S. (nm)	Strain%
0.15	10	46	0.04	73	0.015	–	–
	30	30	0.06	56	0.03	–	–
	50	20	0.07	–	–	29	0.46
	70	–	–	–	–	26	0.51
	100	–	–	–	–	23	0.55
0.25	10	107	0.25	139	0.27	–	–
	30	92	0.5	92	0.52	–	–
	50	37	0.63	–	–	65	0.43
	70	–	–	–	–	53	0.55
	100	–	–	–	–	45	0.88

Table 2
Mean grain size and micro-strain of the annealed powders with different Cr content at the vial speed of 540 rpm.

Phases		α-$MoSi_2$		β-$MoSi_2$	
X_{Cr} mole fraction	Annealing temperature (°C)	G.S. (nm)	Strain%	G.S. (nm)	Strain%
0.15	As milled (50 h)	–	–	29	0.46
	700	–	–	35	0.31
	850	60	0.19	–	–
	1000	73	0.14	–	–
0.25	As milled (50 h)	–	–	65	0.43
	700	–	–	92	0.34
	850	73	0.35	–	–
	1000	126	0.08	–	–

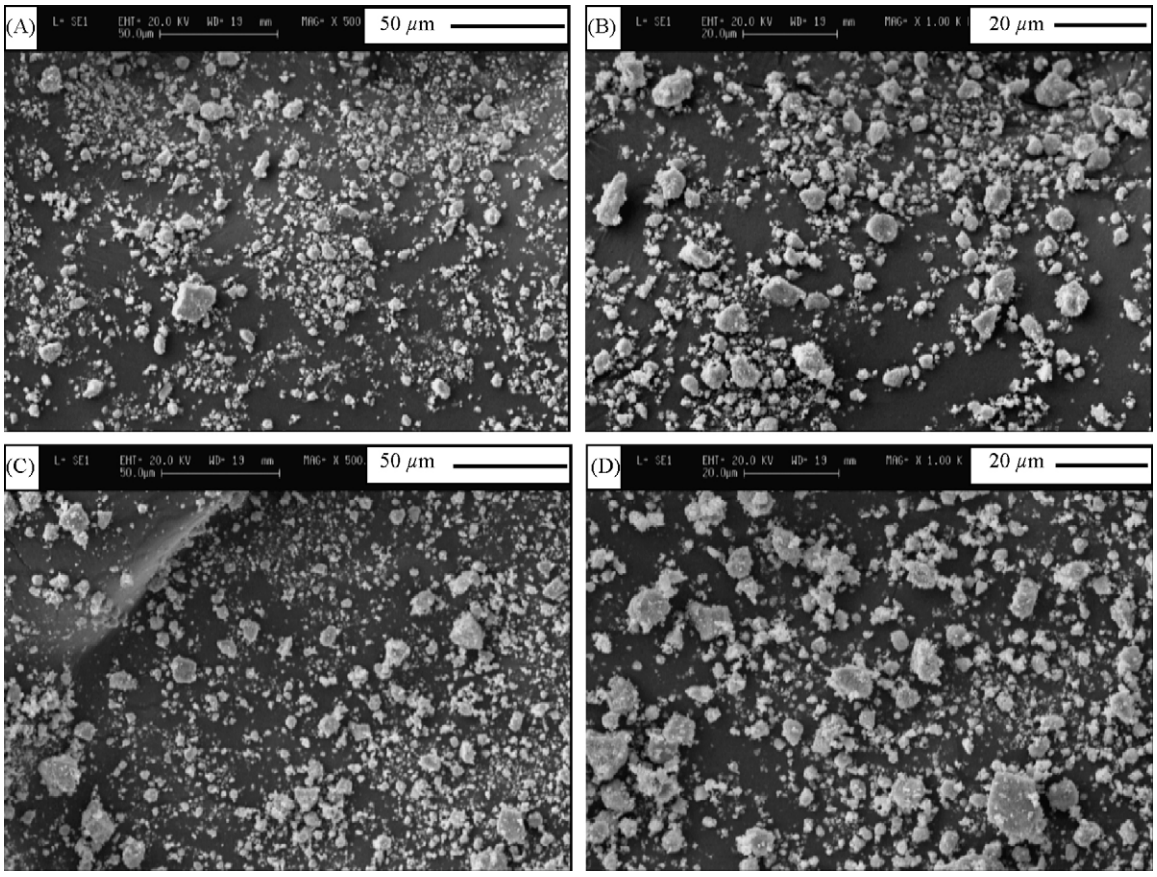

Fig. 6. SEM images of the 50 h milled powders at the cup speed of 540 rpm with different Cr content: (A) 0.15 mole, (B) 0.15 mole at higher magnification, (C) 0.25 mole and (D) 0.25 mole at higher magnification.

reduction. Diffusion in nanometer grain size and dislocations can be performed in higher speeds during annealing. Higher speed diffusion promotes the recovery mechanism during annealing and leads to the grain growth as well as lattice strain release. The results of mean grain size and lattice strain measurement of the annealed phases confirm this. As seen in Table 2, the mean grain size of both polymorphs of $MoSi_2$ increases at high temperature. In spite of this grain growth, both phases maintain their nanocrystalline properties after annealing. As discussed above, strain release is the other effect of the annealing.

Effects of the Cr content on the morphology of the 50 h milled powders are shown in Fig. 6. A distribution of particles and agglomerates can be seen in these samples. But the particles and agglomerate in the sample with 0.15 mole Cr (Fig. 6A and B) are some larger than the samples with 0.25 mole Cr (Fig. 6C and D). Higher Cr content led to more agglomeration of the small particles. The spherical morphology was obtained at this stage of milling is shown in Fig. 7. Heavy plastic deformation of the particles during

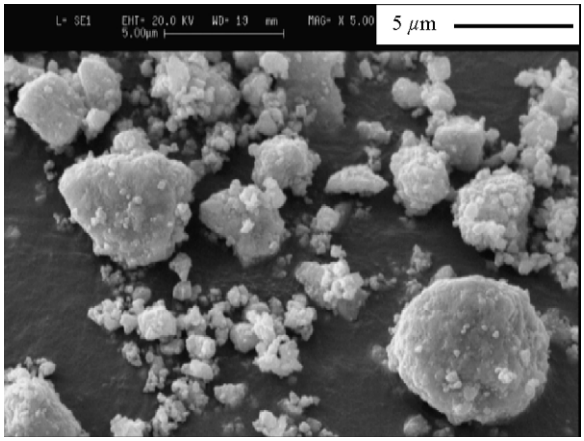

Fig. 7. Spherical particles of the 50 h milled powder at the cup speed of 540 rpm with 0.25 mole Cr.

milling led to the cold-welding and forming of spherical agglomerates.

4. Conclusion

$MoSi_2$–$CrSi_2$ nanocomposite powders with two Cr contents of 0.15 and 0.25 mole were successfully synthesized by mechanical milling of Mo, Si and Cr elemental powders. Formation of these composites begins after 50 h of milling and completes after 70 h of milling. HTP of $MoSi_2$ was formed during milling due to its similar crystal system with $CrSi_2$. $MoSi_2$–$CrSi_2$ nanocomposite powders were also synthesized by combining short milling time (50 h) and low temperature annealing (850 °C). Longer milling time led to smaller grain size as well as larger lattice strain. A mean grain size less than 50 nm was obtained at the end of milling on the basis of peak profile analysis and TEM image. These nanocomposites maintained their nanocrystalline nature after annealing. HTP to LTP transformation was performed during annealing at 1000 °C.

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