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Non-isothermal kinetic studies on the formation of Al_2O_3/Nb composite

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ABSTRACT

The reaction mechanism and activation energy (E_α) of aluminothermic reaction between Al and Nb_2O_5 were investigated under non-isothermal conditions using X-ray diffractometry (XRD) and differential thermal analysis (DTA). It was found that the mechanically alloyed Al–Nb_2O_5 powder mixture was converted to Al_2O_3/Nb composite in three stages and during the reduction, intermediate Nb oxides (NbO_2 and NbO) were formed. Four isoconversional methods, of Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), Tang and Starink, were used to determine the value of E on a conversion fraction of $\alpha = 0.5$ for these three exothermic reactions. The results showed that all methods lead to similar values of E and have a good agreement with one another. Also, the isoconversional method of Starink was used to determine the variation of the activation energy, E_α, for three exothermic reactions with degree of conversion (α). It was revealed that the E_α for the first and third reactions are independent from α while different behavior was observed for the second reaction, where a decrease of E_α occurred in the conversion range of $0.6 \le \alpha \le 0.95$.

1. Introduction

Ceramic–matrix composites have attracted the attention of researchers for many years because of their potential for structural applications. Al_2O_3 reinforced with particles such as Mo, Nb, TiC, WC, SiC, and NbC represent a new class of materials with improved mechanical properties, hardness and wear resistance when compared to monolithic ceramics [1–9]. This new class of materials would be an interesting alternative for the manufacturing of cutting tools, improving their cutting speed and efficiency [10].

The Al–Nb_2O_5 system is well known by the exothermic reaction that it undergoes when submitted to thermal and/or mechanical treatment [11], according to the following stoichiometric reaction:

$$10Al + 3Nb_2O_5 \rightarrow 5Al_2O_3 + 6Nb \quad (1)$$

The final phases, Al_2O_3 and Nb, are formed by an in situ chemical reaction in which Al reduces the niobium oxide. Thermite reactions have become important in the synthesis of composites, in which the individual advantages of each constituent may be utilized to its best, achieving excellent mechanical properties of composite as a whole [12]. Moreover, use of mechanically alloyed (MA'd) Al–Nb_2O_5 powder mixture could potentially ensure complete gradual transformation of Al–Nb_2O_5 powder mixture to Al_2O_3/Nb composite [11].Thermodynamic and kinetic studies of in situ ceramic–matrix composites are important in determining their transport mechanisms and thermal stability. The determination of reliable kinetic parameters for solid-state reactions is a widely discussed topic. Problems arise from the uncritical use of the general kinetic approach, not taking into account the implemented basic assumptions [13]. There are several ways to determine the kinetic parameters such as Coats–Redfern which is a model-fitting method and uses single α–T data, obtained at a certain heating rate [14]. The use of methods that use single α–T data for determination of the kinetic parameters should be avoided [15,16], because they generally cannot distinguish true from false kinetic model and tend to produce highly uncertain values of activation energy (E) and pre-exponential factor (A). On the other hand, conventional kinetic methods do not permit an unambiguous formal analysis. As a rule, several kinetic models provide a similar statistical goodness of data approximation, but the corresponding sets of kinetic parameters are quite different [17,18]. For a successful analysis at least one kinetic parameter must be a priori known. These drawbacks of model-fitting methods can be avoided by using isoconversional (model-free) methods which require α–T data obtained from at least three different heating rates. Isoconversional methods can determine E without the knowledge or assumption of kinetic model and, unlike model-fitting approach, can reveal the dependence of E on α. The dependence of E on α is considered as common sign of the process complexity [19,20].

To our knowledge, no article has been published concerning the kinetic analysis of the non-isothermal formation of Al_2O_3/Nb composite. In this work, kinetic analysis of non-isothermal formation of Al_2O_3/Nb composite was performed using different isoconversional methods.

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2. Experimental procedure

2.1. Sample preparation

Mixtures of pure aluminum (purity > 99%, particle size ≤40 μm) and Nb_2O_5 powders (purity >99.5%, particle size ≤15 μm) in the stoichiometric ratio of 25 wt.% Al were milled in a planetary high energy ball mill. High chromium–carbon hardened steel vial (57 mm diameter and 76 mm height) containing the powders and the balls (15 mm diameter) was fixed onto a rotated disc and rotated in the opposite direction to that of the larger platform. The rotation speeds of the vial and the platform were fixed at 350 and 175 rpm, respectively. The mass of powder charge was 10 g and the weight ratio between steel balls and the powder charge was controlled about 15:1.

2.2. Instrumentation

X-ray diffraction technique was used to follow the structural changes of powders after milling and annealing. A Philips diffractometer (40 kV) with Cu Kα radiation ($\lambda = 0.15406$ nm) was used for XRD measurements. The XRD patterns were recorded in the 2θ range of 30–100° (step size 0.05 degree and time per step 1 s). Differential thermal analysis (DTA) was performed using a Reometric STA 503 differential thermal analyzer, with a temperature accuracy of ±0.1 °C under argon supplied at a rate of 60 ml min^{-1}. Powder samples weighting 30 mg were encapsulated into aluminum pans and heated at constant heating rates ($\beta = 10$, 15, and 20 °C min^{-1}) up to 1200 °C. The heat treatment of the samples was conducted in Ar atmosphere. The separation of the peaks in DTA traces was carried out by fitting a 4-parameter Gaussian equation. The partial area analysis under the exothermic peak was used to calculate the degree of conversion at a given temperature, T, from $\alpha = (S_T/S)$, where S is the total area of the exothermic between the temperature, T_i, where process begins and the temperature, T_f, where the process is completed, and S_T is the area between T_i and T. A computer program has been developed to calculate the conversion fraction using the data obtained from DTA experiments.

3. Theoretical background

Model-free isoconversion methods are the most reliable methods for the calculation of activation energy of thermally activated reactions [20–29]. A large number of isoconversion methods have been conducted for polymer materials, but only a few for studies on thermite reactions [30–33]. For the solid-state reactions that are ruled by a single process, the reaction rate can be expressed by Eq. (2):

$$\frac{d\alpha}{dt} \cong \beta\frac{d\alpha}{dT} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{2}$$

where α is the degree of conversion, β the linear heating rate (°C min^{-1}), T the absolute temperature (K), R the universal gas constant (J mol^{-1} K^{-1}), t the time and A the pre-exponential factor (s^{-1}) and E is the activation energy (kJ mol^{-1}).

This equation can be integrated by separation of variables [25,29,34]:

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)} \approx \frac{AE}{\beta R}\int_{T_0}^{T}\frac{\exp(-y)}{y^2}dy \tag{3}$$

The integral on right-hand side is usually called the temperature integral, $P(y)$, and does not have analytical solution:

$$P(y) = \int_{y_f}^{\infty}\frac{\exp(-y)}{y^2}dy \tag{4}$$

To solve the temperature integral, several approximations were introduced. In general, all of these approximations lead to a direct isoconversion method.

The most popular isoconversion methods used for calculation of activation energy are:

1. The Kissinger–Akahira–Sunose (KAS) method [35–37], which takes the form:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = C_k(\alpha) = \frac{E_\alpha}{RT_{\alpha i}} \tag{5}$$

2. The Flynn–Wall–Ozawa (FWO) method, suggested independently by Flynn and Wall [38] and Ozawa [39]. This method is given by:

$$\ln\beta_i = C_W(\alpha) - 1.0518\frac{E_\alpha}{RT_{\alpha i}} \tag{6}$$

3. The Tang method. A more precise formula for the temperature integral has been suggested by Tang et al. [40], which can be put in the form:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^{1.894661}}\right) = C_T(\alpha) - 1.00145033\frac{E_\alpha}{RT_{\alpha i}} \tag{7}$$

4. The Starink method [25,29], another new method for the derivation of activation energy, which is given by:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^{1.92}}\right) = C_S(\alpha) - 1.0008\frac{E_\alpha}{RT_{\alpha i}} \tag{8}$$

It was shown [25] that this method is an order of magnitude more accurate than the others.

4. Results and discussion

4.1. Reaction mechanism

Fig. 1 shows the XRD patterns of powder mixture (75 wt.% Nb_2O_5 and 25 wt.% Al) before and after 2 h of milling. As seen, the inten-

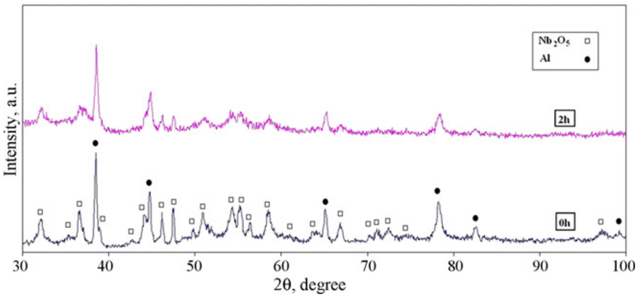

Fig. 1. XRD patterns of Al–Nb_2O_5 powder mixture before and after 2 h of milling.

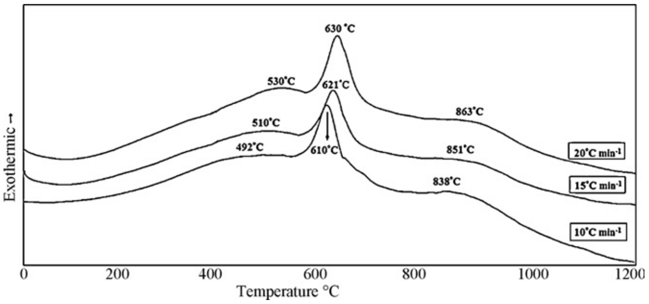

Fig. 2. DTA curves of Al/Nb_2O_5 powder mixture milled for 2 h at different heating rates.

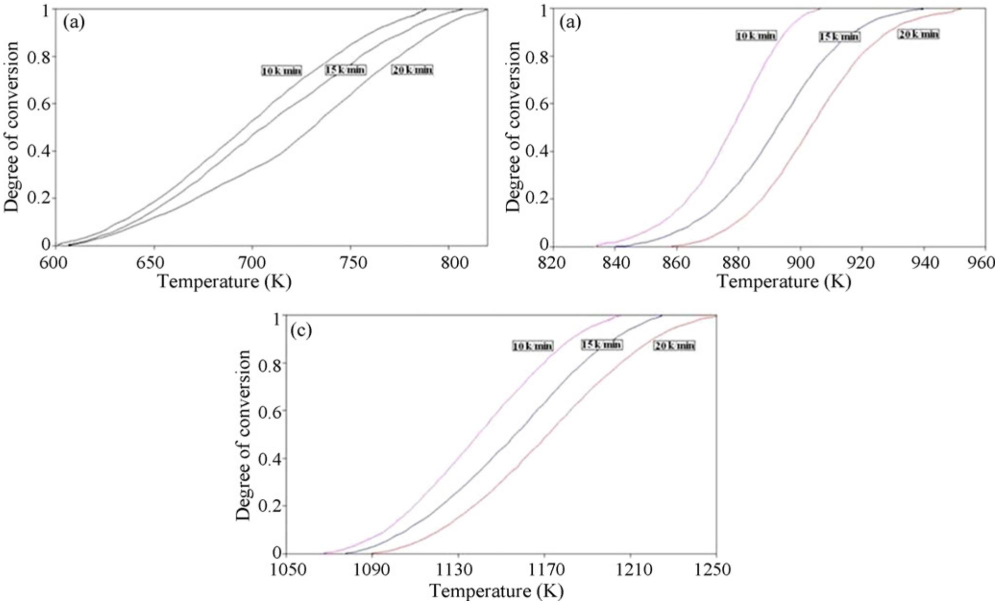

Fig. 3. Degree of conversion as a function of temperature of (a) P_1, (b) P_2, and (c) P_3 at different heating rates.

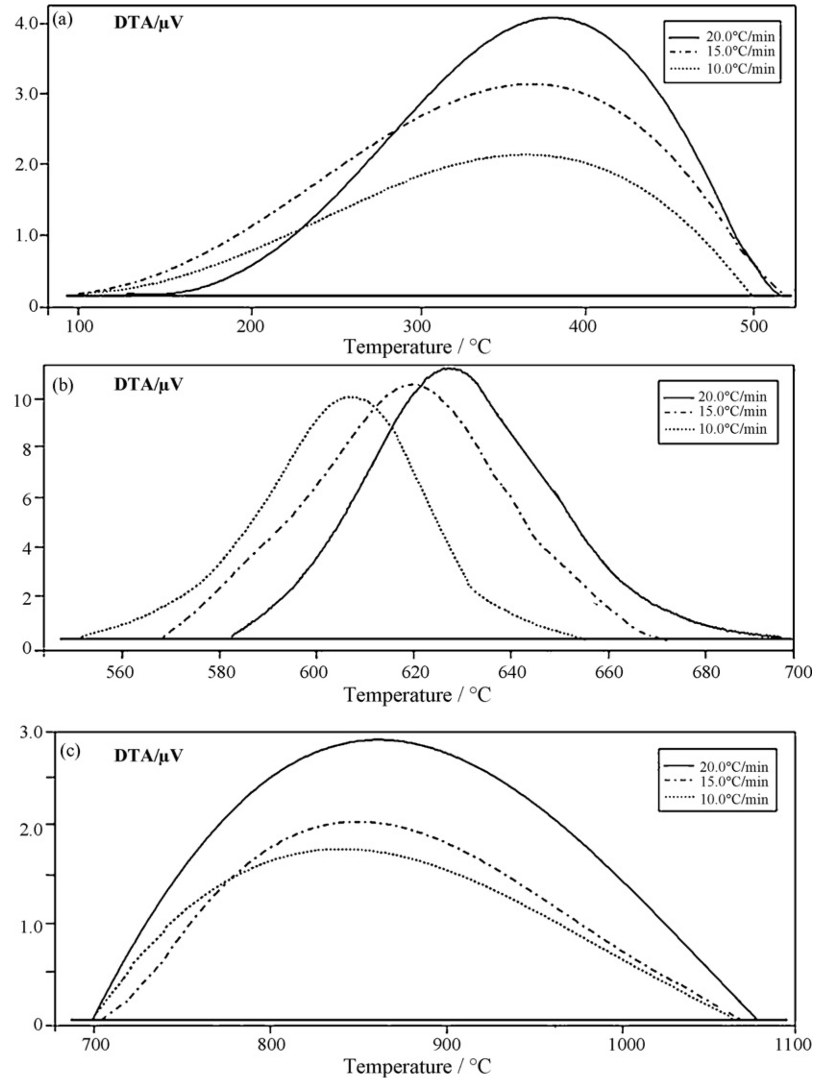

Fig. 4. Three separated exothermic peaks (a) P_1, (b) P_2, and (c) P_3.

Table 1
The value of activation energy for P_1, P_2 and P_3 calculated using Eqs. (5)–(8) at $\alpha = 0.5$.

	KAS	FWO	Tang	Starink
E_{P_1} (kJ mol^{-1})	117 ± 4%	118 ± 4%	117.5 ± 3%	117.7 ± 2.7%
E_{P_2} (kJ mol^{-1})	134.2 ± 2%	136 ± 2%	135 ± 2%	135 ± 1%
E_{P_3} (kJ mol^{-1})	221.5 ± 4%	223 ± 4%	222.2 ± 3%	222.5 ± 2.5%

sity of Nb_2O_5 and Al peaks decrease and they are broadened during milling due to the reduction of crystallite size as well as the microstrain induced in powder particles. In our previous work [11], it was found that the mechanochemical reaction between Al and Nb_2O_5 will be completed after 170 min of mechanical alloying. So the powder mixture of Al and Nb_2O_5 milled for 2 h was selected in order to study the formation kinetic of reaction between Al and Nb_2O_5.

In order to elucidate the mechanism of reaction between Al and niobium oxide, thermal analysis of the MA'd powders were carried out. Fig. 2 shows the results for this mixture. As observed, at the heating rate of 10 °C min^{-1}, there are three exothermic peaks at 492 (P_1), 610 (P_2) and 838 °C (P_3).

The 2 h milled powder samples were heated up to 550 °C, 700 °C and 1000 °C at a heating rate of 10 °C min^{-1} in Ar atmosphere to elucidate the transformation process responsible for these exothermic peaks. It was observed that the reduction of Nb_2O_5 takes place in three stages according to the following reactions:

$$2Al + 3Nb_2O_5 \rightarrow \gamma\text{-}Al_2O_3 + 6NbO_2 \quad (9)$$

$$2Al + 3NbO_2 \rightarrow \alpha\&\gamma\text{-}Al_2O_3 + 3NbO \quad (10)$$

$$2Al + 3NbO \rightarrow \alpha\text{-}Al_2O_3 + 3Nb \quad (11)$$

As it published in our previous work [11], XRD measured showed that NbO_2 and γ-Al_2O_3 are formed after annealing up to 550 °C which indicates that after annealing up to this temperature, reaction (9) takes place. But the main phases in powder mixture milled for 2 h and annealed up to 700 °C, were α-Al_2O_3, γ-Al_2O_3 and NbO indicating that annealing up to this temperature leads to occurrence of reaction (10). α-Al_2O_3 and Nb were the only phases observed in XRD pattern of the sample milled for 2 h and annealed up to 1000 °C, which shows that the reduction of Nb oxide and reactions (9)–(11) were completed.

4.2. Activation energy

Isoconversional method mentioned in (8) was applied to evaluate activation energy for the reactions (9)–(11), $E_\alpha(T)$, and to obtain the dependence of $E_\alpha(T)$ on α for all heating rates applied for the milled Nb_2O_5/Al powder. Three separated exothermic peaks and baselines are shown in Fig. 3.

Graphical representation of the volume fraction crystallized shows typical sigmoid curve as a function of temperature for different heating rates for the three exothermic peaks (see Fig. 4a–c).

Hence, to obtain E, Eqs. (5)–(8) were applied on a conversion fraction of $\alpha = 0.5$ at different heating rates, β_i. The values of the activation energy for P_1, P_2 and P_3 are listed in Table 1. As can be inferred, all methods lead to similar values of E and have a good agreement with each other. Also, the activation energy for the P_3 is the highest.

To evaluate the activation energies for reactions (9)–(11), $E_\alpha(T)$, the isoconversional method in Eq. (8) was used on the overall transformation data to obtain the dependence of $E_\alpha(T)$ on α for all heating rates. Fig. 5 shows the dependence of E_α on α, for P_1, P_2 and P_3, respectively. As can be seen, for P_1 and P_3, E_α, has no dependence on α and is constant during the conversion. But for P_2, E_α is constant in the conversion range of $0.05 \le \alpha \le 0.6$ and then decreases approximately linearly in the conversion range of $0.6 \le \alpha \le 0.95$. It can be interpreted that the endothermic peak corresponding to the melting of remained aluminum in the system has a complete overlap with P_2 which is close to the melting point of aluminum. So, beyond $\alpha = 0.6$, the values of E_α, are not reliable because of the overlapping P_2 and endothermic peak of aluminum melting.

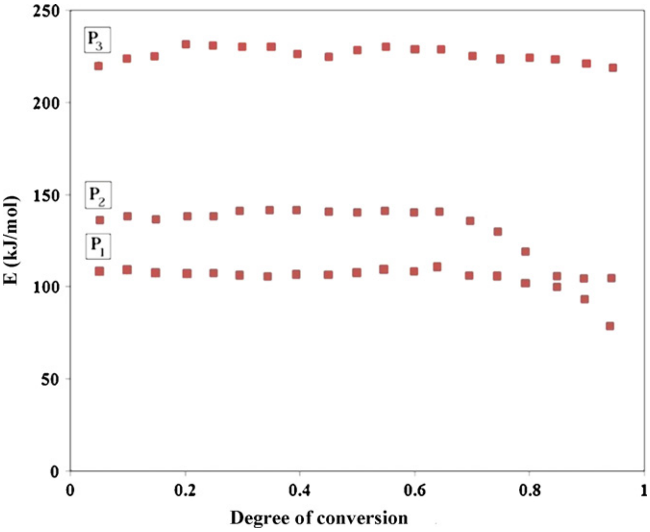

Fig. 5. Dependence of activation energy for reactions (9)–(11), E_α, on the degree of conversion, α (calculated using Starink method).

5. Conclusions

In this study the reaction mechanism and activation energy for aluminothermic reaction between Al and Nb_2O_5 were investigated. It was revealed that the reduction of Nb_2O_5 takes place in three stages and during the reduction, intermediate Nb oxides (NbO_2 and NbO) are formed. The activation energies for three exothermic reactions which lead to the formation of Al_2O_3/Nb composite, E, were estimated by applying four isoconversional methods (KAS, FWO, Tang and Starink). The results showed that all methods lead to similar values of E and have a good agreement with each other. It was found that for P_1 and P_3, E_α, is approximately independent of α, but for P_2 decreases in the conversion range of $0.6 \le \alpha \le 0.95$ because of complete overlapping of P_2 and endothermic peak of aluminum melting.

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