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Mechanism of zinc oxide–aluminum aluminothermic reaction

Ali Maleki · Masoud Panjepour · Behzad Niroumand · Mahmood Meratian

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Abstract In this study, the aluminothermic reaction of a mixture of aluminum and zinc oxide powders ball milled at ambient temperature was investigated employing X-ray diffraction (XRD), differential thermal analysis (DTA), and electron microscopy (SEM) techniques. The kinetics of the reaction was studied based on DTA results to evaluate the mechanism and the activation energy of the reaction. The reaction mechanism was recognized to be an interface controlled one. The activation energy as well as the ignition temperature of the aluminothermic reaction was found to decrease significantly with increasing the milling time. The ignition temperature of the reaction was reduced from 1008 °C for the unmilled mixture to 563 °C for the mixture milled for 60 min. This was rationalized in terms of the microstructural changes observed in the milled mixtures. The activation energy also decreased from 848 kJ/mol for the unmilled mixture to 119 kJ/mol for the mixture milled for 60 min.

Introduction

Thermite reaction is a general term used to describe the displacement reaction between a metal and a metallic oxide to form a more stable oxide and the corresponding metal of the reactant oxide [1]. Aluminothermic reactions are a well-known group of thermite reactions involving reduction of a metallic oxide with elemental aluminum [2]:

$$2x\mathrm{Al} + 3\mathrm{M}_y\mathrm{O}_x \rightarrow 3y\mathrm{M} + x\mathrm{Al}_2\mathrm{O}_3 + \Delta H$$

The reaction products may find applications in certain processes such as welding, coating, and composite synthesis [1, 3]. For instance, the reaction can be utilized to synthesize in situ aluminum/alumina composites, where alumina acts as reinforcement and the reduced metal may be dissolved in the matrix as an alloying element [4]. In fact, researchers have used a host of different metallic oxides for this purpose which include, e.g., TiO_2 [5], MnO_2 [6], SiO_2 [7, 8], CuO [9], B_2O_3 [10], MoO_3 [11], Fe_2O_3 [12], ZnO [13–16], etc.

Many researchers have tried to use zinc oxide as the reactant material to synthesize in situ aluminum/alumina composite. For example, Kobashi and Choh [15] reported that no chemical reaction occurred in the ZnO/Al system as the metal oxide was added into molten aluminum. Chen and Sun [16] studied ZnO/Al reaction by mixing, pressing, and heating the reactants and showed that almost no thermite reaction could take place in the system below 970 °C.

Still many aspects of this process remain unclear. Among these, the authors were not able to find any published work which investigated the kinetics as well as the effect of mechanochemical processing on the thermite reaction of zinc oxide with aluminum. This was the motivation for a study to find out the reasons behind the poor reactivity of zinc oxide with aluminum and to facilitate the reaction through a novel in situ aluminum/alumina composite synthesis method. Some aspects of the study have been published previously [17]. In this article, the mechanochemical reaction and kinetics of ZnO/Al system is investigated. The reaction mechanism is defined, and the activation energy of ZnO/Al reaction before and after mechanical activation is determined.

A. Maleki · M. Panjepour · B. Niroumand · M. Meratian (✉)
Department of Materials Engineering, Isfahan University
of Technology, Isfahan 84156-83111, Iran
e-mail: meratin@cc.iut.ac.ir

Experimental materials and procedures

Commercially pure aluminum powder (99.7% purity, Khorasan PM Co., IRAN) with a particle size of <45 μm and pure zinc oxide powder (>99.9% purity, Merck, Germany) with particle size of less than 0.5 μm were used as raw materials. Mixtures of aluminum and zinc oxide powder with stoichiometric ratio of their aluminothermic reaction ($2Al + 3ZnO \rightarrow Al_2O_3 + 3Zn$) were milled in a planetary ball mill machine (Retsch PM100) using hardened chromium steel vial and balls under argon atmosphere for 20, 40, 60, and 80 min. A ball-to-powder mass ratio of 10 and rotation speed of 600 rpm was employed.

X-ray diffractometry (XRD) was used to detect the phases present in the powders before and after milling. A Philips diffractometer (40 kV) with Cu Kα radiation ($\lambda = 0.15406$ nm) was used for XRD tests. The XRD patterns were recorded in 2θ range of 25–75° with a speed of 3° per minute. To investigate the effect of ball milling duration on the reaction temperature, differential thermal analysis (DTA) was performed on the mixtures under argon atmosphere using a Shimadzu TG/DTA machine. About 10 mg of each mixture was filled in a special alumina crucible. A heating rate of 10 °C/min and temperature range of 25–1200 °C were used. DTA was also performed under similar conditions on pure aluminum powder up to temperatures of 800, 900, and 1000 °C. Zero baseline correction was performed on DTA signals. In addition, XRD patterns of the reaction products (mixtures after DTA) were taken to study the phases formed during heating. The interaction between the powder particles was investigated using Philips XL30 scanning electron microscope (SEM).

Variation of α, the fraction reacted, with temperature for aluminothermic reaction of the aluminum and zinc oxide particles was also studied. α value of the reaction was calculated using DTA graph of the reaction as following [18]:

$$\alpha_T = S_T / S \qquad (1)$$

where α_T, S_T, and S were the fraction reacted at temperature T, the DTA peak area at temperature T, and the total DTA peak area, respectively. The resultant α–T graph was used to determine the reaction mechanism and its activation energy.

Results and discussion

Aluminum and zinc oxide can react in a displacement reaction as following [14]:

$$2Al + 3ZnO \rightarrow Al_2O_3 + 3Zn + \Delta H$$

$$\Delta G^{\circ}_{298K} = -601 \text{ kJ/mol}$$

$$\Delta H^{\circ}_{298K} = -625 \text{ kJ/mol}$$

As can be seen, the change in the free energy of the reaction is negative, and therefore, the reaction is thermodynamically possible. That is, it may ignite even at ambient temperature upon providing the required activation energy. The role of ball milling applied to the mixtures in this study was to provide the activation energy of the reaction.

Figure 1 illustrates XRD patterns of aluminum and zinc oxide mixtures ball milled for 0, 20, 40, 60, and 80 min. As it is evident from the figure, only aluminum and zinc oxide peaks were observed in the diffractogram of the unmilled sample. Ball milling for 20 min yielded a similar pattern only with decreased peaks intensities which is attributed to peak broadening phenomenon, a characteristic feature of ball milling. The same trend was observed for powders ball milled for 40 and 60 min. For these experiments either no new phases have been formed or the amount of new phases formed has been so small that they could not be detected by XRD.

Figure 1 reveals that once ball milling elapses 80 min, a new peak associated with zinc formation appears in the XRD pattern of the ball milled mixture indicating that the reaction has been ignited. In fact when the reaction starts, both zinc and alumina are formed as the reaction products and one should expect new peaks to appear in the corresponding XRD pattern. The new peak observed is the most intensive peak of zinc proving the zinc formation during 80 min ball milling. However, alumina peaks cannot be observed in the pattern. Indeed, it has been demonstrated that the alumina formed at ambient temperature is amorphous and, therefore, does not induce any peak in the XRD pattern [19].

Figure 2 illustrates DTA curves of the mixtures of aluminum and zinc oxide powders activated for 0, 20, 40, and 60 min and heated in a differential thermal analyzer system up to the predefined temperatures of 1000 °C or 1200 °C. Figure 3 exhibits XRD patterns of unmilled mixture after heating up to 1000 °C and 1200 °C and that of the 60 min milled mixture heated up to 1000 °C.

For the unmilled sample, Fig. 2 shows an endothermic peak at about 660 °C, related to the melting of aluminum,

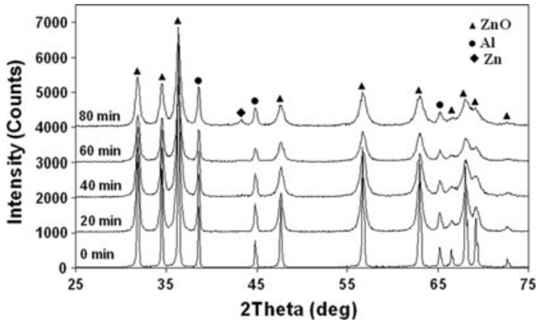


Fig. 1 XRD patterns of aluminum and zinc oxide mixture ball milled for 0, 20, 40, 60, and 80 min

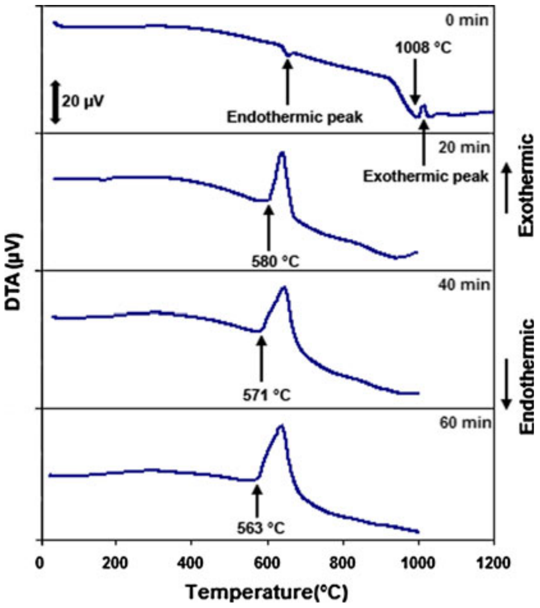


Fig. 2 DTA curves of aluminum and zinc oxide mixture ball milled for 0, 20, 40, and 60 min

and then an exothermic peak beginning at about 1008 °C indicating the start of the aluminothermic reaction. All the peaks in the XRD pattern of the unmilled mixture heated up to 1000 °C (Fig. 3a) are related to aluminum and zinc oxide, which implies that no new phase has been formed up to this temperature. However, when the reactants are heated up to 1200 °C, alumina peaks appear in the XRD pattern (Fig. 3b). It approves that the exothermic peak started at 1008 °C (Fig. 2) is related to the aluminothermic reaction. Since this temperature is fairly higher than the zinc evaporation temperature (907 °C) [20], it seems that all the zinc formed has been evaporated, and therefore, no peak of zinc is detected in the XRD pattern (Fig. 3b).

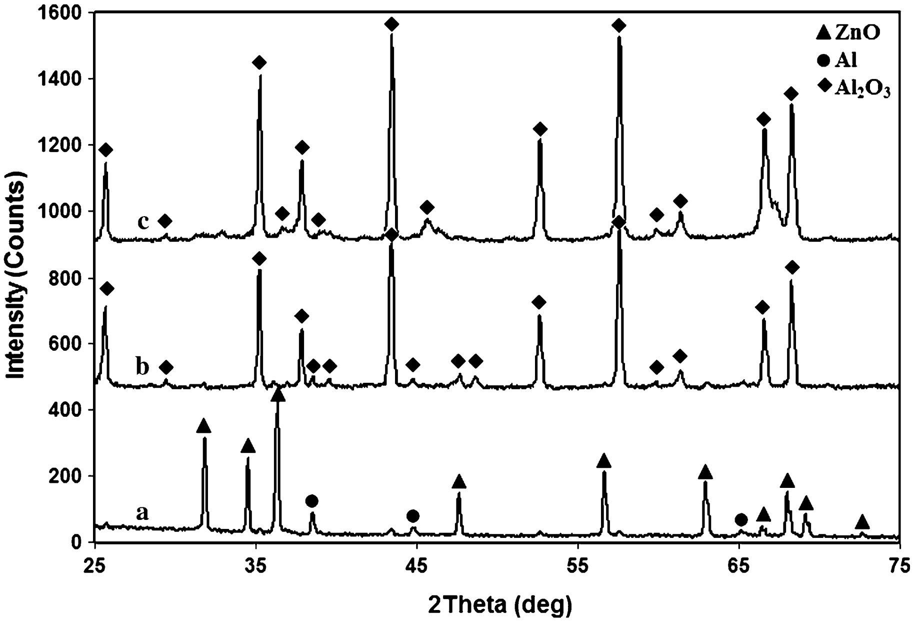
The DTA curve of the mixture milled for 20 min reveals an exothermic peak started at about 580 °C. This means that activation for only 20 min has decreased the ignition temperature of the aluminothermic reaction to temperatures below the melting point of pure aluminum. No endothermic reaction is observed in this graph suggesting that all the aluminum has already been consumed by the reaction before reaching the melting point of the aluminum powder. By extending the milling time to 60 min the ignition temperature decreased even further to about 563 °C. Milling times of more than 60 min resulted in the reaction being ignited in the vial at ambient temperature (Fig. 1).

Figure 3c illustrates the XRD pattern of the reaction products of the 60 min activated powder. A number of alumina peaks are present and no Al or ZnO peak is detected demonstrating the completion of the reaction. No zinc peak is detected in the figure because of the aforementioned reason.

For the aluminothermic reaction to ignite, the zinc oxide particles should come in direct contact with the aluminum particles. However, aluminum particles are usually covered by an aluminum oxide film [3]. Therefore, the aluminothermic reaction cannot ignite before this oxide film is removed or broken. When an aluminum particle is heated up, both the oxide layer and the aluminum inside it start to expand. Since the coefficient of thermal expansion (CTE) of aluminum is higher than its oxide, the oxide film will break at a critical temperature which depends on aluminum particle size and on the thickness of the oxide film.

Figure 4 shows pure aluminum powder particles in as received condition and after heating up to 800, 900, and

Fig. 3 XRD patterns of aluminum and zinc oxide mixture after DTA: **a** unmilled, 1000 °C, **b** unmilled, 1200 °C, **c** 60 min milled, 1000 °C



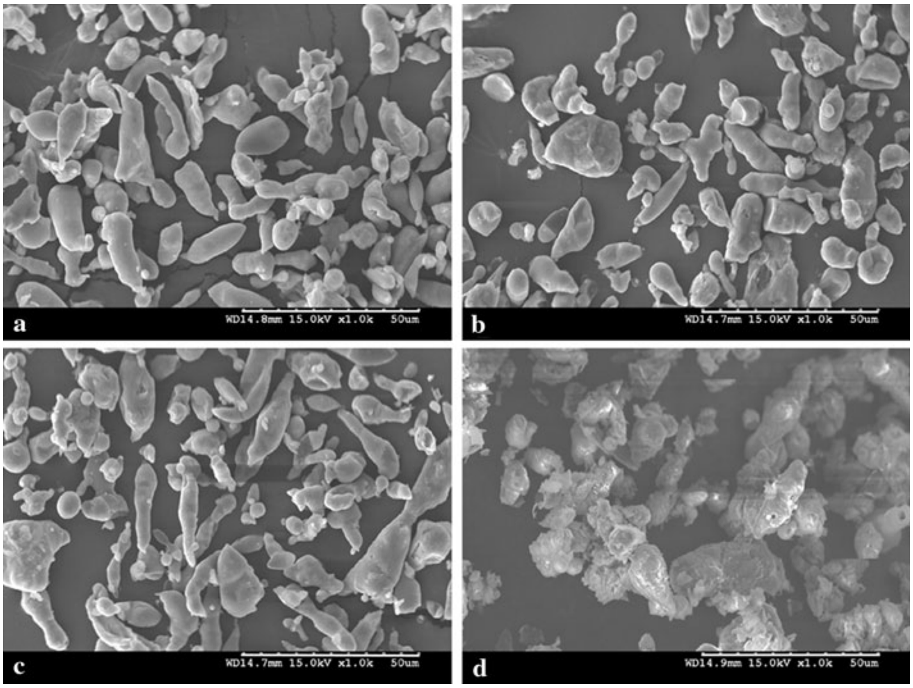


Fig. 4 Pure aluminum powder particles before heating (**a**) and after heating up to 800 °C (**b**), 900 °C (**c**), and 1000 °C (**d**) in a DTA system

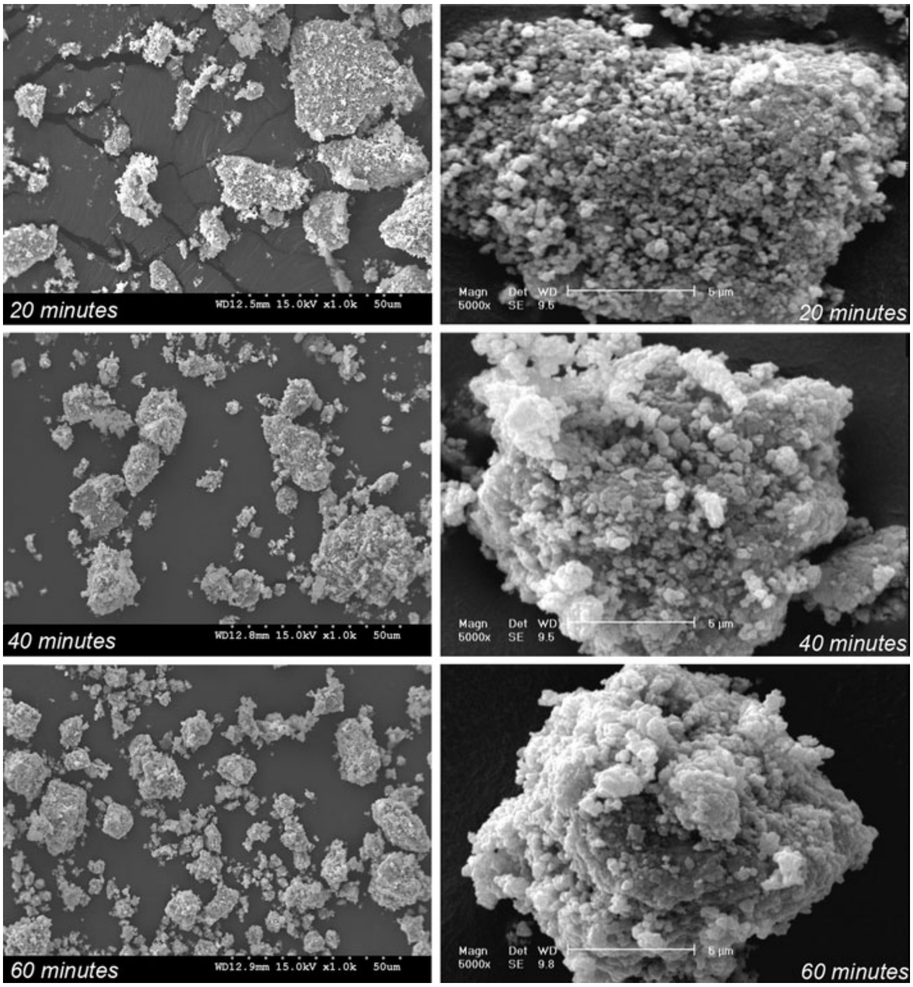


Fig. 5 SEM micrographs of the powder mixture activated for 20, 40, and 60 min with low magnification (*left*) and high magnification (*right*)

1000 °C in a DTA system. Despite the fact that the endothermic melting peak of aluminum powder was detected at about 660 °C, Fig. 4b, c reveals that the shape of aluminum powder particles remained almost unchanged after being heated up to 800 and 900 °C, respectively. Partial agglomeration of aluminum particles resulted from the rupture of oxide films and release of the molten aluminum inside the particles was only visible after heating to 1000 °C (Fig. 4d). This confirms the presence of a surrounding oxide film which prevents the direct contact between the molten aluminum and the zinc oxide particles.

It seems that when the powder mixture is ball milled, on the one hand, the oxide films on the surface of the aluminum particles are mechanically broken and, on the other hand, some of the zinc particles are pushed into the aluminum particles. As a result the zinc oxide particles get in direct contact with aluminum and a good interaction takes place between the aluminum and zinc oxide particles. At such a condition, the reaction kinetics tends to be independent of the critical temperature required for breaking the aluminum oxide film. Thus, the reaction may ignite at lower temperatures.

Figure 5 shows the SEM micrographs of the powder mixture activated for different times. SEM investigations revealed a significant reduction in the size of the aluminum particles by milling. Furthermore, after 20 min of milling, aluminum particles were all covered with a layer of zinc oxide powder while there were still some non-interacting zinc oxide particles left. When milling time was increased to 40 min, not only the aluminum particles were indented more by the zinc oxide particles, but also the number of non-interacting zinc oxide particles decreased as well [17]. Figure 6 shows a cross-section of a 60 min activated aluminum powder particle. The outer surface is the same as micrographs in Fig. 5. It is evident from the cross-section that the zinc oxide particles were indented inside the aluminum powder particles. The best interaction between the powder particles occurred after 60 min of ball milling where in fact a particulate composite of Al/ZnO was formed and the minimum number of non-interacting ZnO particles remained. As the milling was continued, the reaction ignited in the vial as revealed by the XRD pattern corresponding to 80 min ball milling in Fig. 1.

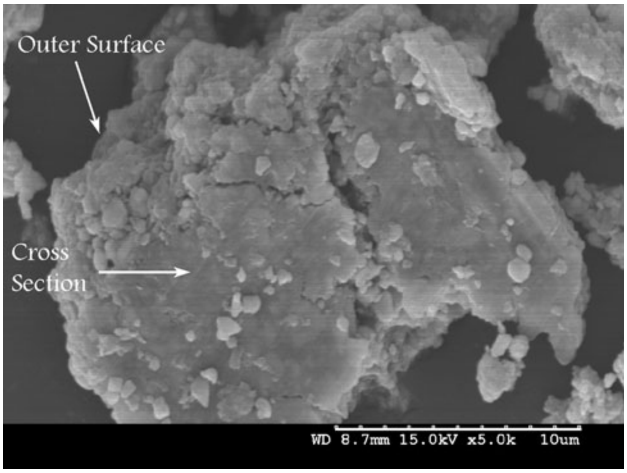


Fig. 6 Cross-section of a 60 min activated aluminum powder indicating indented zinc oxide particles

This interaction brought about by milling not only causes a noticeable fall in the ignition temperature of the reaction but also reduces its required activation energy.

Figure 7 shows the variation of α, the fraction reacted, with temperature for aluminothermic reaction of aluminum and zinc oxide particles. It is evident that for unmilled mixture the reaction starts at a much higher temperature than the milled ones. Furthermore, for the milled samples, the α value at any given temperature is higher for longer milling times. In other words, increasing the milling time promotes the reaction kinetics.

The α–*T* graph can be used for determining the reaction mechanism and its activation energy. Following Sarangis' approach [21], three key equations need to be used for this purpose:

(1) The differential equation as in the conventional kinetics:

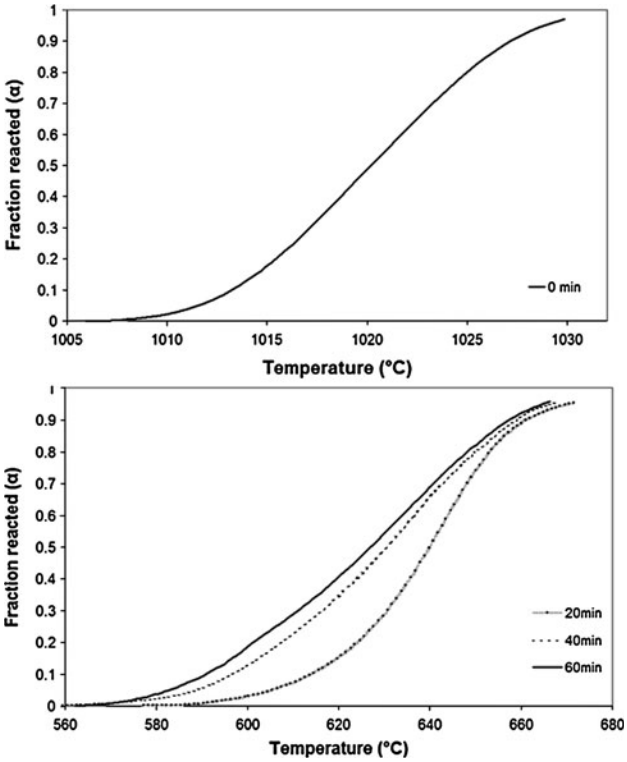


Fig. 7 α–*T* plot for aluminothermic reaction of aluminum and zinc oxide mixture activated for 0, 20, 40, and 60 min

$$\mathrm{d}\alpha/\mathrm{d}t = k \cdot f(\alpha) \tag{2}$$

where α is the fraction reacted, t is time (min), k is a rate constant (min^{-1}), and $f(\alpha)$ is a particular kinetics function whose form should be defined based on the reaction mechanism.

(2) An Arrehenius expression relating the rate constant to temperature:

$$k = A \cdot \exp(-Q/RT) \tag{3}$$

where A is a pre-exponential factor, Q is the activation energy, R is the universal gas constant, and T is temperature.

(3) The temperature variation as a function of time:

$$T = T_0 + \beta \cdot t \tag{4}$$

then

$$\mathrm{d}T/\mathrm{d}t = \beta \tag{5}$$

or

$$\mathrm{d}t = \mathrm{d}T/\beta \tag{6}$$

where T_0 is the initial temperature and β is a constant depending on the heating rate.

Combination of Eqs. 2, 3, and 6 results in Eq. 7:

$$\mathrm{d}\alpha/\mathrm{d}T = (A/\beta) \cdot \exp(-Q/RT) \cdot f(\alpha) \tag{7}$$

From Fig. 7 it can be seen that α-T curve is almost linear at its middle part (for instance 0.2<α<0.8). Therefore, ignoring the initial and final stages of the reaction, $\mathrm{d}\alpha/\mathrm{d}T$ could be considered constant (C).

$$\mathrm{d}\alpha/\mathrm{d}T = C \tag{8}$$

Thus Eq. 7 is written as:

$$f(\alpha) = (\beta \cdot C/A) \cdot \exp(Q/RT) \tag{9}$$

or

$$\ln f(\alpha) = \ln(\beta \cdot C/A) + (Q/RT) \tag{10}$$

Dickinson and Heal [22] have proposed a number of equations for $f(\alpha)$, each of which corresponds to a certain reaction mechanism. Therefore, the mechanism of the aluminothermic reaction in this study can be determined by substitution of different $f(\alpha)$ equations in Eq. 10. The function which results in the most linear graph of $\ln f(\alpha)$ versus $1/T$ will define the reaction mechanism. The activation energy of the reaction will then be easily found by multiplying R by the slope of $\ln f(\alpha)$ − 1/T line (i.e., Q/R).

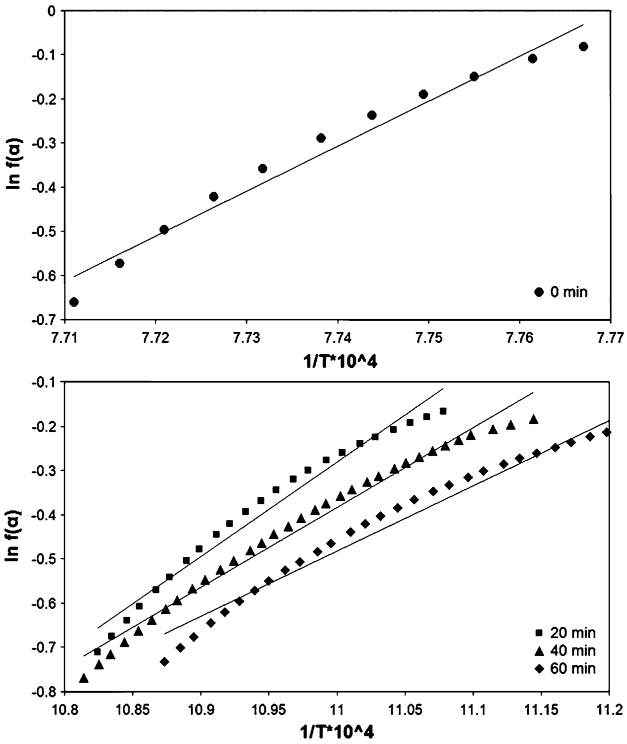


Fig. 8 $\ln f(\alpha) - 1/T$ plot for aluminothermic reaction of aluminum and zinc oxide mixture activated for 0, 20, 40, and 60 min

The mechanism and activation energy of the reaction of unmilled powder mixture and the powder mixture milled for 20, 40, and 60 min were determined using aforementioned approach. It was confirmed, consequently, that the reaction satisfied phase boundary controlled reaction equation (notation $R2$ in reference [22]) better than other equations. It was concluded then that the reaction kinetics was controlled by the interface of the reactants. Figure 8 shows $\ln f(\alpha)$ versus $1/T \times 10^4$ graph for mechanism $R2$ [22]. The corresponding equation for this mechanism is:

$$f(\alpha) = 2(1-\alpha)^{1/2} \tag{11}$$

The phase boundary controlled mechanism for this reaction is in agreement with the experimental observations in this study where reaction of uninteracting (unmilled) aluminum and zinc oxide mixture could only take place at a high temperature. This was due to the fact that the interaction of the interfaces could occur only above a critical temperature where the breakage of aluminum oxide films on the aluminum particles would allow for the wetting of the zinc oxide particles by the released molten aluminum. On the other hand, ball milling caused a mechanically induced interaction between the aluminum and zinc oxide particles which created fresh interfaces capable of reacting at lower temperatures. The decrease in the reaction temperature has been also observed by other researchers when aluminum and zinc oxide were compacted under pressure [13]. This suggests that mechanism $R2$ may also be applicable to the results of those studies.

Table 1 Activation energy of aluminothermic reaction of aluminum and zinc oxide mixture ball milled for different times

Milling time (min)	Activation energy (kJ/mol)
0	848
20	198
40	150
60	119

Table 1 represents the activation energy of the aluminothermic reaction after different milling times of the powder mixture. Evidently mechanical activation significantly decreases the activation energy of the reaction and as the milling time increases, the activation energy decreases. Table 1 shows that the activation energy has decreased from 848 kJ/mol for the unmilled mixture to 119 kJ/mol after 60 min of milling. This is attributed to the increased interface between aluminum and zinc oxide (formation of particulate Al/ZnO composite), as well as to the change of aluminum oxide film breakage mechanism from a temperature-dependant mechanism to a mechanically induced one.

Conclusion

The aluminothermic reaction of an aluminum and zinc oxide mixture with and without mechanical activation was investigated. The results revealed that:

1. The ignition temperature of the aluminothermic reaction of non-activated aluminum and zinc oxide mixture was found to be about 1008 °C which is much higher than the acceptable working temperature range for aluminum melts.
2. Ball milling improved the interaction between aluminum and zinc oxide powders and significantly decreased their reaction temperature. Ball milling could reduce the ignition temperature of the aluminothermic reaction from 1008 °C for the unmilled mixture to 563 °C for the mixture milled for 60 min.
3. The mechanically induced interaction between aluminum and zinc oxide particles decreased the activation energy of the reaction. The activation energy decreased from 848 kJ/mol for the unmilled mixture to 119 kJ/mol after 60 min of milling.
4. Investigation of the reaction kinetics revealed that the aluminothermic reaction was phase boundary controlled (mechanism *R*2) and confirmed that improved interaction between aluminum and zinc oxide particles accompanied by aluminum oxide film breakage could result in decreased ignition temperature and activation energy of the reaction.

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References

1. Mei J, Halldearn RD, Xiao P (1999) Scripta Mater 41:541
2. Huang ZJ, Yang B, Cui H, Duan XJ, Zhang JS (2001) J Mater Sci Lett 20:1749
3. Wang S, Liang K, Zhang X, Li H, Gu S (2002) Key Eng Mater 224–226:745
4. Huang Z, Yang B, Cui H, Zhang (2003) Mater Sci Eng A 351:15
5. Peng HX, Wang DZ, Geng L, Yao CK (1997) Scripta Mater 37:199
6. Maity PC, Chakraborty PN, Panigrahi SC (1994) Mater Lett 20:93
7. Woo KD, Huo HW (2006) Met Mater Int 12:45
8. Woo KD, Na HS, Kim SW, Sato T, Kamio A (2001) Met Mater Int 7:613
9. Maity PC, Chakraborty PN, Panigrahi SC (1997) Mater Lett 30:147
10. Geng K, Lu W, Zhang D (2003) J Mater Sci Lett 22:877
11. Li YF, Qin CD, Ng DHL (1999) J Mater Res 44:2997
12. Subramanian R, McKamey CG, Schneibel JH, Buck LR, Menchhofer PA (1998) Mater Sci Eng A 254:119
13. Yu P, Deng CJ, Ma NG, Ng DHL (2004) Mater Lett 58:679
14. Durai TG, Das K, Das S (2007) Mater Sci Eng A 445–446:100
15. Kobashi M, Choh T (1992) J Jpn Inst Light Metals 42:138
16. Chen G, Sun G (1998) Mater Sci Eng A 244:291
17. Maleki A, Meratian M, Niroumand B, Gupta M (2008) Metall Mater Trans A 39A:3034
18. Haines PJ (2002) Principles of thermal analysis and calorimetry. Royal society of chemistry, Cambridge
19. Wu JM (2001) Mater Lett 48:324
20. Gaskell DR (2003) Introduction to the thermodynamics of materials. Taylor & Francis, London
21. Sarangi B, Sarangi A, Ray HS (1996) ISIJ Int 36:1135
22. Dickinson CF, Heal GR (1999) Thermochim Acta 340–341:89