

Implementation of DSC analysis in reaction kinetics during heating of Ti–50 at.%Al powder mixture

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Received: 27 February 2016 / Accepted: 19 November 2016 / Published online: 2 December 2016
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Abstract In this study, the reactions in Ti–50 at.%Al powder mixture upon heating at constant heating rates were studied using DSC analysis. Heating up the mixture resulted in melting of aluminum at temperatures close to its melting temperature, which was manifested as an endothermic peak in DSC curves. The melting of aluminum was the onset of an intense exothermic reaction, so-called combustion synthesis reaction which results in the formation of titanium aluminide. The shift in exothermic peak temperature in various linear heating rates was used to calculate the apparent activation energy according to Kissinger-type model-free methods. Heating rates of 10, 20, 30, 40, and 50 K min⁻¹ were used to estimate the activation energy based on DSC data. In order to study the effect of ball-milling on reaction behavior, the starting powder mixture was ball-milled for different times, and a comparison was made between non-ball-milled and ball-milled DSC curves. The results showed that ball-milling tends to diminish the endothermic peak of melting of aluminum and shift the exothermic reaction temperature to lower temperatures, apparently altering the mechanism from a solid–liquid to an almost solid–solid one. The activation energy

of the process in the non-ball-milled state was found to be close to the activation energy of diffusion of aluminum in TiAl (220 kJ mol⁻¹). However, the application of same model-free methods to the ball-milled samples showed unexpectedly increased values for activation energy. It would be appropriate to check other methods as well as for calculation of activation energy in the ball-milled systems.

Keywords Intermetallic compound · Reactive synthesis · DSC · Diffusion

Introduction

Titanium aluminides are attractive potential candidates for structural applications due to their high specific strength, good resistance to corrosion and oxidation at high temperatures, as well as good creep resistance [1, 2]. Several novel synthesis processes such as combustion synthesis and mechanical alloying [3–6] have been proposed as alternatives to the costly traditional vacuum melting or powder metallurgy methods. Among these methods, the combustion synthesis of aluminides including titanium aluminides has proved to be a quick, efficient, and low-cost technique. The process has been subdivided into self-propagating high-temperature synthesis (SHS) and thermal explosion (TE) modes and has been used to synthesize various refractory compounds including ceramics and intermetallics [7–9]. The combustion synthesis of intermetallic compounds such as NiAl [10–12], TiAl [13, 14], CoAl [15], and FeAl [16] has been successfully carried out during the past decade. However, the complex nature of the process, high temperature gradients, and high rates of reaction have made it difficult to study the kinetics of the reactions. Methods such as quenching of the sample under reaction has been used to

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study the sequence of reactions [17, 18], but deriving the kinetic parameters such as the overall activation energy is not usually possible through these methods. An effective route to investigate the process from the kinetics point of view is using calorimetric methods such as DSC, which can be used to evaluate kinetic parameters such as reaction activation energy and sequence of physico-chemical processes in highly exothermic reactions [19].

Differential scanning calorimetry has already been used to study the reactions between Ti and Al to form TiAl_3 [18, 20]. DSC investigations on mixtures of Ti and Al other than Ti–75%Al have also been reported in a few studies [21, 22]. The present study has been undertaken to calculate the activation energy of the combustion reaction in a Ti–50 at.%Al powder mixture using DSC analysis. The apparent activation energy has been calculated using a model-free method. There were no published data found in the literature to make a comparison between DSC curves in Ti–Al powder mixtures with and without preliminary ball-milling treatment. In this study, the effect of mechanical activation on the reaction mechanism has been studied by comparing the DSC results of milled and unmilled starting powders. The results showed that low-energy ball-milling can promote the reactions and decrease the ignition times in systems like Ti and Al mixture, which show low exothermicity during reaction.

Experimental

Ti (99.9%, <45 μm , High Purity Chemicals, Japan) and Al (99.99%, <45 μm , High Purity Chemicals, Japan) elemental powders with 1:1 molar ratio were thoroughly hand-mixed. The powder mixture (2 g) was subsequently pressed using a 50 kN force to form compacted disks with green densities of 83–85% of the theoretical density. Specimens with the mass of 25 mg were separated from the disks for DSC experiments. A calibrated heat-flux-type DSC apparatus (DSC Nanotechnology Inc., Exstar 6000, Japan) working under argon atmosphere was used to perform calorimetric studies. Pure $\alpha\text{-Al}_2\text{O}_3$ was used as reference sample. Heating rates of 10, 20, 30, 40, and 50 K min^{-1} were used. After each DSC experiment, the products were analyzed by a Rigaku XRD using $\text{Cu-K}\alpha$ radiation to identify the phases. Portions of similar powder mixture were ball-milled for 1, 2, 4, 7, and 10 h using a Nitto ball-mill (Nitto Kagaku Co., Japan). A cylindrical steel vial with internal diameter of 16 cm and height of 20 cm containing 8 mm stainless steel balls was used. The vial was purged with argon for 1 h before the beginning of ball-milling. The ball-milled powder specimens were analyzed by DSC and XRD. A VEGA-TESCAN SEM was used to study the powder mixture before and after ball-milling.

Results and discussion

Figure 1 shows the non-isothermal DSC curves of Ti–50 at.%Al at different heating rates of 10, 20, 30, 40, and 50 K min^{-1} . The DSC curves show the occurrence of an endothermic and an exothermic reaction. The endothermic

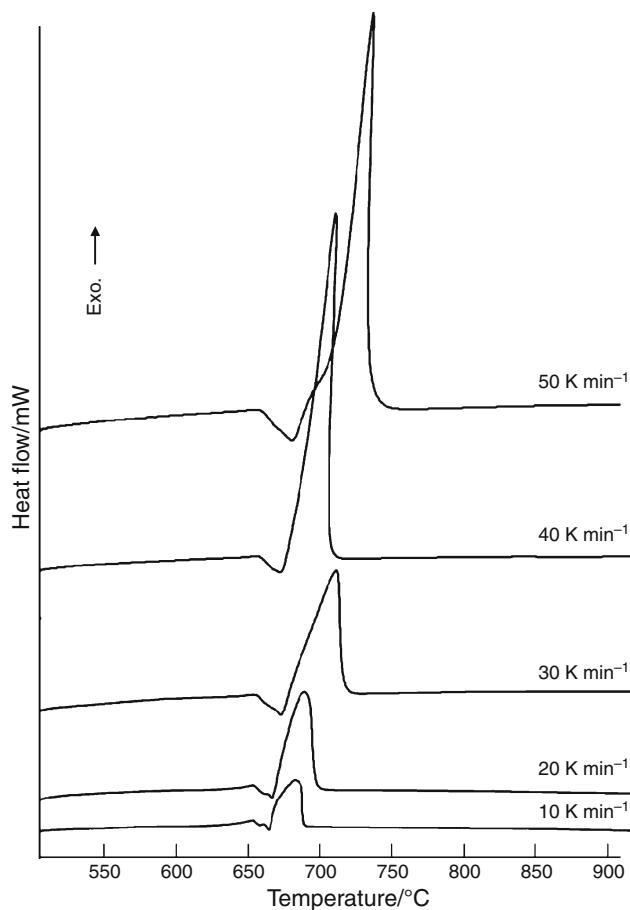


Fig. 1 DSC curves at constant heating rates of 10, 20, 30, 40, and 50 K min^{-1} for Ti–50%Al

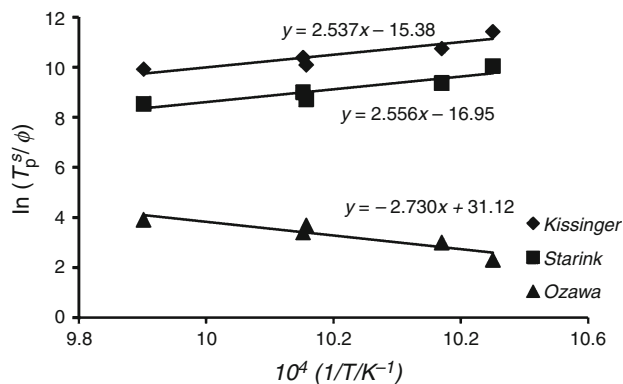


Fig. 2 Plots of $\ln\left(\frac{T_p^s}{\phi}\right)$ versus $\left(\frac{1}{T_p}\right)$ for Ti–50 at.%Al exothermic mixture

peak is observed at around the melting point of aluminum (660 °C). The sharp exothermic peak thereafter is related to the combustion reaction between titanium and aluminum, to form titanium aluminide. The sequence of reaction is in agreement with findings of other researchers [23, 24], who have reported that the combustion synthesis

of aluminides begins with the melting of aluminum, and the molten aluminum engulfs the higher melting particles of the other element. The reaction proceeds due to interfacial reactions as well as the diffusion of elements in the intermetallic layer formed at the interface. Several intermediate phases other than the final intermetallic phases can

Table 1 Calculated activation energies for the combustion synthesis of TiAl from starting mixture of Ti–50 at.%Al

Starting mixture	Apparent activation energy/kJ mol ⁻¹		
	Kissinger method	Starink method	Ozawa method
Ti–50 at.%Al	210.9	211.7	215.8

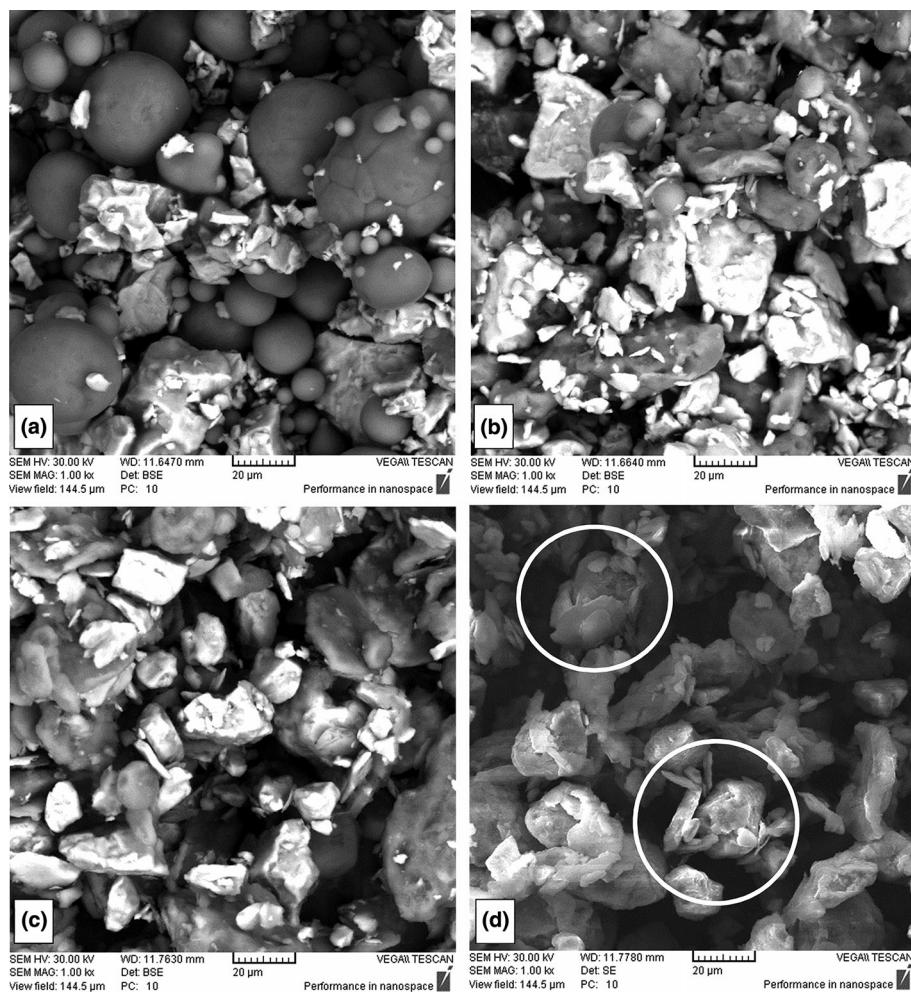


Fig. 3 SEM micrographs showing the Ti–50 at.%Al powder mixture, **a** before ball-milling, after ball-milling for **b** 4 h, **c** 10 h, **d** secondary electron micrographs showing fracture and joining of the particles and signs of cold welding after 10 h of ball-milling

be formed during this process. If these phases do not have a prohibiting effect on the diffusion processes, they will finally dissolve and the process will continue, leaving behind the desirable intermetallic product. Otherwise, some unreacted particles might remain in the final microstructure.

At all heating rates, same endothermic and exothermic peaks are observed; however, the heating rate affects the exothermic reaction temperature. Temperature peak variation at different heating rates can be used to evaluate the kinetic parameters of the process.

The kinetic analysis of chemical reactions is generally performed based on the following kinetic equation [25]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the degree of conversion, k is the chemical reaction rate constant, t is time and T is temperature. It has been assumed in Eq. (1) that the dependence of k on T can be isolated from the kinetic model of the reaction, $f(\alpha)$. Assuming an Arrhenius-type k - T relation, Eq. (1) could be rewritten as follows:

$$\frac{d\alpha}{dt} = k_0 \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (2)$$

where k_0 is the apparent pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. Both model-fitting and model-free methods have been used on the basis of Eq. (2) to analyze kinetic data and calculate the apparent activation energy. However, in non-isothermal thermoanalytical methods in which T and α change simultaneously, there could be an extensive error in the

calculations of Arrhenius parameters. Among different model-free methods, the integral methods based on Kissinger equation [26] have been vastly used to evaluate the apparent activation energy by performing DSC or DTA analyses at different heating rates. Based on these methods, the following equation should be satisfied [4]:

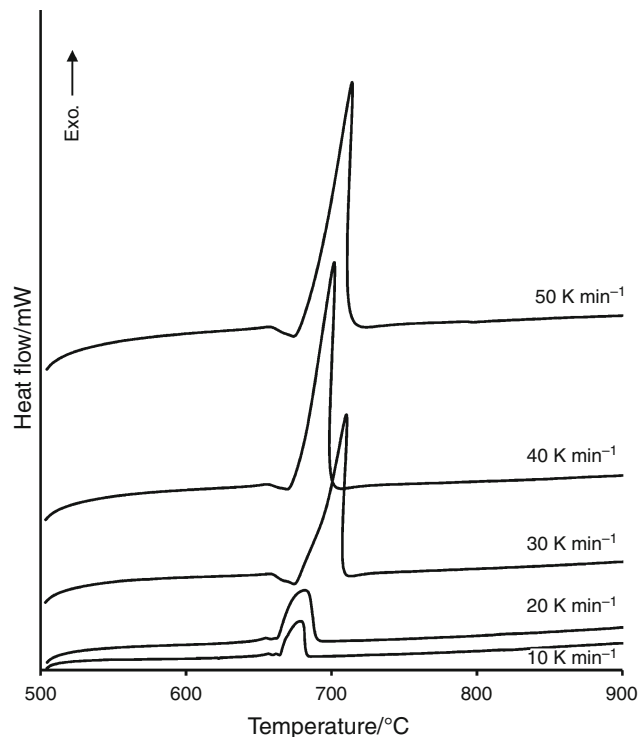
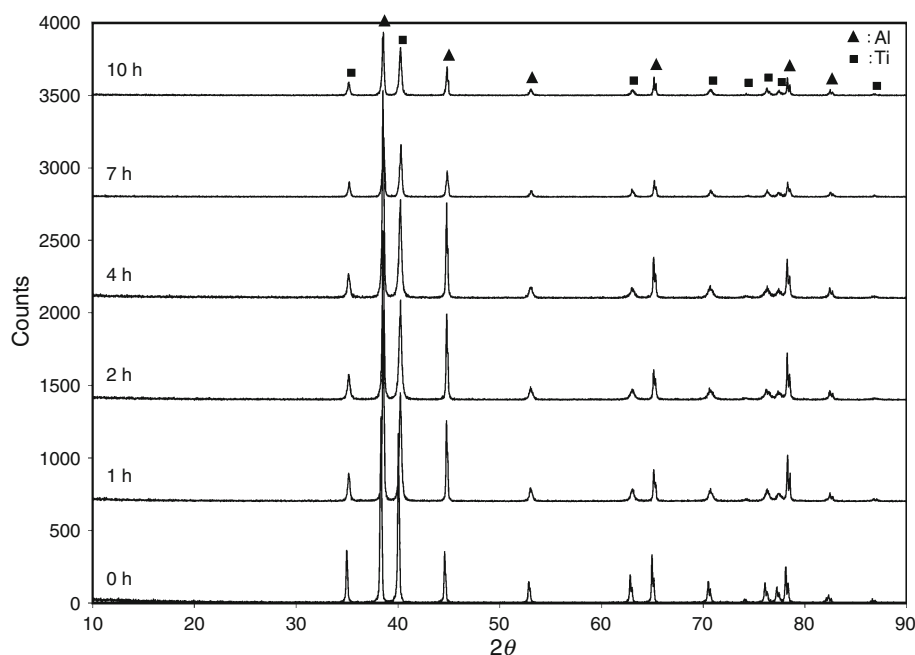


Fig. 5 DSC curves at different heating rates for Ti-50 at.%Al mixture after ball-milling for 1 h

Fig. 4 XRD patterns of the powder mixtures before and after ball-milling



$$\ln\left(\frac{T_p^S}{\varphi}\right) = A \frac{E_a}{RT_p} + \text{constant} \quad (3)$$

where T_p is the peak temperature in DSC or DTA curves (K), φ is the linear heating rate [dT/dt (K min^{-1})], E_a is the apparent activation energy of the reaction (J mol^{-1}), and R is the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$). S and A are constants for which different values have been numerically approximated and reported by researchers. In present research, the values reported by Kissinger ($S = 2$ and $A = 1$) [26], Starink ($S = 1.8$ and $A = 1.0008$) [27], and Ozawa ($S = 0$ and $A = (-)1.0518$) [28] have been used to calculate the apparent activation energy. According to Eq. (3), a plot of $\ln\left(\frac{T_p^S}{\varphi}\right)$ versus $\left(\frac{1}{T_p}\right)$ should give a line with the slope of $A \frac{E_a}{R}$. Figure 2 shows the lines plotted using Kissinger, Starink, and Ozawa methods.

The values of apparent activation energy were calculated as listed in Table 1.

The values of apparent activation energy obtained from the three methods are relatively close and are comparable to the value of activation energy of diffusion of aluminum in TiAl phase (220 kJ mol^{-1}) as reported in the literature [29], which means that the total reaction rate is probably controlled by the diffusion of Al in the TiAl layer formed at the Al/Ti interface.

To investigate the effect of ball-milling on DSC analysis, appropriate portions of the elemental mixture were ball-milled for 1, 2, 4, 7, and 10 h. The aim of ball-milling under argon atmosphere in an ordinary ball-mill was refinement of particles and providing a better contact between the elements. In order to prevent solid-state reactions which readily occur during ball-milling, high-energy ball-milling and the resulting mechanical activation was avoided in this work. SEM micrographs presented in Fig. 3 show the powder mixture particles before and after ball-milling. Mechanical deformation of aluminum granules (dark particles) and titanium particles (light particles) as well as cold welding and fracturing of surface oxide layers are expected to provide significant enhancement of chemical reactivity. The ball-milling also produces a lot of vacancies, dislocations, and other lattice defects which are supposed to induce considerable enhancement in the kinetics of reaction [30–32].

In order to make sure that no chemical reactions happen during ball-milling, the powder mixture was analyzed by XRD after each ball-milling step. The XRD patterns for the ball-milled powders (Fig. 4) show that no new phases were formed. Slight broadening and shortening of Ti and Al peaks happened due to refinement of particles.

Figures 5–8 show the DSC curves of samples ball-milled for 1, 4, 7, and 10 h. As seen in the figures, there is an overall shift in the exothermic peak to lower temperatures

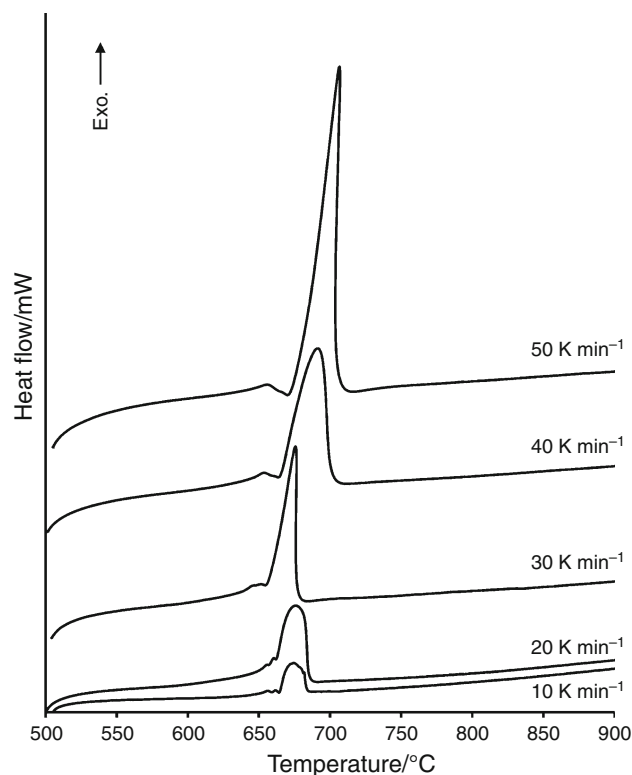


Fig. 6 DSC curves at different heating rates for Ti-50 at.%Al mixture after ball-milling for 4 h

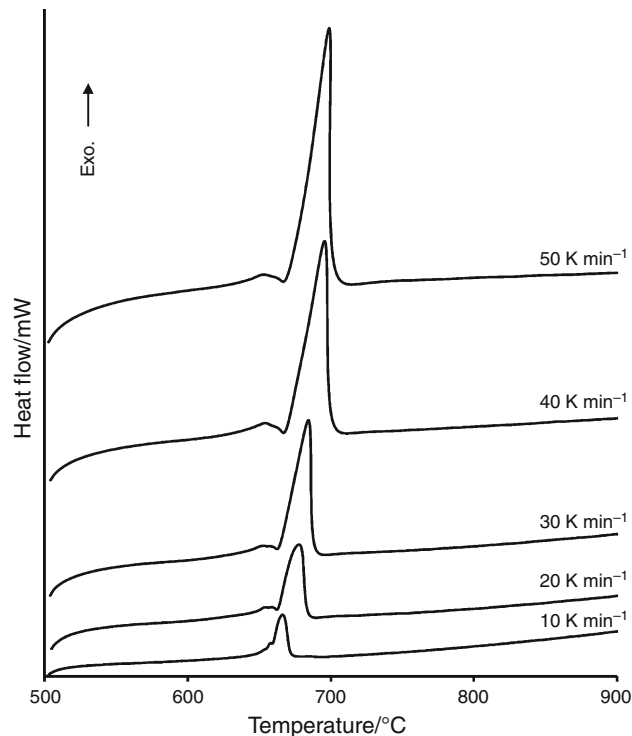


Fig. 7 DSC curves at different heating rates for Ti-50 at.%Al mixture after ball-milling for 7 h

as compared to Fig. 1. The sequence of the reaction seems to be same as before: The melting of aluminum occurs first, making the main exothermic reaction possible. However, by increasing milling time, the endothermic peak tends to diminish specially at low heating rates. By ball-milling of the starting powders for 10 h, the endothermic peak related to the melting of aluminum almost disappears at all heating rates, and apparently the exothermic peak takes its place.

For simplicity of comparison, the DSC curves at heating rate of 50 K min^{-1} for powder mixtures ball-milled at different times are presented in Fig. 9.

As seen in this figure, ball-milling longer than 7 h tends to eliminate the endothermic peak related to the melting of aluminum. As the maximum temperature has shifted to temperatures more close to the melting of aluminum, it could be deduced that either the reaction mechanism has altered from solid–liquid reaction to solid–solid reactions or melting of a small portion of aluminum is adequate for the activated mixture to develop the exothermic reaction. In the latter case, it is possible that the endothermic peak is concealed in the stronger exothermic one. The exothermic peaks also lost their sharpness by increased ball-milling times.

The observed phenomena show that the combustion reactions between Ti and Al could be ignited at lower temperatures even with low-energy ball-milling, which could be beneficial in synthesizing this compounds considering the relatively low exothermicity of the reaction between Ti and Al. High-energy ball-milling could

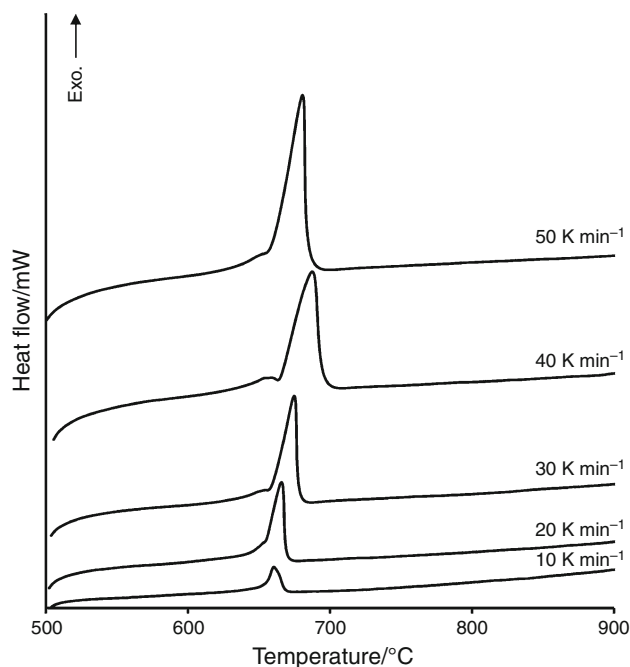


Fig. 8 DSC curves at different heating rates for Ti–50 at.%Al mixture after ball-milling for 10 h

certainly have an even more remarkable effect. Nepapushev et al. [33] showed that in the synthesis of nickel aluminide, high-energy ball-milling leads to a remarkable decrease in reaction onset temperature, as well as a decrease in apparent activation energy. The high density of non-equilibrium defects induced by mechanical processing of the powders, as well as refining, local joining, and clustering of the particles, is supposed to decrease the overall activation energy of the process. Such a

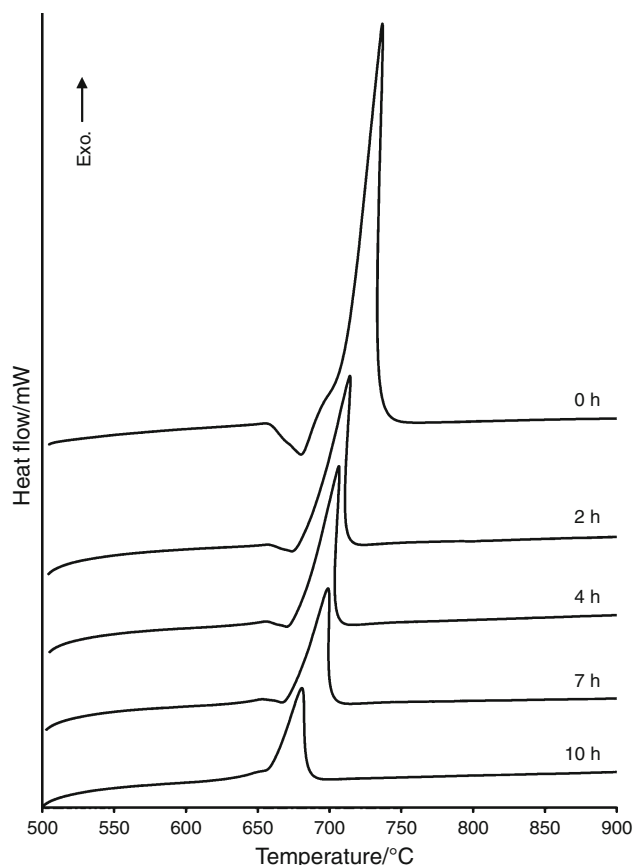


Fig. 9 DSC curves of non-ball-milled powder mixture compared to mixtures ball-milled for different times at heating rate of 50 K min^{-1}

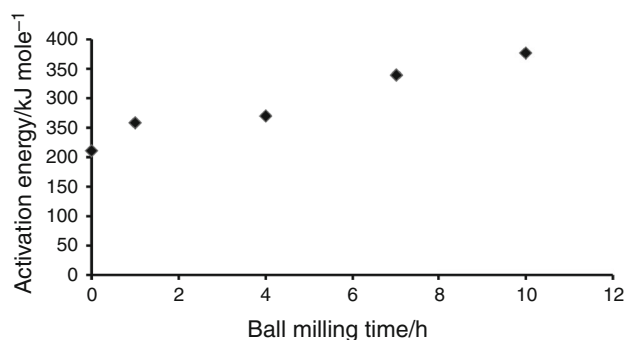
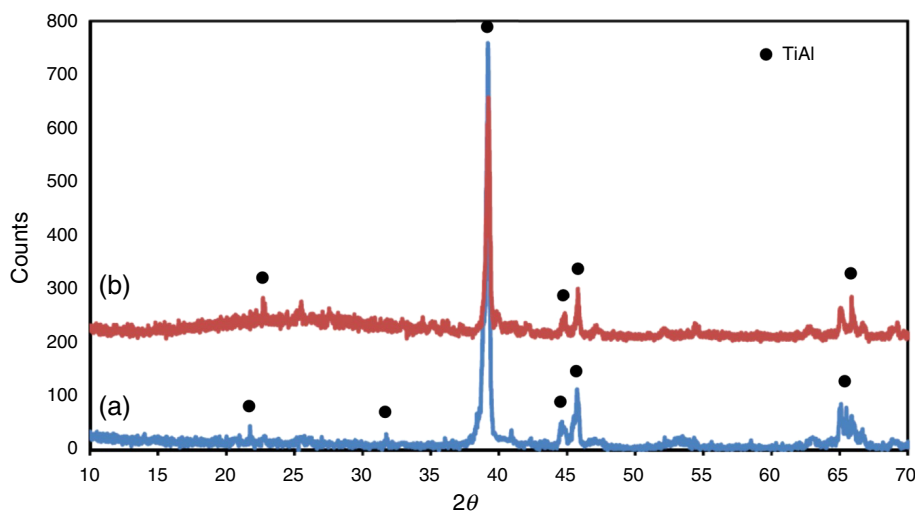


Fig. 10 Values of calculated apparent activation energy versus ball-milling time

Fig. 11 Typical XRD patterns of the reaction products after DSC analysis, *a* unmilled starting powder mixture, *b* powder mixture ball-milled for 7 h (linear heating rate = 50 K min⁻¹)



decrease in activation energy by ball-milling has also been reported in synthesis of non-metallic compounds such as PbTiO₃ [34]. However, in our experiments, the calculated activation energies showed a significant increase in the ball-milled samples. Figure 10 shows the values of activation energy versus time of ball-milling using Kissinger method. The calculated activation energy approached 380 kJ mol⁻¹ after 10 h of ball-milling.

As typically shown in Fig. 11, XRD analysis showed that the main phase detected in products of both ball-milled and non-ball-milled sample was TiAl.

The obtained results show the probability of a change in reaction mechanism due to ball-milling of starting powders. Since no significant melting of aluminum happens in the ball-milled samples, this may be evidence that diffusional, solid-state reactions with much higher activation energies have a more significant role in the process when ball-milled powder mixtures are used. It is also probable that the application of such model-free methods might not be appropriate for the calculation of activation energy in mechanically treated systems, and other methods should be examined.

Conclusions

Non-isothermal DSC was used to investigate the reaction between Ti and Al in Ti–50 at.%Al mixture. Kissinger-type model-free methods were used to calculate the apparent activation energy of the process. The focus of discussion in this paper is the differences between the DSC curves in ball-milled and non-ball-milled condition of powder mixture. The findings can be summarized as follows:

1. DSC analyses showed that the reaction between titanium and aluminum in non-ball-milled powder mixture starts with the melting of aluminum (endothermic reaction), followed by the main exothermic reaction between molten aluminum and solid titanium particles.
2. Performing DSC experiments at different heating rates introduces a shift in peak temperatures which can be related to the apparent activation energy according to Kissinger-type methods. The apparent activation energies for the reaction were calculated to be 210.9, 211.7, and 215.8 kJ mol⁻¹ using Kissinger, Starink, and Ozawa methods, respectively.
3. The calculated activation energies are close to the value reported for the diffusion of aluminum in TiAl phase (220 kJ mol⁻¹), which determines this step as the overall rate-controlling step.
4. Comparison between DSC curves of milled and unmilled samples showed that the endothermic peak of melting of aluminum tends to be eliminated by ball-milling, which means that either the mechanism of reaction switches to solid–solid instead of solid–liquid or melting of a small portion of aluminum is sufficient to begin the intense exothermic reaction. Since the reaction peak temperatures move to lower temperatures, it can be deduced that even a few hours of low-energy ball-milling can help combustion reactions with lower exothermicity.
5. The calculated activation energies in ball-milled condition were unexpectedly higher than the values in non-ball-milled condition, which may prove the significance of solid-state reactions. It is also probable that applying such methods for the evaluation of the activation energy in mechanically treated powder mixtures may not be appropriate.

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