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Kinetics analysis of mechano-chemically and thermally synthesized Cu by Johnson–Mehl–Avrami model

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Abstract

In this paper, the isothermal reduction process kinetics of Cu_2O with carbon under high vacuum for a non-activated sample and mechanically activated samples has been studied. The influence of milling time on the apparent activation energy was analyzed using Johnson–Mehl–Avrami (JMA) model. In order to gain a deeper insight into the possible mechanisms that govern mechanochemical solid-state reduction of Cu_2O, the kinetic of the process was investigated using a similar model. It was found that in temperature range of 550–650 °C, the rate determining step of the thermal reduction is chemical reaction. But in the range of 650–750 °C, the rate determining step seems to be diffusion. Analyzing the relevant experimental results and comparison of the thermal and mechanochemical reduction kinetics showed that the mechanical activation induced by milling may decrease the required reaction activation energy by increasing defect sites. However, it appears that the thermal and mechanical activation induce different transformation rates, but the transformation paths are the same.

Keywords: Kinetics; Mechanochemical; Reaction mechanism; JMA model

1. Introduction

Mechanical alloying and mechanochemistry are novel solid state processing routes for producing metals, alloys and intermetallics in the nanocrystalline scale. The mechanochemistry includes exchange reactions, reduction/oxidation reactions, decomposition of compounds and phase transformations. Solid state reactions involve the formation of a product phase at the interfaces of the reactants. Subsequently, further growth of the product phase involves diffusion of the reactant atoms through the product phase, which constitutes a barrier layer preventing further diffusion. Hence, high temperature is required for the reaction to occur at a reasonable rate. Mechanical milling increases the reaction kinetics due to the generation of clean and fresh surfaces, increased defect density and reduction of particles size [1].

Although the mechanochemical synthesis is known as a very useful technique, it suffers from theoretical principles. One of the most important limitations is the ambiguity of the mechanism and evaluation of mechanical activation as well as a suitable characterisation of transformation paths [2]. Therefore, the transformation kinetics in the intermediate stages of milling continue to gather extensive attention in the field of solid state chemistry and materials science and has been the target of some investigations.

In the solid state reactions, determination of kinetics equation, rate controlling steps and kinetics parameters such as activation energy will provide a valuable insight in the mechanism of the process [3]. Many research works have been carried out on mechanical alloying and mechanical activation kinetics and the way which mechanical energy affects the reaction rate. There are studies on the kinetics of thermal decomposition of mechanically activated compounds [2,4,5], chemical leaching of mechanically activated minerals [6–8] and formation of solid solution and/or amorphous alloys by mechanical alloying, and crystallization of the as-milled amorphous powders [9–14]. However, the activation energies and mechanisms of displacement reactions as a function of milling time need more investigation. The possibility of mechanochemical reduction

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of cuprite (Cu_2O) with graphite has been already investigated [15], but the kinetics of mechanochemical reduction and thermal reduction of mechanically activated powder mixtures have not been studied thoroughly.

This paper presents detailed descriptions of the effects of mechanochemical activation on the Cu_2O reduction with graphite and production of Cu. Furthermore, comparison of the reduction kinetics in thermal and mechanochemical production of Cu was employed to understand the mechanism of the reaction in both routes.

2. Experimental procedure

High purity Cu_2O (99%, 5–30 μm) and graphite (99.9%, 10–50 μm) were used as precursors and milling was performed in a high-energy Fritsch P5 planetary ball mill, with a speed of 300 rpm for various milling times. Ball to powder weight ratio was adjusted to 35. Cu_2O with 40 mol% of extra carbon was reduced according to the reaction (1):

$$2Cu_2O + C \rightarrow 4Cu + CO_2\uparrow \qquad (1)$$

Phase identification was examined by X-ray diffraction (XRD) analysis (Philips PW-1730) using Cu Kα radiation. According to the literature, the degree of structure disorder, F, is defined as below [2]:

$$F = \frac{(\mathrm{IB})_t}{(\mathrm{IB})_0} \qquad (2)$$

where $(\mathrm{IB})_t$ is the integral width corresponding to the disordered sample after milling time t and $(\mathrm{IB})_0$ is the integral width corresponding to the non-disordered sample. Meanwhile, IB can be calculated from the following equation:

$$\mathrm{IB} = \frac{A}{I_{\max}} \qquad (3)$$

where A is the area under the diffraction peak whose maximum intensity is $I_{\max}$.

Unmilled sample and three samples milled for 2, 4 and 6 h were used for isothermal reduction experiments. Three grams of each sample was pressed in a cylindrical mould to obtain a density of about 1.50 g cm^{-3}. The pressed samples were dried at 110 °C for 2 h in a vacuum tube furnace. The dried samples were gradually heated at a rate of 40 K min^{-1} using a programmable vacuum tube furnace equipped with thermogravimetric system, at 100 Pa. These samples were heat treated at 550, 600, 650, 700 and 750 °C, for 5–120 min. The changes of weight in each sample were measured continuously. The extent of the reaction, α, in each sample was calculated using the following equation [5]:

$$\alpha = \frac{w_0 - w_t}{f w_0} \qquad (4)$$

where w_0 and w_t are the weights of the initial sample and the one milled for time t, respectively. f is the fraction of weight loss for complete reduction of Cu_2O according to the reaction (1).

3. Results and discussion

3.1. Kinetics modeling of isothermal reduction at the high temperature annealing

Fig. 1(a)–(e) shows the variation of extent of reduction versus time for unmilled and 2, 4 and 6 h milled samples heated at 550, 600, 650, 700 and 750 °C. A remarkable effect of milling on the kinetics of reduction can be seen between unmilled and milled samples, especially at 550 and 600 °C. Furthermore, prolonged milling and mechanical activation resulted in much higher copper production and reduction rates. The results illustrate that temperature significantly affected the reduction rate, as well. For example, the reaction conversion after 60 min thermal reduction at 600 °C for unmilled sample is 0.11, whereas at 700 °C this value increases to 0.69.

In the present work, it was found appropriate to use the Johnson–Mehl–Avrami (JMA) equation to determine the kinetics of the reaction. This equation describes a wide variety of isothermal solid state transformations and generally it is used to determine the mechanisms which govern the nucleation and growth [10,14]. This equation has general form of:

$$\alpha(t) = 1 - \exp[-(Kt)^n] \qquad (5)$$

where $\alpha(t)$ is the extent of the reduction after time t, n is the Avrami exponent, which depends on the growth mechanism and the dimensionality [10]. K is the reaction rate constant whose temperature dependence is usually given by an Arrhenius equation in terms of the apparent activation energy. Large values of K imply rapid transformations. The values of n and K provide a clue to the type of reaction mechanisms which dominate during the reaction and also show how fast these mechanisms work [12].

For analyzing the results, Eq. (5) may be rewritten in the form of following equation:

$$\ln(-\ln(1-\alpha)) = n \ln K + n \ln t \qquad (6)$$

The constants values of K and n can be calculated by plotting a linear plot of $\ln(-\ln(1-\alpha))$ as a function of $\ln t$, Avrami plot. Fig. 2(a)–(e) shows the Avrami plots for samples at 550, 600, 650, 700 and 750 °C, respectively.

As seen from Fig. 2 in all the cases a good linear fit is observed. It shows that the JMA model accurately describes the isothermal Cu formation from the unmilled and milled Cu_2O–C mixtures. The kinetics parameters, n and K, can be extracted from the slopes and intercepts of the plots. Table 1 gives these parameters for these mixtures. In all the cases a good linear fit was observed because correlation coefficients, r, are greater than 0.99.

In Table 1 it can be seen that in every constant temperature, n and K increase with milling time. But, mechanical activation increases K at low temperature more significantly. For example, activation of the mixtures for 6 h increase the reaction rate constant in order of 10^9 at 550 °C, but it is only 2.5 at 700 °C. Additionally, higher values of n for much activated samples indicate that mechanical activation induces a promoting nucleation effect. This is due to the fact that the structure refining to the nanoscale during milling, introduces various defects which are convenient nucleation sites.

The activation energy for the reaction may be obtained using the Arrhenius equation in the following form:

$$\ln K = \ln A - \frac{E_a}{RT} \qquad (7)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gases constant and T is the absolute temperature. Fig. 3 shows the lines fitted on $\ln K$ versus T^{-1} plot for each activated samples. E_a can be obtained from slope of lines in each temperature range.

The Arrhenius plots in Fig. 3 indicate a change in reaction mechanism at $T = 650$ °C which is manifested by the slope

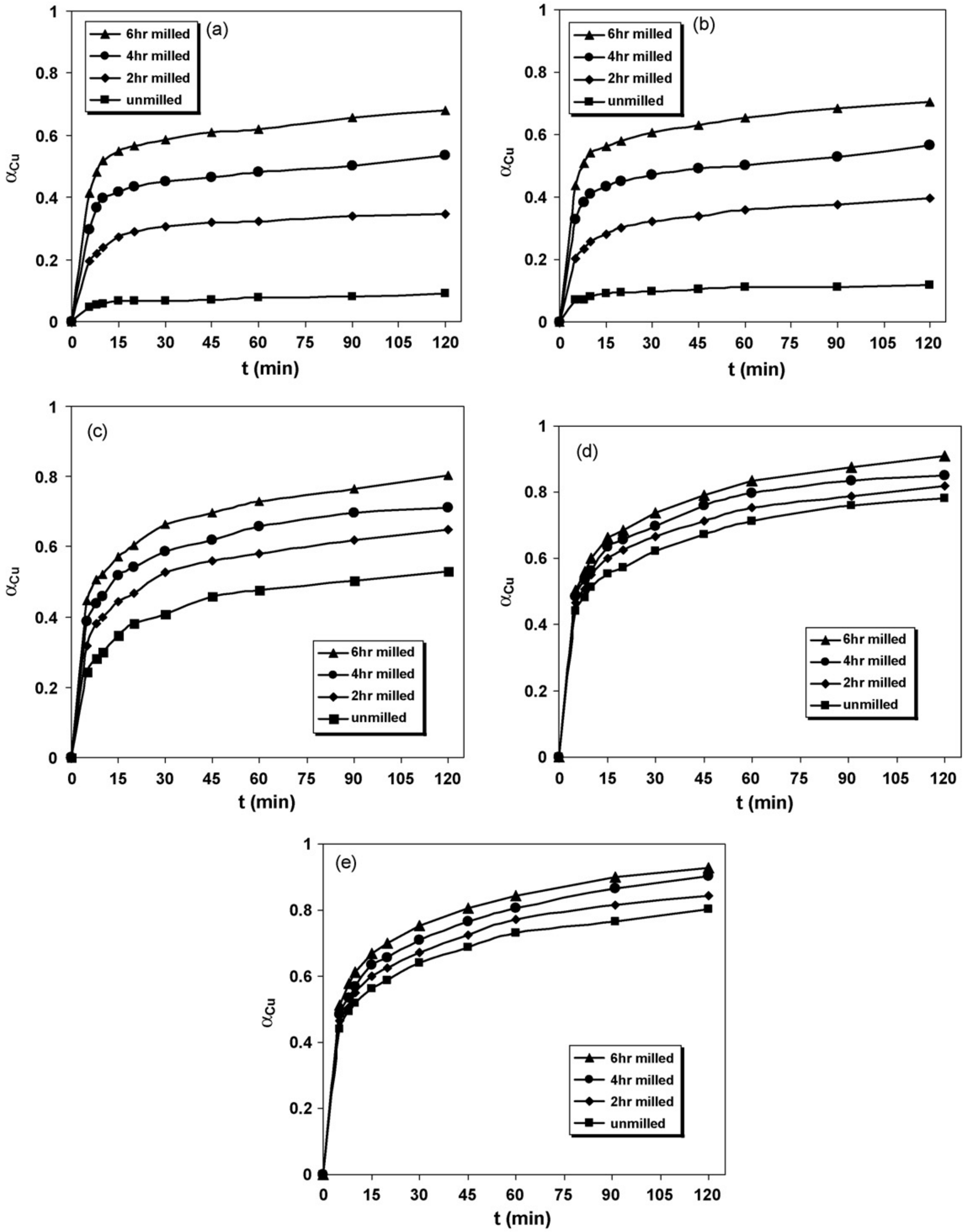

Fig. 1. Extent of the reaction for different samples heated at (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C and (e) 750 °C as a function of annealing time.

change for unmilled and mechanically activated samples for 2 and 4 h. Therefore, the reduction mechanism probably changes from chemical controlled at low temperature to diffusion controlled at high temperature [16]. Table 2 shows the apparent activation energy values obtained for reduction reaction in various conditions. Since the correlation coefficient is very close to 1 ($r > 0.99$), the optimized values were calculated with the best-fit lines.

It is found that although the reduction kinetics at 550–650 °C for unmilled, 2 and 4 h milled mixtures is surface chemical controlled, at 650–750 °C is diffusion controlled. The reason is that at low temperatures the rate of chemical reaction is so slow that it is much less than the rate of diffusion. At high temperatures, the rate of chemical reaction accelerated with rise in temperature and it becomes much faster than the rate of diffusion, i.e., it becomes diffusion controlled [16]. Rapid formation of dense Cu layer at high temperature surrounding the unreacted Cu_2O core could be another reason for change in mechanism by increasing temperature. Therefore, carbon and CO_2 have to diffuse through this layer. Thus, the process becomes diffusion controlled, although

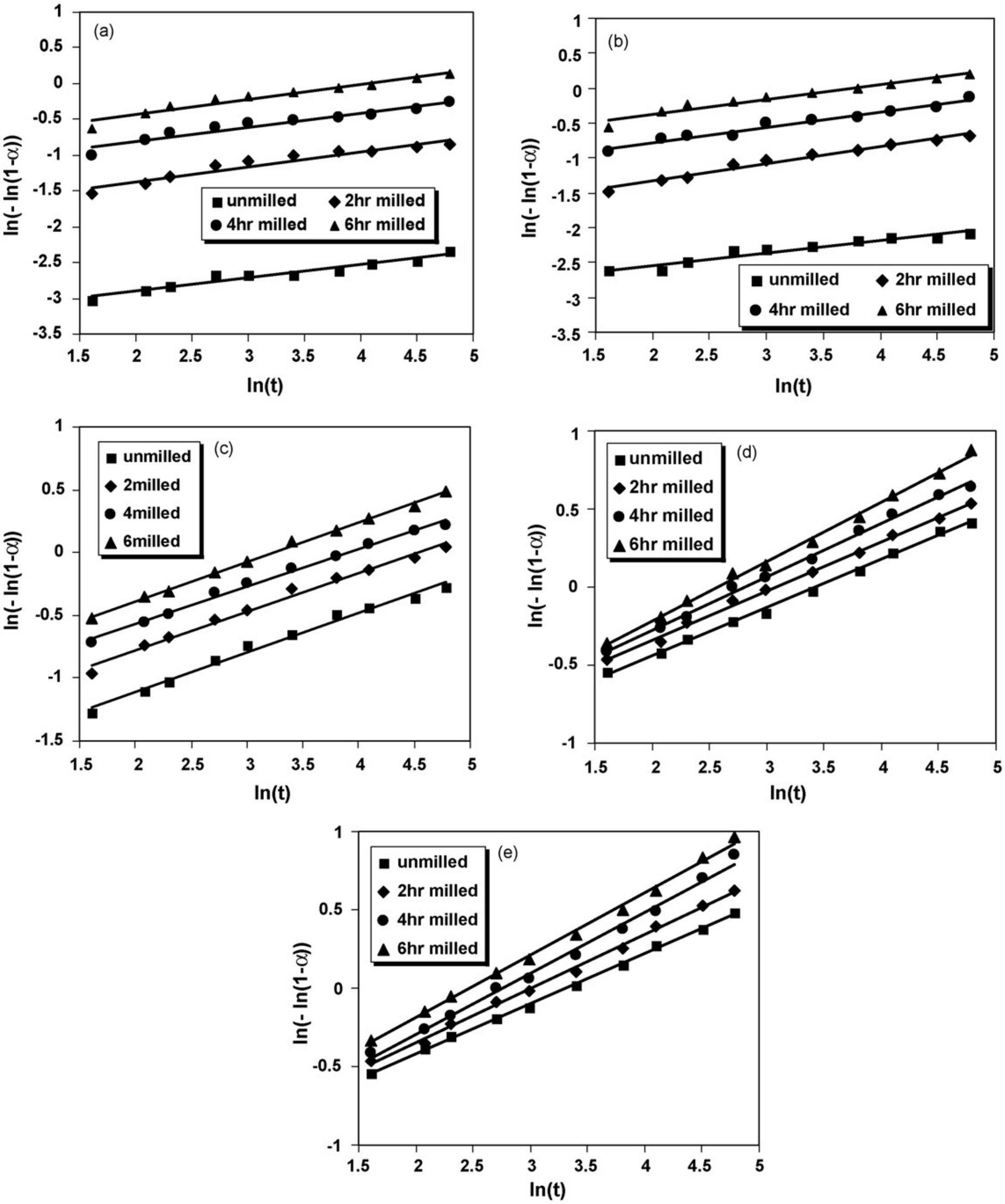

Fig. 2. The Avrami plot of $\ln(-\ln(1-\alpha))$ vs. $\ln t$ for samples heated at (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C and (e) 750 °C.

it is chemically controlled at low temperatures. In this process both reasons are plausible.

In Table 2 it can also be seen that increasing the milling time decreases the activation energies for both determining steps (surface chemical and diffusion steps), i.e., promotes the reaction kinetics. This may be explained by the shorter diffusion paths provided by reduced particle sizes and defects formation in the particles by mechanical activation. On the other hand, it can be found that from apparent activation energy for 6 h milled sample, the rate determining step in temperature range of 550–750 °C is diffusion. It means that the mechanical activation shifts the mechanism change temperature (Arrhenius plot break) to lower temperature, when compared with other samples. This effect may be attributed to enhanced reactivity by increasing surface area, S_A, and the degree of structural disorder, F. Structural disorder means changes in lattice strain and in crystallite size increased with milling time. The changes in F with milling time can be plotted using Eq. (2). In Fig. 4 it can be seen that up to 6 h of milling, the degree of F increases by 5.6 times. These results are consistent with literature for the rate of thermal decomposition reactions in minerals [2]. The influence of S_A and F has been expressed by an empirical coefficient in the form of S_AF by means of the following relation [2]:

$$K = a + bS_AF \tag{8}$$

Table 1
Kinetics parameters for unmilled and milled mixtures extracted from Avrami plots at different temperatures

Milling time (h)	n	K (min^{-1})	r
$T = 550\,^\circ$C			
0	0.1184	6.56×10^{-12}	0.996
2	0.1237	6.43×10^{-8}	0.991
4	0.1363	2.75×10^{-5}	0.995
6	0.1401	6.74×10^{-3}	0.998
$T = 600\,^\circ$C			
0	0.1318	1.36×10^{-7}	0.997
2	0.1347	2.90×10^{-5}	0.994
4	0.1386	1.51×10^{-3}	0.992
6	0.1426	21.23×10^{-3}	0.996
$T = 650\,^\circ$C			
0	0.3034	4.29×10^{-3}	0.992
2	0.3051	10.98×10^{-3}	0.996
4	0.3086	22.07×10^{-3}	0.994
6	0.3183	39.04×10^{-3}	0.998
$T = 700\,^\circ$C			
0	0.2950	30.25×10^{-3}	0.995
2	0.3223	46.72×10^{-3}	0.993
4	0.3453	61.40×10^{-3}	0.997
6	0.3685	75.66×10^{-3}	0.994
$T = 750\,^\circ$C			
0	0.3206	40.71×10^{-3}	0.996
2	0.3466	67.53×10^{-3}	0.995
4	0.3683	78.29×10^{-3}	0.998
6	0.3787	91.23×10^{-3}	0.997

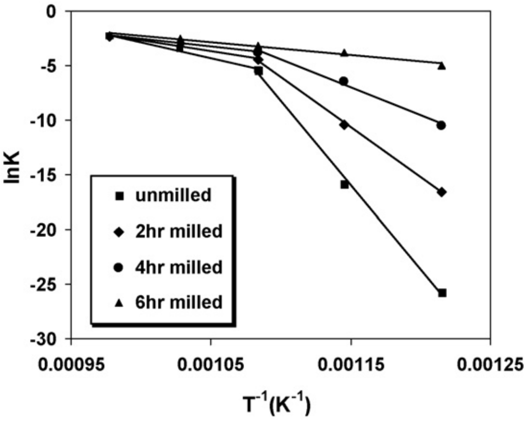

Fig. 3. Arrhenius plots for thermal reduction of Cu_2O with carbon at temperature = 550–750 °C.

Table 2
The apparent activation energy values of unmilled and mechanically activated samples

Milling time (h)	E (kJ mol^{-1})	
	$T = 550$–$650\,^\circ$C	$T = 650$–$750\,^\circ$C
0	1387.47, $r = 0.996$	291.76, $r = 0.998$
2	795.24, $r = 0.994$	216.19, $r = 0.997$
4	359.51, $r = 0.996$	152.77, $r = 0.995$
6	94.98, $r = 0.997$	

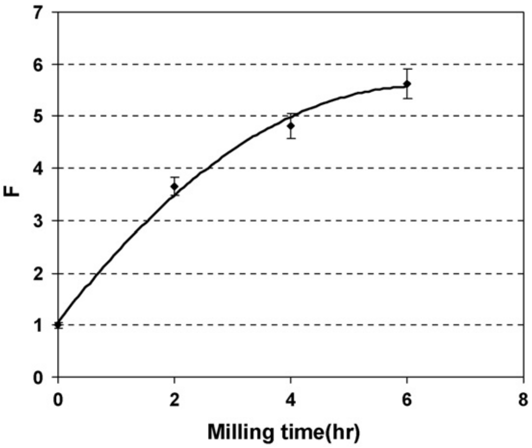

Fig. 4. Influence of milling time on structural disorder of the Cu_2O.

where a and b are constant values. Hence, increment of F results in an increase in K. Moreover, thermal reduction of Cu_2O is a heterogeneous reaction, the rate of which increases with the surface area of the sample.

3.2. Kinetics modeling of mechanochemical reduction during the room temperature milling

Fig. 5 shows XRD patterns of the samples milled for various times, revealing the structural evolution as milling progressed in the powder mixture. With an increase in the milling time, the peaks of Cu_2O were gradually broadened and their intensities decreased. The asymmetry of the second peak of the 6-h pattern clearly suggests the presence of some Cu. Further milling increased the Cu peaks intensities, and single phase Cu was obtained after 30 h of milling.

Fig. 6 shows the progress of the reduction reaction during milling (shown by experimental data), measured by the ratio of the areas under the largest XRD peaks of Cu and Cu_2O. As it was pointed out previously [15], the Cu formation curve in Fig. 6 indicates that the mechanochemical reduction of Cu_2O and Cu

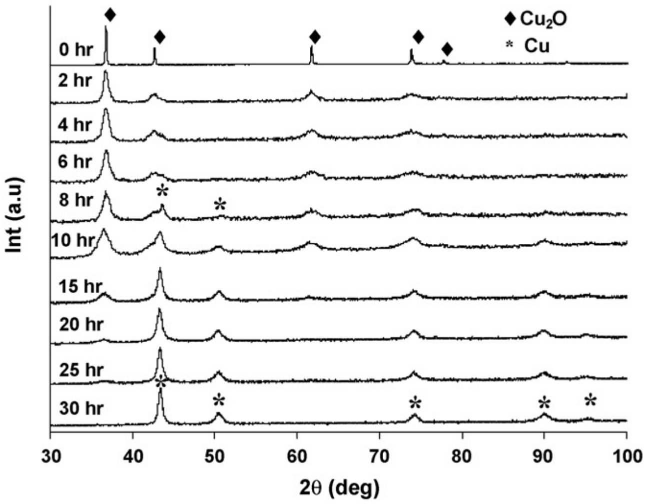

Fig. 5. XRD patterns of the samples milled for various milling times.

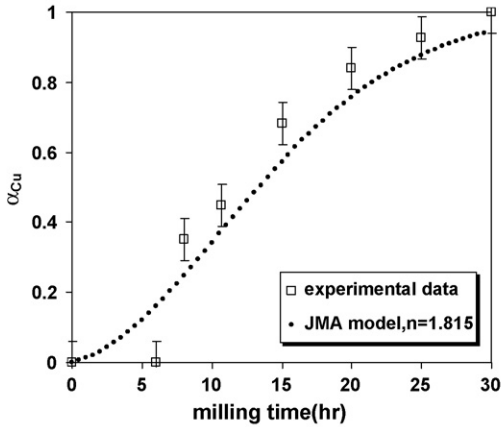

Fig. 6. Relative fraction of copper produced as a function of the milling time at room temperature in compared with JMA model corresponding to the average Avrami exponent of 1.815.

formation occurs via a nucleation and growth mechanism. The above figure shows an incubation time of nearly 6 h after which the reduction reaction starts with a sharply rising rate. The rate of the reaction diminishes slowly with prolonged milling. This suggests that the process occurs via a nucleation and growth mechanism [17]. Moreover, the initial incubation period probably corresponds to grain refinement and mixing. It should be mentioned that the real incubation time might be less than 6 h and tiny amounts of Cu may be produced earlier than 6 h. However, the related peaks could not be detected probably due to the minor amount of Cu and limitation of the XRD resolution. Furthermore, within the first 15 h of milling, most of the Cu_2O (70%) reacts with carbon with a high reaction rate after which the reaction rate decreases with further milling. Consequently, the JMA model is used for kinetics analysis of this process as well.

Fig. 7 shows the Avrami plot for mechanochemical synthesis of Cu, where α was determined from Fig. 6 and t is milling time in hour. In view of the fact that α value was assumed to be zero until 6 h of milling, Avrami plot began at this time. The average Avrami exponent, n_{av}, was calculated as 1.815 from the slope of fitted line.

For comparison, α is plotted corresponding to the n_{av} (see Fig. 6). According to this figure, the JMA model can be identified as a good description of kinetics for mechanochemical synthesis of Cu. It should be noted that, the deviations are probably related to the extraction of experimental data from XRD results, especially up to 6 h. Considering an average value of $n = 1.815$ and using Avrami plot the reaction rate constant, $K = 9.994 \times 10^{-4}\ \text{min}^{-1}$ is calculated for this process. Therefore, the kinetics equation for mechanochemical reduction of Cu_2O to Cu under mentioned conditions may be written as below:

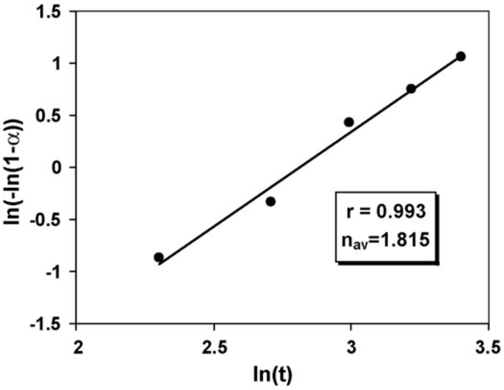

Fig. 7. The Avrami plot of $\ln(-\ln(1-\alpha))$ vs. $\ln t$ for mechanochemical formation of Cu.

$$\alpha(t) = 1 - \exp[-(9.994 \times 10^{-4} t)^{1.815}] \tag{9}$$

where t is milling time in minutes and α is the fraction of produced Cu.

3.3. Comparison between kinetics modeling of high temperature thermal and mechanochemical reduction

Since solid state reactions occur at the reactant–product interface, the reaction rate is proportional to the surface area of the unreacted part of the material as well as nucleation process. The lower Avrami exponents of the high temperature thermal reduction indicate that the surface of each particle is covered by a layer of the final product in the initial stages and the reaction proceeds by diffusion-controlled growth in three dimensions, where nucleation cannot take place during the process. On the other hand, for mechanochemical reduction, the refining of grain size during mechanical milling introduces a large percentage of grain and interphase boundaries and various defects, all of which could promote the accelerated reduction reaction. Under the above conditions, the number of the nucleation sites and diffusion paths increased progressively as compared with the high temperature thermal reduction. Additionally, milling can remove the product layer from the surface of each particle continuously. These lead to the extremely higher value of Avrami exponent [12,13].

It appears from the modeling results that although different activation factors induce different transformation rates, the process does not proceed through different transformation paths, since the JMA model describes both reduction paths accurately, and both thermal and mechanical activation increase Avrami exponent and decrease diffusion barriers. Thus, the inference of different reaction pathways may depend on the different periods which activation factors can overcome on the barriers. For example, mechanical activation can create suitable nucleation sites much faster than thermal activation, but thermal activation can remove chemical interface reaction barrier much more convenient than mechanical activation. In thermal activation diffusion coefficient varies exponentially with temperature and increasing the temperature results in removing diffusion barrier. On the other hand, mechanical activation provides short diffusion paths due to the formation of defects and removing product layer between reactants. It may be concluded that, although the activation mechanisms are different in thermal and mechanical activation, the mechanism of the Cu_2O reduction seems to be similar in both rates.

4. Conclusions

It was shown that the JMA model accurately describes the thermal and mechanochemical Cu formation from Cu_2O–C mixture. The break of Arrhenius plot in thermal reduction at 650 °C indicates a change in reduction mechanism for unmilled, 2 and 4 h milled mixtures involving a transition from surface chemical reaction to diffusion. For 6 h milled sample the reaction becomes diffusion controlled at 550–750 °C. The higher Avrami exponent of mechanochemical reduction in comparison with the exponent of the high temperature thermal reduction is related to the continuous formation of the lattice defects and grain boundaries in addition to activated fresh surface areas during milling, which are suitable nucleation sites for Cu. Moreover, creation of structural defects may increase the diffusion rate of atoms. It appears from the modeling results that although different activation factors induce different transformation rates, the process does not proceed through different transformation paths. In other words, although the activation mechanisms are different in thermal and mechanical activation, the mechanism of the Cu_2O reduction seems to be similar in both ways.

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