The effect of aluminothermic reaction on the progress of carbothermic reaction in simultaneous mechanochemical reduction of CuO and ZnO

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ABSTRACT

In this research, the effect of aluminothermic reaction on the progress of carbothermic reaction in simultaneous mechanochemical reduction of CuO and ZnO has been studied. A mixture of CuO and ZnO powders along with different amounts of aluminum and graphite was milled in a planetary ball-milling machine. The adiabatic temperature and overall reaction enthalpy were varied by changing the aluminum/carbon ratio. The results showed that by increasing the amount of aluminum, the exothermic aluminothermic reaction provided the required heat for the endothermic carbothermic reactions. Consequently the oxide powders were entirely reduced during ball-milling process and α-brass–Al_2O_3 nanostructured composites were obtained. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the final products. By utilizing the Scherrer's method, the mean grain size of the products was calculated to be in the nanometer range, further confirmed by TEM observations.

1. Introduction

Reduction of metal oxides is usually carried out at high temperatures in appropriate conditions with respect to equilibrium thermodynamics. However, because of the high activity of fresh surfaces, mechanochemical reduction is possible [1]. During mechanical alloying repeated welding and fracturing of powder particles increases the area of contact between the reactant powder particles due to a reduction in particle size and allows fresh surfaces to come into contact repeatedly; this allows the reaction to proceed without the necessity for diffusion through the product layer [2]. The redox reactions in powder mixtures of oxide and pure metal during reactive milling allow both the refining of metals and the direct production of alloys from their respective oxides, thus attracting much attention [3].

In the past couple of decades, reduction of many metallic oxides by solid metallic reducing agents (metallothermic reduction) through mechanical alloying has been extensively studied. Solid state reduction of CuO by Ca, Al, Mg, Ti, Mn, Si, Fe, Ni [2–8] and ZnO by Al [9], Ca [3], Ti [10] and Mg [11] have been investigated up to now. Schaffer and McCormic also applied the reaction between CuO, ZnO and Ca to synthesize β′-brass [3].

In addition to metallothermic reduction, carbothermic reduction can take place during mechanical alloying. Yang et al. [12] and Tokumitsu [1] have reported the possibility of mechanochemical reduction of CuO by C. But according to the author's investigation, the effect of metallothermic reaction on carbothermic reaction during mechanical alloying has not been studied yet.

In this work, we have used CuO/ZnO powders as starting materials and Al/carbon as reducing agents and studied the effect of aluminothermic reaction on carbothermic reaction during simultaneous reduction of mentioned oxides and formation of α-brass.

2. Experimental work

CuO (96% purity, Merck 102761), ZnO (99% purity, Fluka 96484), Al (99.5% purity, Mashhad Powder Metallurgy Co.) and C (99.5% purity, Mashhad Powder Metallurgy Co.) powders were mixed to give the following desired stoichiometric composition:

$$0.3ZnO + 0.7CuO + (1-3x)C + 2xAl \rightarrow 0.3Zn + 0.7Cu + (1-3x)CO + xAl_2O_3 \quad (1)$$
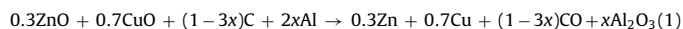
where x is a variable. Changing the value of x will influence the weight percent of the primary carbon and aluminum, which consequently affects the adiabatic temperature of the reaction.

Adiabatic temperature can be calculated from the following equation [13]:

$$\Delta H^{\circ}_{298} = \sum \left[\int_{298}^{T^i_m} C^i_{ps}\, dT \right] + \sum (\Delta H^i_m) + \sum \left[\int_{T^i_m}^{T^i_{ad}} C^i_{pl}\, dT \right] \quad (2)$$

where ΔH°_{298} is the standard enthalpy of reaction, T^i_m is the melting point of product i, C^i_{ps} is the heat capacity of product i in the solid state, ΔH^i_m is the enthalpy of fusion of product i and C^i_{pl} is the heat capacity of product i in the liquid state. If vaporizing of product i occurs, heat capacity of product i in the vapor state (C^i_{pv}) and enthalpy of vaporization of product i (ΔH^i_v) should be included in Eq. (2). The change in the adiabatic temperature vs. x, by using Eq. (2) is plotted in Fig. 1. Four different starting compositions were chosen for the experiments. x, T_{ad}, and the content of primary Al and C for each studied composition are shown in Table 1.

Mechanical alloying (MA) was performed under argon atmosphere in a planetary ball-mill at room temperature with a rotation speed of 260 rpm. The milling media

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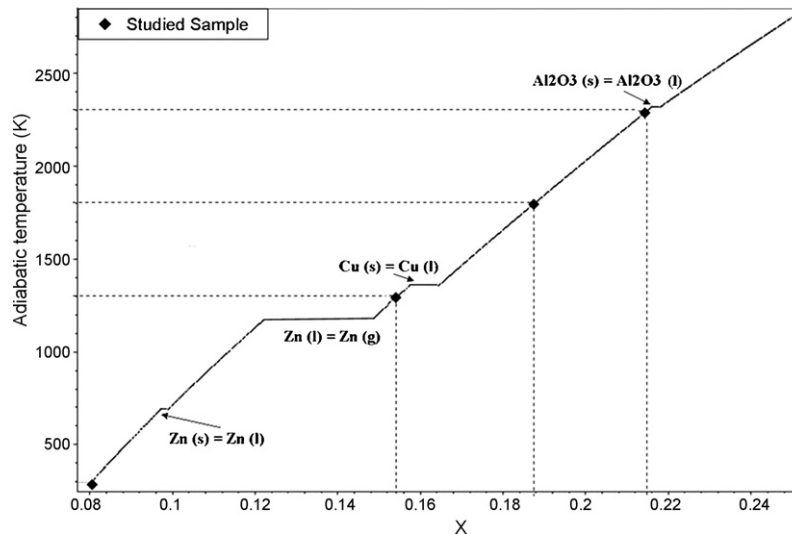
Fig. 1. The change in the adiabatic temperature for different values of *x*.

was two types of bearing steel balls with diameters of 10 and 12 mm and the chosen weight ratio of the balls to the powder (BPR) was 40:1. In each run, the total amount of milled powder mixture was 7.5 g.

The reduction progress in the ball-milled powders was characterized by means of X-ray diffraction (XRD) with Cu Kα (λ = 1.54060 Å). The microstructure and morphology of the reacted powders was studied by transmission electron microscopy (TEM) (LEO 912 AB). The sample chosen for TEM observation was prepared by mixing the powders with ethanol in an ultrasound stirrer and mounting the suspended powders on a carbon coated grid. The crystallite size of the powders was calculated using the Scherrer method from the line broadening of the diffraction lines in the XRD patterns [2]:

$$d = \frac{0.9\lambda}{B\cos\theta} \tag{3}$$

where *d* is the average grain size (nm), λ the Cu Kα wavelength (nm), *B* the diffraction peak width at half maximum intensity (rad) and θ the Bragg diffraction angle.

3. Results and discussion

3.1. Reduction by aluminum and carbon

The first step was to ensure that the copper and zinc oxides could be simultaneously reduced during the mechanochemical process; in this regard, sample 1 was ball-milled for different time periods. The adiabatic temperature in this sample was calculated to be 2300 K, and according to Merzhanov's criteria (T_{ad} > 1800 K), occurrence of self-propagating high temperature synthesis (SHS) is possible [14]. Therefore, there is a high probability that the heat produced by the metallothermic reaction is sufficient to activate the carbothermic reduction reaction. Fig. 2 shows the XRD results obtained from this sample.

As can be seen in Fig. 2, after 2 h of ball-milling, no new peaks were seen in the XRD pattern i.e. no detectable chemical reaction has occurred. But after 3 h of ball-milling, the peaks corresponding to the starting materials have disappeared and new peaks corresponding to α-brass and α-Al₂O₃ can be seen. This fact indicates

Table 1
T_{ad} and the amount of primary aluminum and carbon for different values of *x* in four studied samples.

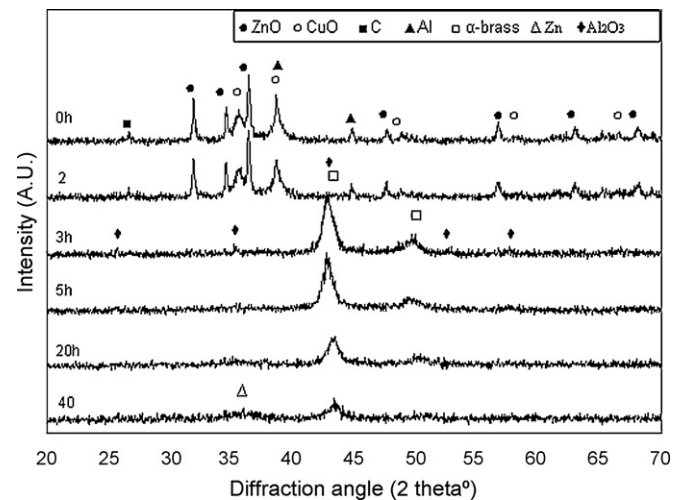| Sample no.	*x*	T_{ad} (K)	Primary Al weight percent	Primary C weight percent
1	0.215	2300	12.09%	4.44%
2	0.188	1800	10.62%	5.57%
3	0.155	1300	8.81%	6.77%
4	0.08	298	4.61%	9.74%

Fig. 2. XRD patterns of sample 1 ball-milled for different time periods.

that the reaction occurs as an SHS and the aluminothermic reaction is responsible for activating the carbothermic reaction.

The changes in the (1 1 1) α-brass peak caused by increasing the ball-milling time are shown in Fig. 3. By increasing the ball-milling time a slight broadening could be seen in the (1 1 1) peak, its inten-
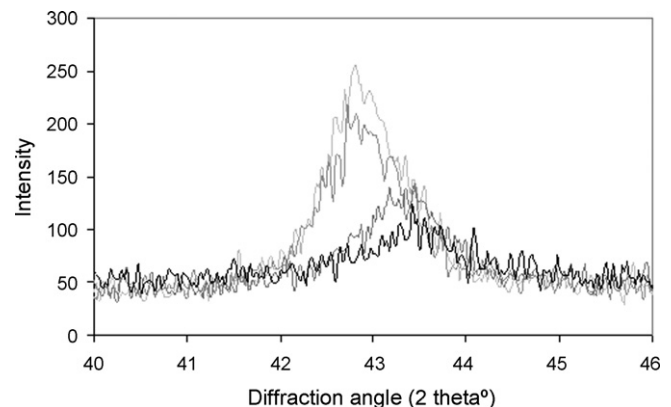

Fig. 3. Changes of (1 1 1) α-brass peak vs. ball-milling time for sample 1.
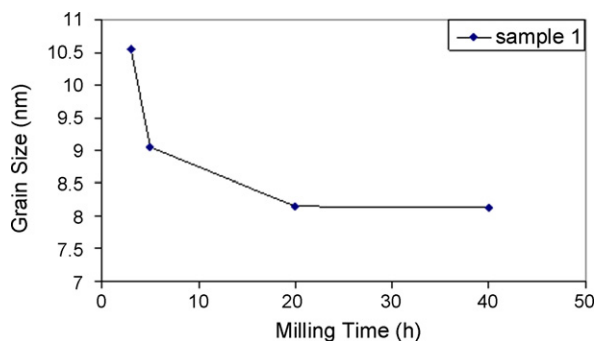
Fig. 4. Average grain size of α-brass vs. the milling duration for sample 1.

sity decreases and the peak is displaced to a higher Bragg angle. The broadening and decrease in intensity of the peak could be related to the decrease in α-brass grain size and increase in lattice microstrain. Fig. 4 displays the average grain size of α-brass vs. ball-milling time. The reduction in grain size and attainment of a steady-state grain size are the result of interplay and balance between several mechanisms occurring simultaneously during the milling process. For instance, at first, formation of new defects particularly dislocations might result in formation of high dislocation density regions in the grains, pile up at the grain boundaries or irregular clusters in the grains which results in reduction of crystalline size [15]. This mechanism is followed by work hardening and recovery mechanisms [15]. Displacement of the peak to higher Bragg angles is related to the decrease in the lattice parameter caused by the gradual departure of small amounts of zinc from the brass alloy [16]. The XRD results also confirm this fact, such that after 40 h of ball-milling, peaks corresponding to zinc could clearly be spotted (Fig. 1).

3.2. Effect of aluminothermic reduction on carbothermic reduction

In order to study the effect of the aluminothermic reduction reaction on the progression of the carbothermic reaction, samples 2, 3 and 4 were ball-milled for 20 h (under the same conditions as sample 1) and the results were compared with sample 1. Fig. 5 shows the XRD patterns obtained from these samples.

α-Brass peaks could be found in sample 2 which had a calculated adiabatic temperature equal to 1800 K. Also, the peaks corresponding to CuO have been eliminated and ZnO peaks have been intensely reduced which indicate that the carbothermic reaction has been activated in this sample. But due to the fact that the heat produced by the aluminothermic reaction was low (because the adiabatic temperature was low), the carbothermic reaction has not been completed. Peaks corresponding to α-Al_2O_3 could not be seen in the XRD pattern in Fig. 5 for samples 1 and 2. This could be because of
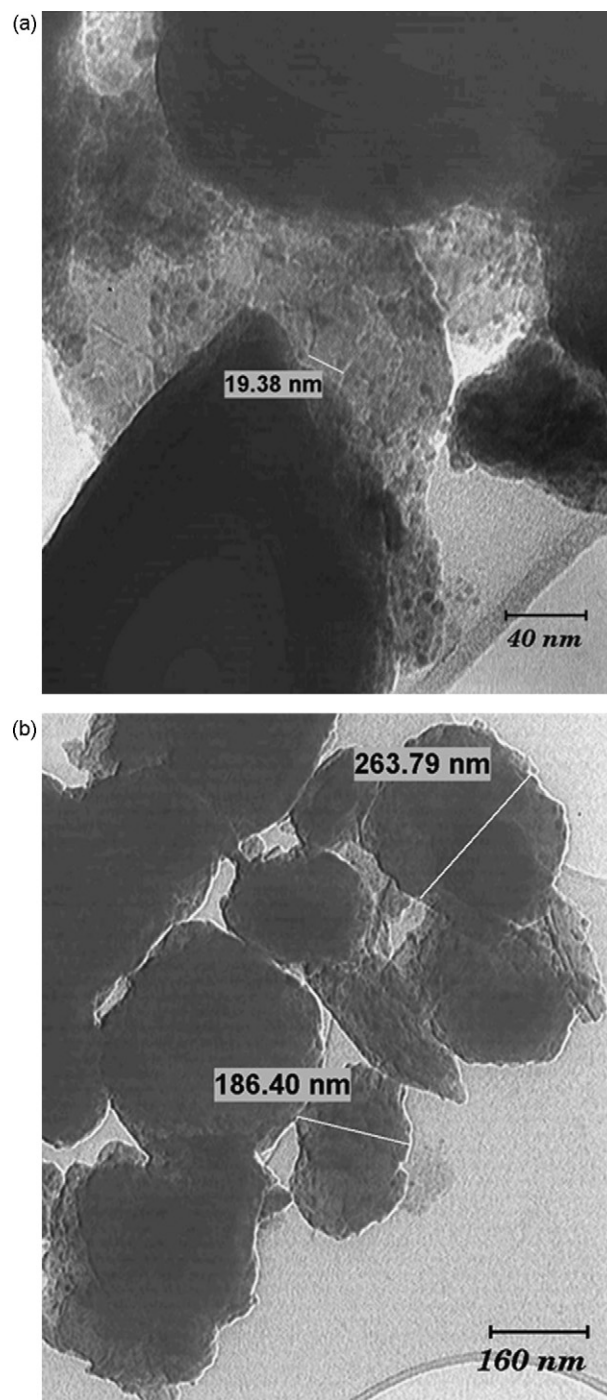

Fig. 5. XRD patterns of samples ball-milled for 20 h.

Fig. 6. TEM images of sample 1 ball-milled for 20 h; (a) size of grains; (b) size of particles.

the small size of Al_2O_3 particles and the fact that they are caught in the dense copper matrix as reported by Ying and Zhang [17] and Hwang and Lee [18].

The adiabatic temperature in sample 3 is calculated to be 1300 K; therefore, SHS did not occur. Low intensity Cu peak in this sample, suggesting that the aluminothermic reaction took place gradually. A gradual aluminothermic reaction did not supply the required temperature for occurrence of carbothermic reaction. Hence, even after 20 h of ball-milling, CuO was partially reduced. The same behavior was observed in sample 4. Because low amounts of aluminum were used in sample 4, the Cu peaks in the XRD pattern had very low intensities. Although the carbothermic reaction did
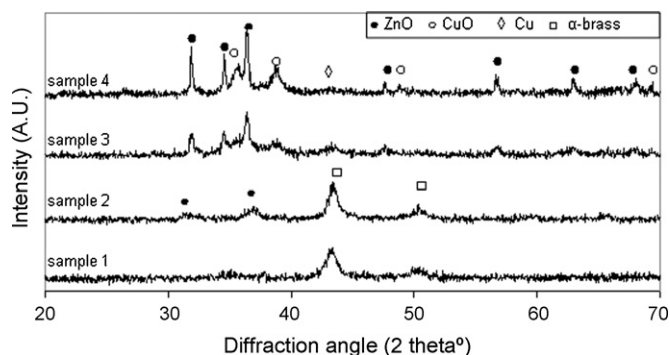
not take place in samples 3 and 4, the peaks corresponding to carbon were eliminated in the XRD patterns. Elimination of carbon peaks is associated with its intense deformation during ball-milling [19,13]. When ball-milling systems containing several phases, the phase with the softest crystal structure undergoes more deformation compared to phases with harder crystal structures. Therefore, the carbon peaks gradually decreased in intensity and completely disappeared after 20 h of ball-milling. In this state, carbon particles are believed to have an amorphous structure [19–23].

In order to study the microstructure and particle size of the synthesized brass, transmission electron microscopy (TEM) was utilized. Fig. 6 shows bright field images of sample 3 which was ball-milled for 20 h. As can be recognize from Fig. 6a, the mean grain size is about 20 nm while the grain size obtained from the XRD pattern (using the Scherrer method) is about 10 nm. The possible reason for this distinction can be physical differences in values being determined [24]. The X-ray structural method actually allows us to determine a size of coherently scattering domains connected with internal grain areas having a weakly distorted crystal lattice, whereas the TEM method measures a complete grain size which includes near boundary strongly distorted [24]. This distinction in grain size can also be related to ignoring the effect of stacking faults on broadening/shift of peak positions. Brass alloys have low stacking fault energy, so high density of stacking fault in (1 1 1) planes during mechanical alloying is expected. These faults can cause anomalous hkl-dependent peak bordering in the X-ray diffraction patterns. Nevertheless, in calculating grain size by Scherrer's equation, it was assumed that the peak bordering is only due to small grain size [2].

The particles do not have a constant and similar morphology and the size of the particles was within 0.2–0.3 μm range (Fig. 6b).

4. Conclusion

Simultaneous mechanochemical reduction of copper and zinc oxides in the presence of carbon and aluminum was successfully performed. It was observed that by changing the aluminum/carbon ratio and consequently changing the adiabatic temperature, the reduction reactions could take place in two different modes: gradually and instantaneously. In order to activate the carbothermic reduction reaction and the aluminothermic reduction reaction simultaneously, the adiabatic temperature must be over 1800 K and the aluminothermic reaction must occur instantaneously. After 3 h of ball-milling, the peaks corresponding to the starting materials were eliminated and brass peaks appeared in the sample which had a 2300 K adiabatic temperature. While, even after 20 h of ball-milling, complete reduction did not occur in the other samples.

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