DSC RESEARCH ON CRITICAL TEMPERATURE IN THERMAL EXPLOSION SYNTHESIS REACTION Ti+3Al→TiAl₃

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Abstract

The critical furnace chamber temperature (T'_{ign}) of the thermal explosion synthesis reaction Ti+3Al→TiAl₃ is studied by isothermal and non-isothermal DSC. The reaction product is characterized by using the X-ray powder diffraction. The value of T'_{ign} is between 740 and 745°C obtained from the isothermal DSC observations, and 729°C obtained from non-isothermal DSC curves. It shows that these two values have a good consistency. With the help of the apparent activation energy of the reaction obtained by Friedman method and the value of $T'_{ign\,0}$ by the multiple linear regression of the T'_{ign}s at different heating rates (β), the critical temperature (T_b) of thermal explosion for Ti–75at%Al mixture is estimated to be 785°C.

Introduction

Combustion synthesis provides energy- and cost-saving advantages over the conventional processing routes for the production of refractory ceramic and intermetallic compounds [1]. Formally, it can be sub-divided into 'self-propagating high-temperature synthesis (SHS)' and 'thermal explosion (TE)' modes [2]. TE mode has been found to be more suitable to produce less exothermic intermetallic systems such as Ti–Al, Ni–Al and Ti–Ni [3–5].

Applications of TE synthesis are numerous [3–5], but its ignition phenomena have rarely been reported, though the ignition temperature is an important parameter for TE synthesis. Bowen and Derby [6] once attempted to estimate the ignition temperature for the (3TiO₂+4Al+3C) mixture simply by locating the onset of deviation from the baseline on a non-isothermal differential thermal analysis (DTA) curve. Unfortunately, their method is irrational for lack of the necessary support of combustion theories. This suggests that a reliable thermal analysis methodology on the ignition temperature of TE synthesis is still needed.

In combustion literature [7–9], two critical temperatures are frequently mentioned: critical temperature (T'_{ign}) of TE furnace chamber and corresponding critical temperature of thermal explosion (T_b) or ignition temperature (T'_{ign}) of reacting mixture. There is a little discrepancy between the values of T'_{ign} and T_{ign} (or T_b). For a TE system with the activation energy of 168 kJ mol^{-1} at T'_{ign} of 1000 K, T_{ign} is 50 K higher than T'_{ign} [7]. T'_{ign} is more helpful for the practical operation of TE synthesis.

In the light of the phenomenological description of TE [7, 9], there is always some critical temperature (T'_{ign}) of the furnace chamber during the process of TE, at which the rate of heat generation equals the loss rate and the temperature is T_{ing} in reacting mixture. After such a critical point, the excess heat increases the mixture temperature, which, in turn, leads to a higher reaction rate. The mixture temperature rises continuously and acceleratively until a high heat evolution rate is attained. Ignition of TE is then said to have occurred. In reality, as soon as the TE starts, the accelerative rise of temperature is quite abrupt, the previously invisible slow subcritical reaction suddenly becomes visible and measurable supercritical TE [7].

As stated above, an isothermal approach can be utilized to evaluate T'_{ign} of TE synthesis for intermetallic systems using DTA or DSC. The reacting mixtures are hold at different predetermined temperatures in DTA or DSC apparatus to observe whether the reactions are characterized as TE mode according to the shape of the exothermic peak. Obviously, if the peaks of those isothermal thermal analysis curves for TE reacting mixture are sharp and abrupt, greatly different from the characteristic flat shape of subcritical conditions, those holding temperatures are certainly higher than T'_{ign}. So T'_{ign} can be considered as the holding temperature, at which reaction changes into supercritical TE mode form subcritical slow non-TE mode.

On the other hand, according to the analysis of the plot of Semenov's thermal balance [7], the value of the second derivative of temperature (d^2T/dt^2) of reacting mixture is equal to zero at the ignition point of TE. Once the temperature of furnace chamber exceeds T'_{ign}, the reaction will proceed in TE mode. Adopting this conclusion to the research on the compatibility of explosives using non-isothermal thermal analysis method, Hu *et al.* [10] have evaluated the T'_{ign} of TE for explosives by locating the onset of $d^3H/dt^3=0$ in a single linearly heating differential scanning calorimetry (DSC) curve or $d^2(\Delta T)/dt^2=0$ in the DTA curve. Such a non-isothermal approach is simpler than the isothermal one in experimental respect, because only a single non-isothermal thermoanalytical curve is needed for the evaluation of T'_{ign}.

For Ti+3Al→TiAl$_3$, one of the typical binary TE synthesis reactions, both applied [3] and kinetic investigations [11, 12] were carried out over the past years. In this paper, the Ti–75at%Al system was chosen to be studied for estimating T'_{ign} of Ti+3Al→TiAl$_3$ reaction by both isothermal and non-isothermal DSC methods.

Experimental

Titanium (99% purity, 39 μm) and aluminum (99% purity, 260 μm) powders of 1:3 atomic ratio were thoroughly mixed in a glass bottle fixed in a roller for 24 h. The mixture of about 25 mg was pressed into a cylindrical tablet with diameter of 5 mm

and height of about 0.6 mm under a pressure of 500 MPa. A heat flux type DSC apparatus, NETZSCH-STA409C, was used in this work. Its operation temperature is up to 1500°C with a maximum heating rate of 40°C min^{-1}. All samples were heated in argon atmosphere. α-Al$_2$O$_3$ was used as reference sample. The heating-up stages of non-isothermal and isothermal DSC were operated at a heating rate of 40°C min^{-1}. The non-isothermal samples were heated up to 1200°C. The isothermal DSC experiments were performed at predetermined holding temperatures from 690 to 760°C until the completion of an obvious exothermic peak, or for 5 h if no exothermic peak occurred in DSC curves. After DSC experiments, each product was analyzed by the X-ray diffraction (XRD) to identify the phases and assess the completeness of conversion.

Results and discussion

Figure 1 shows the curves at 690 and 740°C are quite flat without the characteristic exothermic peaks of the TE mode of the solid state reaction Ti+3Al→TiAl$_3$, whereas the curves at 745, 750 and 760°C present the sharp and abrupt exothermic peaks of synthesizing TiAl$_3$ compound. According to the above-mentioned phenomenological description of the difference between subcritical and supercritical conditions of TE process, the reaction of Ti–75at%Al mixture hold at 690 and 740°C is in the slow and immeasurable subcritical non-TE mode, and those at the holding temperatures higher than 745°C are conducted in the violent supercritical TE mode. So, T'_{ign} of Ti–75at%Al TE synthesis is evaluated between 740 and 745°C. It has been reported that the best temperature range for the kinetic analysis of isothermal DSC of Ti–75at%Al system is 690~740°C, beyond which isothermal experiments cannot be carried out isothermally owing to the rapid rate of heat generation [10].
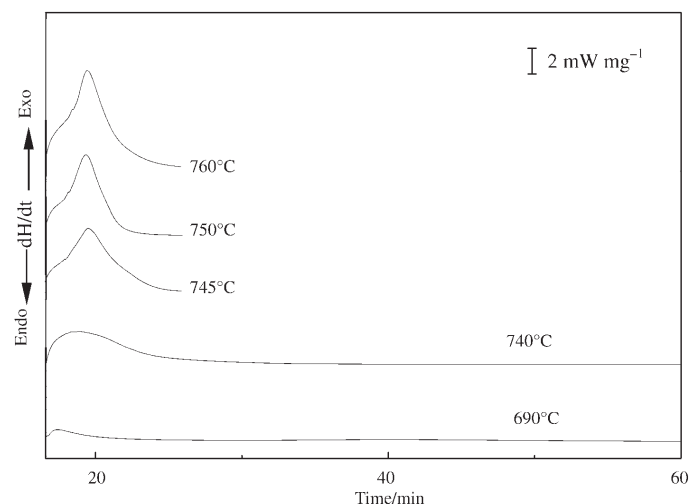

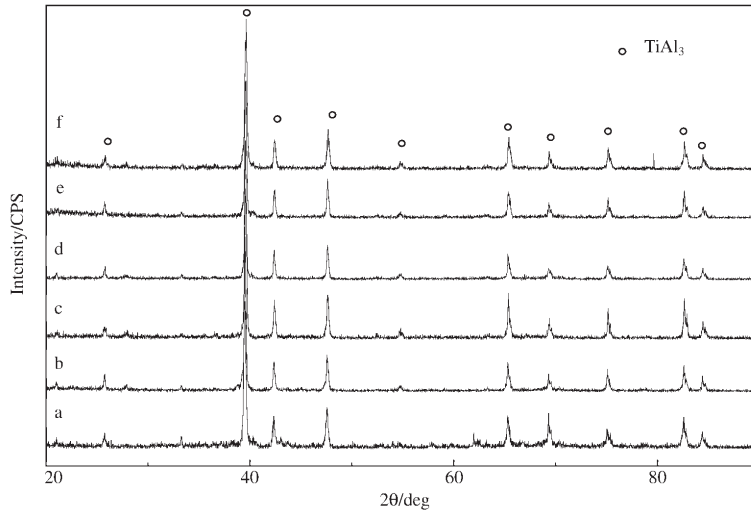**Fig. 1** The isothermal DSC curves at 690, 740, 745, 750 and 760°C of Ti–75at%Al TE system

Fig. 2 X-ray diffraction patterns of products of Ti–75at%Al pellets using (a)
non-isothermal DSC at a heating rate of 40°C min^{-1} and isothermal DSC at (b)
690, (c)740, (d) 745, (e) 750 and (f) 760°C

XRD patterns for samples after the isothermal DSC experiments at 690, 740, 745, 750, 760°C are illustrated in Fig. 2. The results of XRD identification indicate that all samples turned into mono-phase of TiAl$_3$ compound. Namely, the solid state reaction Ti+3Al→TiAl$_3$, undergone in either subcritical non-TE or supercritical TE mode transited completely.

Figure 3 represents the non-isothermal DSC curve of Ti–75at%Al system at a heating rate of 40°C min^{-1}. There is an endothermic peak at 655°C which is due to

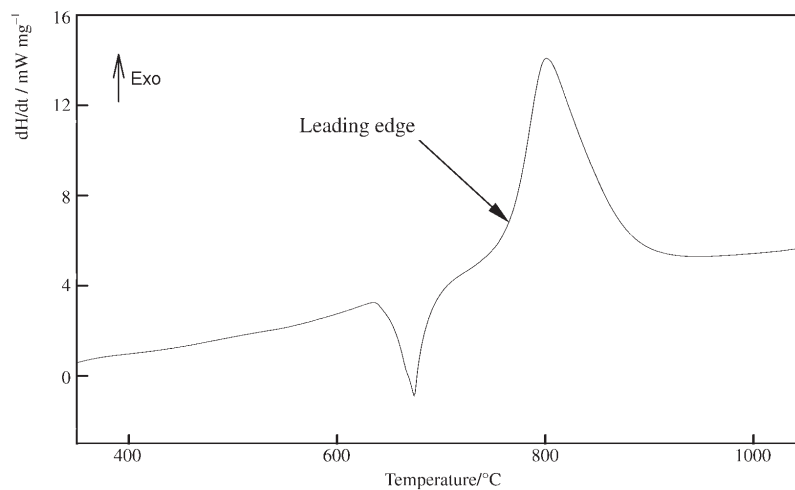**Fig. 3** The non-isothermal DSC curve of Ti–75at%Al TE system at a heating rate of 40°C min^{-1}

melting of aluminum phase. On heating to higher temperatures a strong exothermic peak is observed at 800°C corresponding to the TE reaction of Ti+3Al→TiAl$_3$. The reaction product of this non-isothermal DSC experiment was measured by XRD and identified as mono-phase TiAl$_3$ compound.

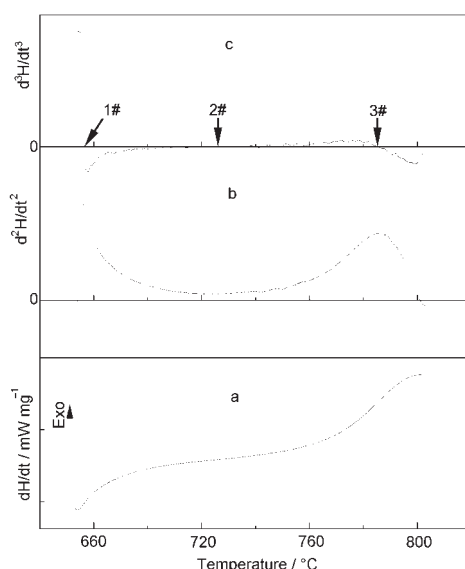**Fig. 4** Curves of (a) the leading edge of the exothermic peak of the DSC at a heating rate of 40°C min^{-1} for Ti–75at%Al system and (b) its first, (c) second order derivatives

The range of the leading edge of the non-isothermal DSC curve at 40°C min^{-1} is indicated in Fig. 3. The leading edge and its first and second order derivatives are shown in Fig. 4. The points 1#, 2# and 3# corresponding to d^{3}H/dt^3=0 in Fig. 4 are the maximum acceleration of the melting of Al, the adjoining point between the melting of Al and the reaction of Ti+3Al→TiAl$_3$, as well as the ignition of Ti+3Al→TiAl$_3$, respectively. The temperature (T'_{ign}) corresponding to point 3# at different linearly heating rates (β) is listed in Table 1.

Table 1 The value of T'_{ign} at different heating rates

β/°C min^{-1}	T'_{ign}/°C
40	785
20	757
15	749
10	737

β – heating rate; T'_{ign} – temperature corresponding to d^{3}H/dt^3=0

By substituting the experimental data (β_i, $T'_{\mathrm{ign}\,i}$, i=1, 2, 3, 4) listed in Table 1 into expression (1),

$$T'_{\mathrm{ign}} = a + b\beta + c\beta^2 + d\beta^3 \tag{1}$$

where a, b, c and d are parameters of MLR, normal Eqs (2)–(5), are obtained

$$a+10b+100c+1000d=737 \tag{2}$$

$$a+15b+225c+3375d=749 \tag{3}$$

$$a+20b+400c+8000d=757 \tag{4}$$

$$a+40b+1600c+64000d=785 \tag{5}$$

From Eqs (2)–(5), we obtain

$$T'_{\mathrm{ign}} = 728.9 + 4.8 \cdot 10^{-8}\beta + 0.1054\beta^2 - 0.00176\beta^3 \tag{6}$$

Substituting $\beta=0°C$ min^{-1} into Eq. (6), the value of $T'_{\mathrm{ign}\,0}$ of 729°C of Ti–75at%Al system under isothermal condition is obtained. This temperature approaches the result of isothermal observation.

Zhang *et al.* [13] have derived a method for estimating critical temperature (T_b) of thermal explosion for energetic materials from Semenov's thermal explosion theory and non-isothermal kinetic equation $d\alpha/dt = Af(\alpha)e^{-E/RT}$ using reasonable hypothesis. The final formula can be expressed as Eq. (7)

$$T_b = \frac{E - \sqrt{E^2 - 4ERT'_{\mathrm{ign}\,0}}}{2R} \tag{7}$$

where E is the apparent activation energy of exothermic reaction in J mol^{-1}.

In order to obtain E used to calculate the critical temperature (T_b) of thermal explosion for Ti–75at%Al mixture, Friedman's method [14] is employed because it is applicable to thermoanalytical data in which the programmed temperature conditions have been distorted by self-heating effects [15]. The calculated value of E is determined to be 165 kJ mol^{-1} for low extent of reaction [12]. By substituting the values of E and $T'_{\mathrm{ign}\,0}$ into Eq. (7), the value of T_b of 785°C is obtained.

Conclusions

• The value of T'_{ign} of Ti–75at%Al TE synthesis system is between 740 and 745°C by the observation of isothermal DSC, and 729°C obtained from non-isothermal DSC curves at various heating rates.
• Two methods have a good consistency in the evaluation of the critical temperature (T'_{ign}) of TE synthesis for binary intermetallic systems like Ti–75at%Al.
• The critical temperature of thermal explosion of Ti–75at%Al mixture is 785°C.

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