

A New Approach to Mechanochemically Synthesizing Al₂O₃/Cu-Cr Nanocomposites

Elahe Hosseini Nezhad, Niloofar Heidari, Mohammadali Ghorbani, and Alireza Heidari

Abstract—In this study, through the mechanochemical synthesis, the nanocomposite Al₂O₃/Cu-Cr was fabricated from a primary mixture of CuO, Al, Cu, and Cr₂O₃ with different percentages by means of the energetic milling. The fabrication of this nanocomposite was based on the regenerative reactions. Such that, the chromium oxide and the copper oxide are regenerated by the aluminum oxide during the process and the final product is a metal matrix composite including the supersaturated chromium solution in copper as the base and the aluminum oxide as the booster phase. Using the extra metallic copper in the primary mixture as the diluent provides the possibility of controlling the adiabatic temperature and the reaction rate. The results of the computation of the lattice parameter based on the XRD data indicate that, for the copper, this parameter changes during the milling process. These changes in the lattice constant are related to the dissolution phenomenon of the chromium and the formation of the supersaturated chromium solution in the copper. Also, the results of the XRD show that, as the primary composition of the powdery mixture and consequently, the adiabatic temperature of the tested samples are changed, the progress of the reactions rate changes. The SEM results demonstrate that, over a 30-to-48-hour period of milling, the fragmentation phenomenon of particles (the shrinking of particles) predominates in comparison to the surface welding of particles (the agglomeration phenomenon of particles). After 48 hours of milling, a nanocomposite containing particles with the approximate size of 30 nm is achieved.

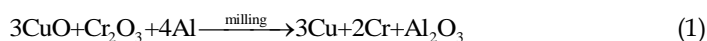
Index Terms—Al₂O₃/Cu-Cr, energetic milling, mechanochemical synthesis, nanocomposite, regenerative reactions

1 INTRODUCTION

Thanks to the abundant applications in the engineering materials, the metal-ceramic composites have been widely investigated by researchers in recent years. The metal-metal oxide composites also account for a subcategory of the metal-ceramic composites. Al₂O₃ is widely used in the fabrication of the metal-metal oxide composites owing to its low price, high chemical stability, high resistance against oxidation, and high temperature resistance that Al₂O₃/Cu-Cr is one of those composites. This composite with the metallic base of copper-chromium, in which the hard particles of Al₂O₃ are dispersed, possesses the excellent thermal and electrical conductivity of Cu-Cr and the strength, the chemical and the thermal stability of Al₂O₃ together. The Al₂O₃/Cu-Cr composite has been widely applied on account of its very high strength in high temperatures, abrasion resistance, and desirable electrical properties [1], [2], [3].

One of the essential and main aspects of the fabrication process of these composites is that, the oxide particles should be miniaturized as far as possible and dispersed uniformly in the metallic base. This necessity cannot be fulfilled completely through the conventional melting and casting methods. Hence, the powder metallurgy is utilized to fabricate these composites. The first step in fabricating this category of composites through the powder metallurgy is the preparation of composite powder. The composite powders containing oxide particles can be fabricated through the internal

oxidation method, but the composite powder Al₂O₃/Cu-Cr fabricated by this method is not uniform and the volume percent of Al₂O₃ is limited. Therefore, the flash freezing and the mechanochemical synthesis are proposed to fabricate this kind of composite powders [3], [4]. However, the classical application of the mechanical alloying is to fabricate the alloys from the basic elements, the several reports show that, by virtue of the mechanical alloying, a wide range of chemical reactions can be performed. Therefore, many researchers have successfully employed the mechanical alloying to activate the oxidation-regeneration reactions including a proper oxidizer and also a proper regenerator [4]. The fabrication of the composite Al₂O₃/Cu-Cr through the mechanochemical synthesis is based on the below reaction:



The product of the above reaction will be a composite with the copper-chromium base and the scattered booster particles of Al₂O₃. With regards to the huge difference in the heat of formation of Al₂O₃, CuO, and Cr₂O₃ oxides, the reaction among the active metals of Al, CuO, and Cr₂O₃ is highly pyrogenic and categorized as the self-propagating high-temperature synthesis (SHS). The various reports indicate that, in some cases, this regenerative reaction in the mechanical alloying system has been performed spontaneously and combustively or mechanically induced self-propagating reaction (MSR). Rising the temperature during the milling process near to the adiabatic temperature of the reaction causes the Al₂O₃ particles to melt and; consequently, to become coarse which affects the mechanical and physical properties of the composite [3], [5]. Hence, many studies have been conducted in order to perceive the governing mechanisms of this reaction [6], [7] and to achieve a

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method for controlling the chemical reaction among Al, CuO, and Cr₂O₃ [3], [8].

The purpose of this study is to investigate the possibility of fabricating these composites through the energetic milling, and the Merzhanov criterion is utilized to predict how the reactions perform. In this study, the mixture of Al-Cr₂O₃-CuO-Cu is used and the composites Al₂O₃-Cr-Cu containing different volume percentages of the Al₂O₃ particles (16-23%) are fabricated through the mechanochemical synthesis. Using different values of metallic copper in the above mixture provides the possibility for controlling the adiabatic temperature, and consequently, for controlling the size of the oxide particles. Moreover, by means of this method, the proportion of the oxide phase dispersed in the base will be controllable. The properties of the fabricated composite powders are investigated by the scanning electron microscope (SEM) and the X-ray diffraction analysis (XRD).

2 THERMODYNAMIC INVESTIGATION OF THE SYSTEM

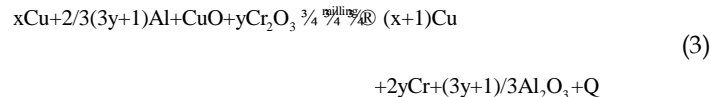
The regenerative substitution reactions as the general form of:



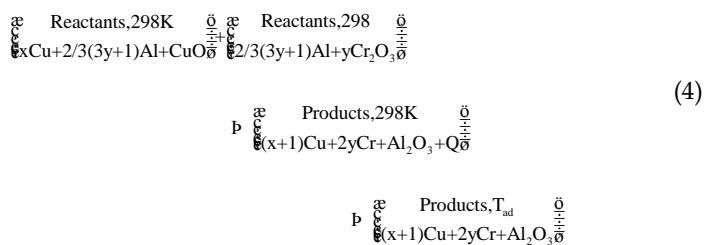
are abundantly applied to prepare the engineering materials and especially the metal-ceramic composites. In this category, one of the important reactions is the thermite reaction during which the oxide of a less active metal is regenerated by Al and forms Al₂O₃. If there is an above average difference between the enthalpies of formation of the metal oxide and Al₂O₃, the regenerative substitution reaction will be pyrogenic and categorized as the SHS reactions. If the required activation energy to reach the ignition temperature (T_{ig}), which is necessary to initiate the reaction, can be provided through the milling process, the reaction is classified as the MSR. In order to categorize easier this type of reactions, the Merzhanov criterion (T_{ad}>1800 K) is used, which is mainly used for the SHS reactions. With regards to the Merzhanov criterion, the reactions whose adiabatic temperature is more than 1800 K can be performed through the MSR method. It is worth mentioning that, there is also a same criterion which introduces a simpler prerequisite ((ΔH₂₉₈/C₂₉₈)>2000 K) to perform the reactions according to the MSR. In the second criterion, the high heat capacity of the reaction's components is not considered. This criterion gives a general overview of the initial moment of the reaction [9].

The results of the studies on the Al-Cr₂O₃-CuO system with the energetic milling SPEX demonstrate that, one to two minutes later the beginning of the milling process, the combustion is performed and the heat released is such that, leads to the evaporation of an amount of copper and the melt of Al₂O₃, and makes the reaction difficult to be controlled during the milling process [5]. To solve this problem, in the system considered in this study, different values of the metallic copper as the diluent and the reaction controller are added to the primary composition and the composite Al₂O₃-

Cr-Cu is fabricated during the milling process and according to the below reaction:



The metallic copper added to the above system increases the heat capacity of the powdery composition; consequently, decreases the temperature rise caused by the combustion. Also, with reducing the direct contact between the particles of CuO, Cr₂O₃, and Al, it controls the reaction rate. Certainly, should be noted that, adding too much copper decreases the system's tendency towards the MSR. In order to investigate the impact of adding copper, the system's adiabatic temperature for different values of the extra copper is calculated according to the below equation, and based on the Merzhanov criterion, the borderline of the MSR reaction is determined. The computation of the system's adiabatic temperature is performed in accordance with the below illustrated path:



Since the reaction is assumed adiabatic, it can be written:

$$\Delta Q = \Delta H_{298}^{\circ}(\text{reaction}) + \int_{298}^{T_{ad}} C_p(\text{products}) \cdot dT = 0 \quad (5)$$

Table 1 indicates the computed values of the adiabatic temperature according to the extra mole of copper. With the addition of the copper to the primary mixture, the adiabatic temperature can be increased through preheating the primary mixture. Therefore, if a reaction is not within the range of the MSR T_{ad}>1800 K, the possibility of performing the process as the MSR can be provided by preheating the primary composition.

3 MATERIALS AND RESEARCH METHOD

The materials used in this study are produced by the powder metallurgy company Institute for Advanced Studies (AIS), and include the copper powder with a purity of 99.78%, the aluminum powder with a purity of 99.15%, and the copper and chromium oxide powders with a purity of more than 99%. The total weight of the powdery mixture containing Cu-Al-Cr₂O₃-CuO is 20 g in each test. The samples S₁ to S₄ are milled for the time periods of 5, 10, 20, and 48 hours until the regenerative reactions are completed (certainly, providing that

the regenerative reaction is completed, the milling process is stopped). The milling process is performed by the 24 stainless steel balls with the diameters of 8 to 16 mm in a closed steel milling container. The ball-to-powder weight ratio is 20:1 and the milling process is performed in a continuous energetic mill. After milling, the samples are investigated by the SEM microscope equipped with the EDX and the XRD phase analysis. The composition of the primary mixture and the composition of the final product after completing the reaction in the tested samples are indicated in Table 1.

TABLE 1										
THE PRIMARY AND FABRICATED COMPOSITIONS (WEIGHT PERCENT) AND THE CALCULATED ADIABATIC TEMPERATURE										
$X\text{Cu}+\text{CuO}+y\text{Cr}_2\text{O}_3+2/3(3y+1)\text{Al} \rightarrow (3y+1)/3 \text{Al}_2\text{O}_3+(X+1)\text{Cu}+2y\text{Cr}$										
Sample	X	Y	Primary composition (%Wt)			Synthesized composition (%Wt)				T_{ad} (K)
			%Cu	%CuO	%Cr ₂ O ₃	%Al	%Al ₂ O ₃	%Cu	%Cr	
S ₁	1.5	1	24	20	38	18	34	40	26	2034
S ₂	2.18	0.283	47	27	15	11	21	69	10	2480
S ₃	0	1	0	26	50	24	45	21	34	2877
S ₄	6	0.2	73	15	6	6	10	86	4	1604

4 RESULTS AND DISCUSSION

The X-ray diffraction pattern relating to the samples with the primary compositions of S₁, S₂, S₃, and S₄ with different time periods of milling are illustrated in Fig. 1. In this study, considering that the investigation of the reactions' progress during the milling process is based on the XRD's results, the XRD result of the S₁ to S₄ samples is indicated in Fig. 1. By means of investigating these results, it can be observed that, in the samples of S₁ and S₄ after 10 hours of milling and in the sample S₂ after 48 hours of milling, the regenerative reaction is completed and the composite is fabricated. In the sample S₃, the regenerative reactions are not completed even after 48 hours of milling.

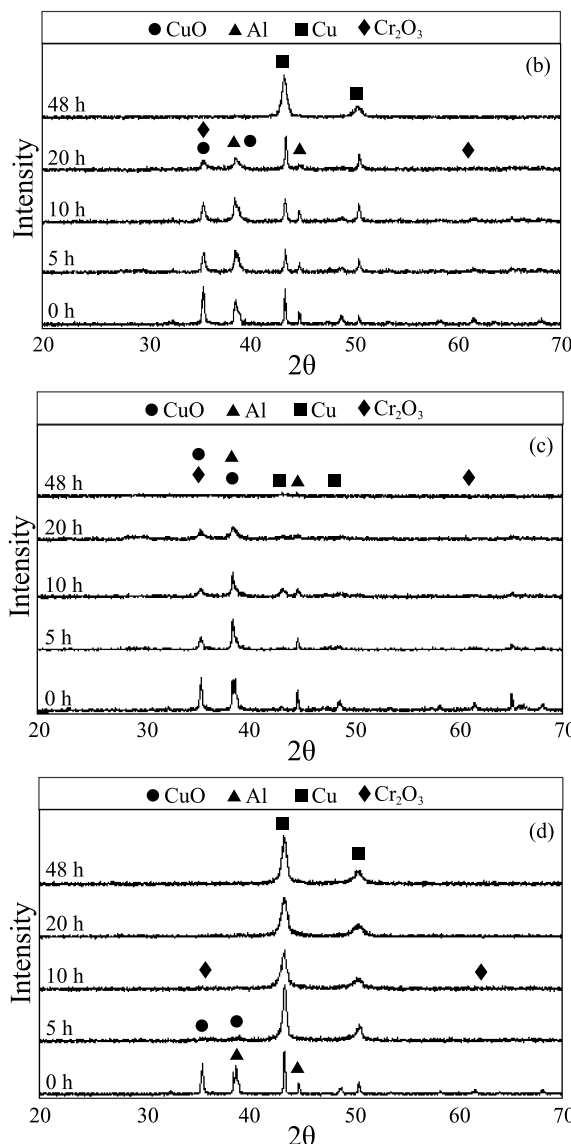
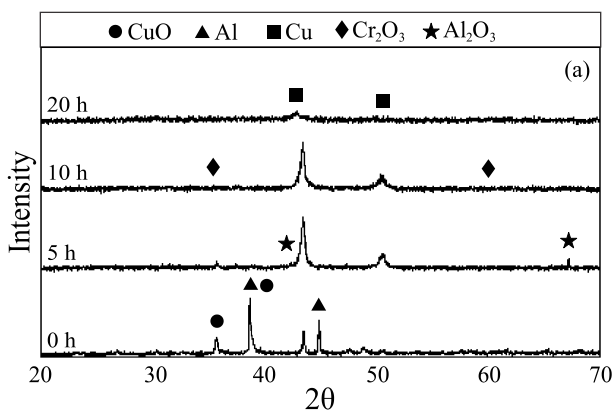


Fig. 1. The XRD pattern of the samples (a) S₁, (b) S₂, (c) S₃, and (d) S₄.

The X-ray diffraction patterns of the sample S₂, which is milled for different periods of time, are illustrated in Fig. 1b. For instance, after five hours of milling, the composition of the phases does not change, and the only considerable phenomenon is that, the peaks of CuO, Al, and Cr₂O₃ shorten due to the mechanical work. As the milling process resumes, the peaks of CuO and Cr₂O₃ gradually weaken, and disappear completely in the 48-hour sample. During the milling process, the peaks of Cu {111} and Cu {200} shorten and widen due to the strain accumulation on the structure and the particle size reduction. Another considerable phenomenon is the movement of copper peaks during the milling process. This commutation resumes approaching sharper angles until 20 hours of milling and returns to the pure copper's position in the 48-hour sample. The commutation phenomenon of the copper peaks can be attributed to the dissolution of the chromium in the copper; since, as can be observed in the equilibrium phase diagram of Cu-Cr, the approximate 8

atomic percent of the chromium in the copper lattice is as a soluble solid solution [10]. The reason of the increase in the copper lattice constant is a distortion which the chromium atoms with the bigger atomic radius in comparison to the copper impose on the unit cell of copper during the substitution dissolution and increase the lattice constant. Therefore, the solution of chromium as a solid solution in the copper lattice can be investigated through measuring the commutation of the copper peaks [11], [12]. Through measuring the distance between the layers d , using the relations between d and the lattice constant (a), using Eqs. (6) and (7) and from the X-ray diffraction pattern, the lattice constant increase can be measured [13]:

$$d = \frac{\lambda}{2\sin\theta} \quad (6)$$

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (7)$$

From Eqs. (6) and (7), it can be concluded that, the lattice constant increase will lead to the commutation of peak toward sharper angles. With regards to the X-ray diffraction images in Fig. 1, the position of the peak of Cu {111} changes from $2\theta=43.32$ (before milling) to $2\theta=43.12$ after 20 hours of milling. This condition demonstrates that, the lattice constant for the 24-hour-milled sample changes from 3.614 to 3.630. The increase of 0.45% in the lattice constant for the 20-hour-milled sample reflects the fact that, the chromium dissolves in the copper lattice and the substitution solid solution forms (Fig. 2).

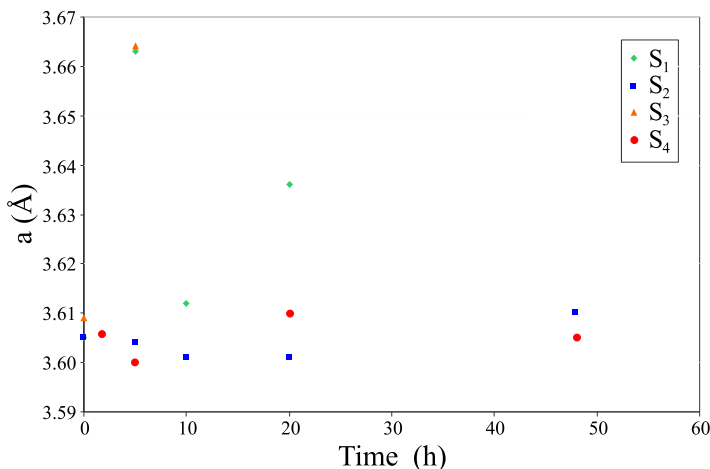


Fig. 2. The changes in the copper lattice's parameter according to the time period of milling.

According to the results of investigating the X-ray diffraction of the milled samples and considering the commutation of the copper peaks and also the disappearance of the peaks of CuO, Cr₂O₃, and Al, it can be concluded that, in the first 24 hours of milling, the chromium dissolves in the copper lattice substitutionally, the solid solution of Cu(Cr) forms and simultaneously, the fracture and crush of oxide particles cause the respective peaks to weaken. As the mechanical alloying

resumes, the size of the particles reduces and the accumulation of structural defects occurs which increases the energy of the system gradually. At this stage (after 20 hours of milling), being provided the thermodynamic conditions, the regenerative substitution reaction starts and the very fine particles of Al₂O₃ form. With the regenerative reaction between the atomic aluminum and the copper, the copper peaks return to the pure copper peaks' position. With regards to the presented mechanism for the reaction, the formed Al₂O₃ will be extremely fine and is not traceable in the X-ray diffraction patterns. The absence of the Al₂O₃ peaks in the final sample is justifiable owing to the same reasons [3], [8].

Comparing the images of Fig. 1, any significant difference cannot be observed in the reaction progress of the samples containing different compositions. In all the three samples with the different percentages of the extra copper, it seems that, the reaction progress is gradual, and even in the sample S₃ with the adiabatic temperature of 2877 K, there is not an abrupt reaction or in the form of MSR which can be recognizable. These results show that, in the prediction of the system's behavior and the determination of the mechanism of the reactions during the milling process, that possesses an intrinsic complexity in which many variables are involved, we cannot simply judge based on the Merzhanov criterion ($T_{ad} > 1800$ K), and this criterion is solely a prerequisite for a pyrogenic reaction to occur as the MSR. This difference in the behavior is more clearly visible when the extra and diluent components are added to the system and the numerous reports about the complexities of the MSR system including a neutral phase support this fact [9]. In this study, the presence of the extra copper in the primary composition, which is added in order to reduce the system's tendency to the combustive reaction, in addition to the confirmation of the predictions of the increasing required time to reach the ignition temperature (T_{ig}), prevents the reaction from performing combustively (the sample S₁). The reasons for this fact can be justified such that; firstly, the high heat capacity of copper increases the heat capacity of the system and decreases T_{ad} and the proportion $\Delta H/C$; secondly, the presence of the copper particles in the primary composition reduces the direct contact between the particles of CuO, Al, and Cr₂O₃, and decreases the reaction rate by positioning between the reacting powders. Overall, the addition of the diluent to the primary materials affects the heat capacity, the collision and contact between the powder particles and the milling container's wall and balls and other parameters. Although using the diluent provides the possibility of controlling the chemical composition in the final product, it causes the reaction to be gradual instead of the MSR.

The changes in the copper grain size (crystal) in the milled samples are obtained from the Cu {111} peaks' width and by means of the Scherer's equation (8) and the William-Hall equation (9):

$$d = \frac{0.9\lambda}{B \cdot \cos\theta} \quad (8)$$

$$B.\cos\theta = \frac{0.9\lambda}{d} + \eta.\sin\theta \quad (9)$$

where d is the crystal size, λ is the X-ray wavelength, B is the peak width at half height, θ is the Bragg peak angle, and η is the lattice strain rate. The remarkable point about the Scherer's equation is that, based on this equation, the widening of the peak is entirely related to the getting tiny of the crystals whereas in the milling process, which the mechanical collisions deeply affect the powder properties, the created strain on the powder particles plays an important role in the widening of the peaks. The considerations demonstrate that, a composition of the two above factors, the getting tiny of the particles and crystals and the particle strain due to the cold working during the milling, has a basic role to play in the widening of the peaks in the X-ray diffraction figures [13]. Now, if $B.\cos\theta$ is plotted according to $\sin\theta$, a straight line will be achieved whose slope equals the lattice strain and its y-intercept will be $0.9\lambda/d$. Therefore, the lattice strain rate can be separated from the changes in the crystal size [15]. The changes in the grain size and the strain rate according to the milling time interval for the sample S_2 are calculated through Eq. (9). The impact of the mechanical alloying on the microstructure and on the crystals' size reduction, also, the effect of the milling process on the deformation phenomenon and on the hardness of work of the particles, which leads to the lattice strain, are illustrated clearly in Figs. 3 and 4. As the milling time interval increases from 5 to 48 hours, the size of the crystals decreases from 120 to 40 nm and the lattice strain rate rises from 0.027 to 0.25. Hence, after 48 hours of milling, the size of the copper crystals becomes nanometric and the composite $Al_2O_3-(Cu-Cr)$ will consequently have a nanometric structure. The SEM images of the powdery mixture with the composition S_2 , before and after the different time periods of milling, are indicated in Fig. 5. The investigation of these images shows that, in the initial time periods of milling, the cold welding occurs and causes the particles to join together and become coarse such that, the size of the agglomerated particles after 10 hours of milling (Fig. 5c) increases within the range of 20-50 μm . As the milling process and the continuous and extensive deformation resume, the hardness of work occurs and results in the fracture and the size reduction of the particles. The considerable size reduction of the particles is this fact's reason. In the 20-hour-milled sample (Figs. 5d and 5e), the size of the particles is less than 20 μm , and in the 48-hour-milled sample, the size of the particles reaches to 30 μm .

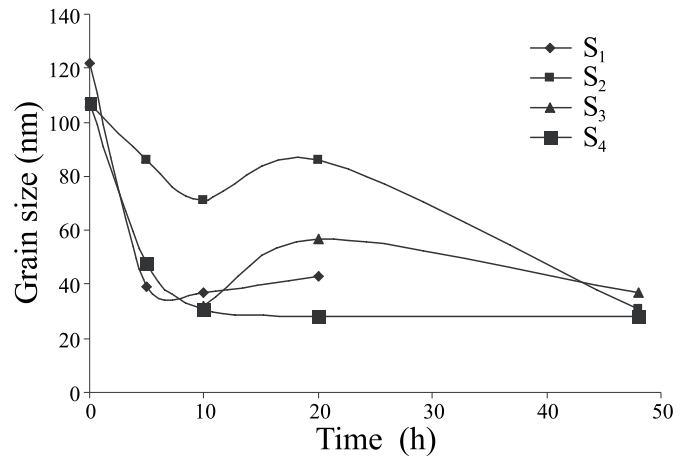


Fig. 3. The change in the crystal size with the time change of milling.

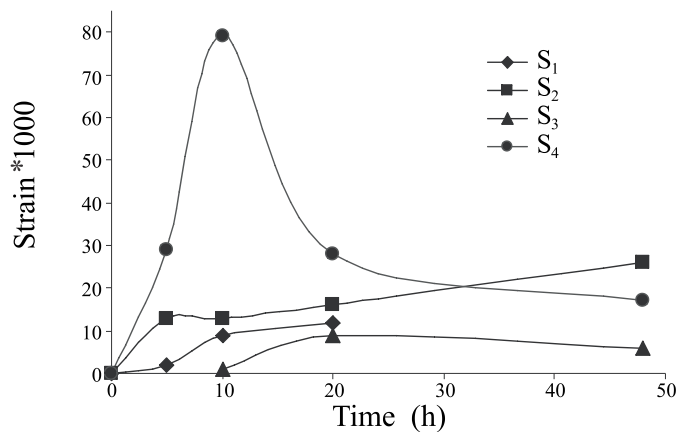
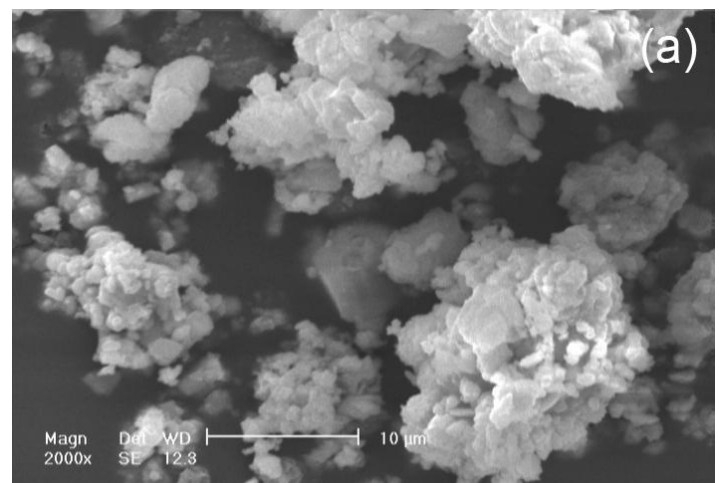


Fig. 4. The change in the lattice strain according to the time change of milling.



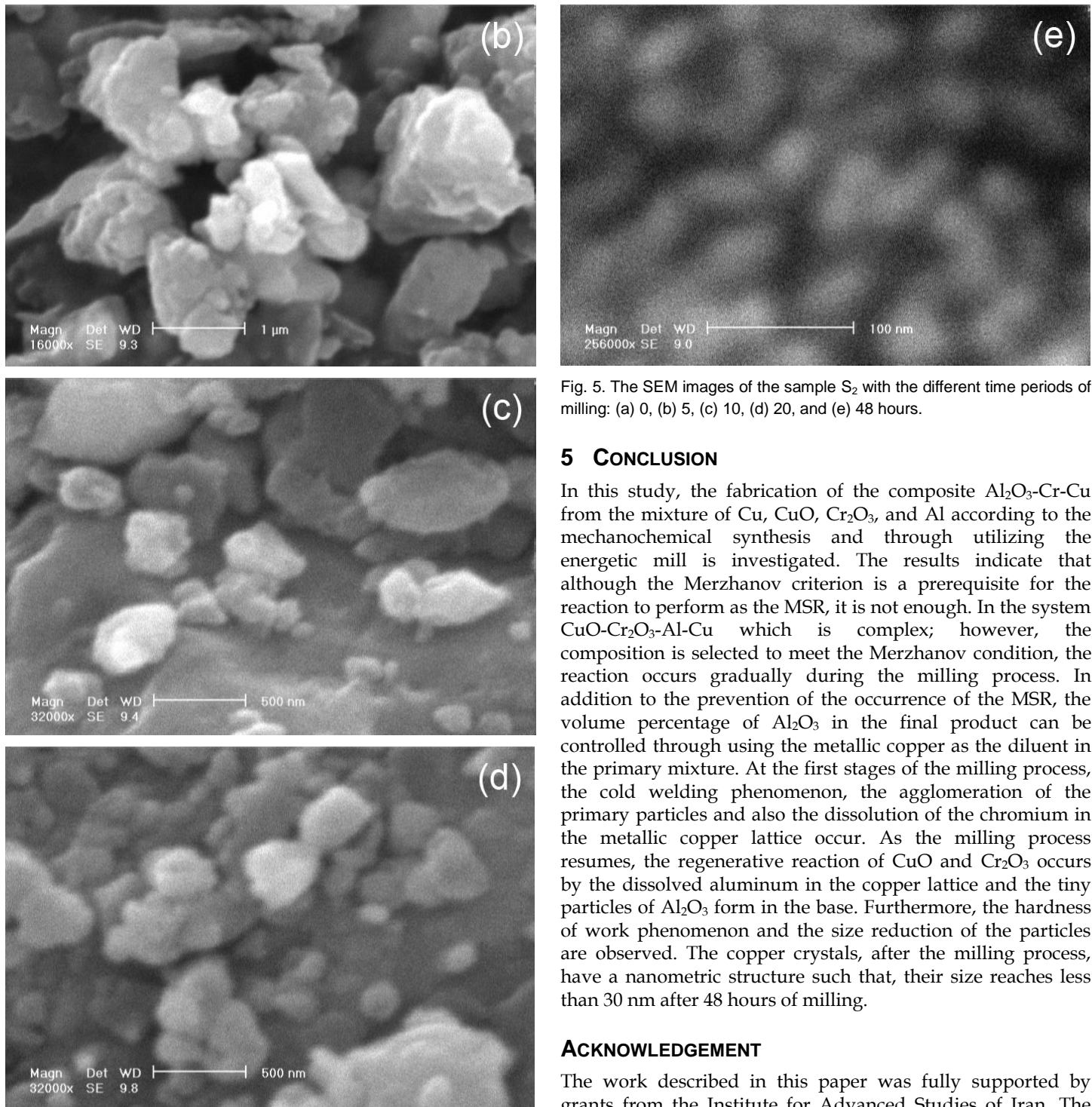


Fig. 5. The SEM images of the sample S₂ with the different time periods of milling: (a) 0, (b) 5, (c) 10, (d) 20, and (e) 48 hours.

5 CONCLUSION

In this study, the fabrication of the composite Al₂O₃-Cr-Cu from the mixture of Cu, CuO, Cr₂O₃, and Al according to the mechanochemical synthesis and through utilizing the energetic mill is investigated. The results indicate that although the Merzhanov criterion is a prerequisite for the reaction to perform as the MSR, it is not enough. In the system CuO-Cr₂O₃-Al-Cu which is complex; however, the composition is selected to meet the Merzhanov condition, the reaction occurs gradually during the milling process. In addition to the prevention of the occurrence of the MSR, the volume percentage of Al₂O₃ in the final product can be controlled through using the metallic copper as the diluent in the primary mixture. At the first stages of the milling process, the cold welding phenomenon, the agglomeration of the primary particles and also the dissolution of the chromium in the metallic copper lattice occur. As the milling process resumes, the regenerative reaction of CuO and Cr₂O₃ occurs by the dissolved aluminum in the copper lattice and the tiny particles of Al₂O₃ form in the base. Furthermore, the hardness of work phenomenon and the size reduction of the particles are observed. The copper crystals, after the milling process, have a nanometric structure such that, their size reaches less than 30 nm after 48 hours of milling.

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