ACTIVATION ENERGY OF SELF-HEATING PROCESS STUDIED BY DSC
Combustion synthesis mixture of Ti–75 at% Al

T. Wang[*]*, R. Y. Liu, M. L. Zhu and J. S. Zhang*

Department of Materials Engineering, Dalian University of Technology, Dalian 116024, People's Republic of China

Abstract

In order to identify the kinetic process of self-heating in DSC experiment for Ti+3Al→TiAl$_3$ reaction, two approaches, linear-fitting approach developed from Semenov's theory of spontaneous ignition and variation of Friedman method, were carried out with cylindrical Ti–75 at% Al samples. Following these approaches, two identical activation energies are obtained as 169±15 kJ mol^{-1} and 170±5 kJ mol^{-1}, respectively. Compared with the activation energies of reactions and interdiffusions between Ti and Al, the possible rate-controlling process of self-heating in DSC experiment for Ti+3Al→TiAl$_3$ reaction is the interdiffusion between Ti and Al through TiAl$_3$-layer.

Keywords: activation energy, DSC, self-heating, Semenov's theory of spontaneous ignition

Introduction

Combustion synthesis (CS), first introduced by Merzhanov and Borovinskaya, provides energy- and cost-saving advantages over the conventional processing routes for 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]. Generally CS reactions are characterized by high reaction temperatures up to 4000 K, short reaction durations, a few seconds for TE and combustion wave velocity of up to 250 mm s^{-1} for SHS and in the case of SHS extremely large thermal gradients, ~10^5–10^6 K m^{-1} [3]. These two reaction modes can be represented schematically by the SHS diagram shown in Fig. 1 [4].

Over the past 30 years, applications of CS to producing a variety of materials are numerous [1, 5], while its reaction kinetics has rarely been reported because of the complex nature of combustion reaction: non-equilibrium conditions, higher-temperature and extremely large temperature gradients. Recently, in order to gain an insight

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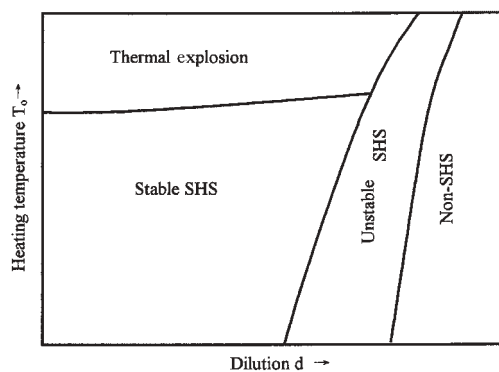*   Author for correspondence: E-mail: wangmang_tao@hotmail.com

Fig. 1 SHS graph

into the reaction kinetics and mechanism of CS, various analytical methods were applied, including time-resolved X-ray diffraction [6], quantitative X-ray diffraction [7], electrical thermal explosion [8], high-temperature thermoanalytical (TA) methods (such as DSC [9, 10], DTA [11] and so on), combustion wave velocity [12, 13] and temperature profile investigations [14, 15]. Among these methods, TA is more reliable and preferable over others for their advantages on experimental condition adjustment, continuous measurement and standardized data processing methods.

In some conventional TA methods, the heating rate of the sample or reference materials is controlled to be constant by programming. Thus, some kinetic analyses of TA curves has been carried out by assuming a constant heating rate of variation of the sample temperature in order to simplify the numerical processing [16]. Due to the inherent exothermic nature, the self-heating phenomena are frequently observed in DSC (or DTA) experiments of CS samples [9]. Therefore, the assumption of a constant heating rate for CS samples is not justified, which might be one of the most serious problems in thermoanalytical investigations of CS reaction. To deal with such a problem, further study on self-heating kinetics is necessary. For $Ti+3Al \rightarrow TiAl_3$, one of the typical intermetallic CS reactions, both applied [5, 17] and kinetic investigations [9, 10], were carried out over the past years. In the present paper, Ti–75 at% Al sample was investigated for the self-heating of $Ti+3Al \rightarrow TiAl_3$ during DSC by both a linear fitting method developed from Semenov' theory of spontaneous ignition and a variant of Friedman method. And these two approaches are introduced as possible methods for evaluation of the activation energy of self-heating process.

Experimental

Titanium (99% purity, 39 μm) and aluminum (99% purity, 100 μm) powders of 1:3 atomic ratio were thoroughly mixed in a glass bottle fixed in a roller for 24 h. The mixtures of various masses were pressed into 16 cylindrical samples with diameter of 5 mm and the four different heights under the pressure of 500 MPa for the analysis using linear fitting method. Among them, there were 4 samples for each approximate height, 0.8, 1.26, 1.68 or 2.6 mm. And the samples for Friedman method were 5 mm

in diameter and 0.6 in height prepared after the same procedures as those samples for linear fitting method. A heat flux type DSC apparatus, NETZSCH-STA409C, was used in this work. Its operation temperature is up to 1773 K with a maximum heating rate of 40 K min^{-1}. All samples were heated in argon atmosphere. α-Al$_2$O$_3$ was used as reference sample. Each 4 sample with different approximate height of 0.8, 1.26, 1.68 and 2.6 mm was labeled as a group of samples. The samples in the same groups were heated up to 1273 K at a fixed linear heating rate, 10, 20, 30, or 40 K min^{-1}, representing a specific heating condition, respectively. The non-isothermal DSC experiments for Friedman method were performed at the heating rates of 8, 10 and 15 K min^{-1} with the same atmosphere protection and reference samples as those for linear fitting approach. The Arrhenius parameters have been estimated by Friedman method with the NETZSCH Thermokinetics software. After DSC experiments, each product was also analyzed by X-ray diffraction (XRD) to identify the phases and assess the completeness of conversion.

Results and discussion

Evaluation of self-heating activation energy using Semenov theory of spontaneous ignition

Semenov theory of spontaneous ignition

The self-heating process is a mini-type of auto-ignition in a TA experiment. During a TA experiment of an exothermic sample, if the overplus between heat generation and heat loss is beyond the amount for heating sample to the programmed sample temperature, the sample will be self-heated, namely the self-heating process is ignited.

According to Semenov's theory of spontaneous ignition, consider a combustible sample [18] of volume V, surface S, heat capacity C and density ρ. The overall energy conservation is given by Eq. (1).

$$\rho CV \frac{\mathrm{d}T}{\mathrm{d}t} = \dot{q}_g - \dot{q}_1 \tag{1}$$

where T, $\dot{q}_g$ and $\dot{q}_1$ are the sample temperature, the heat generation rate and heat loss rate, respectively. The $\dot{q}_g$ and $\dot{q}_1$ can be obtained as

$$\dot{q}_g = VQAc^n \exp\left(-\frac{E}{RT}\right) \tag{2}$$

$$\dot{q}_1 = \lambda S(T - T_0) \tag{3}$$

where Q stands for the liberated heat of the TE synthesis, A for the pre-exponential factor, c for the reactant concentration, n for the overall reaction order, E for apparent activation energy, R for gas constant, λ for the heat transfer coefficient associated with heat transfer from the sample to the furnace chamber and T_0 for the temperature of furnace chamber.

The sufficient and necessary condition for the ignition of TE is $\dot{q}_g$ curve tangential with $\dot{q}_1$ line, which also might be expressed as

$$(\dot{q}_g)_c = (\dot{q}_1)_c \qquad (4)$$

$$\left(\frac{d\dot{q}_g}{dT}\right)_c = \left(\frac{d\dot{q}_1}{dT}\right)_c \qquad (5)$$

Combining Eqs (1), (4) and (5), we obtain

$$\left(\frac{dT}{dt}\right)_c = 0 \qquad (6)$$

$$\left(\frac{d^2T}{dt^2}\right)_c = 0 \qquad (7)$$

Adopting this conclusion to the research on the compatibility of explosives using non-isothermal thermal analysis method, Hu *et al.* [19, 20] have successfully evaluated the critical temperature of environment ($T_{0\,cr}$) in TE for explosives by locating the onset of $d^3H/dt^3 = 0$ in a single linearly heating DSC curve or $d^2(\Delta T)/dt^2 = 0$ in the DTA curve.

Substituting Eqs (2) and (3) into (4) and (5) and processing by exponential approximation, one obtains [21, 22]

$$\varphi_{cr} = \left[\frac{QV\rho EA}{\lambda SRT_0^2}\exp\left(-\frac{E}{RT_0}\right)\right]_c = constant \qquad (8)$$

Namely, the critical condition for a Semenov TE system can be expressed as that the non-dimensional Semenov number φ is a constant [20, 22].

Logarithmically,

$$2\ln T_{0\,cr} - \ln\left(\frac{V}{S}\right) = \ln\frac{Q\rho EA}{\phi_{cr}\lambda R} - \frac{E}{RT_{0\,cr}} \qquad (9)$$

For a cylindrical sample, $V = \pi r^2 h$, $S = 2\pi r^2 + 2\pi rh$, where r and h represent the radius and height of cylinder, Eq. (9) can be rewritten into

$$2\ln T_{0\,cr} + \ln\left(\frac{1}{r} + \frac{1}{h}\right) = \ln\frac{Q\rho EA}{\phi_{cr}\lambda R} - \frac{E}{RT_{0\,cr}} \qquad (10)$$

or

$$2\ln T_{0\,cr} + \ln\left(\frac{1}{r} + \frac{1}{h}\right) = B - \frac{E}{RT_{0\,cr}} \qquad (11)$$

where B is a constant related to reaction conditions. Plotting $2\ln T_{0\,cr} + \ln(1/r + 1/h)$ on the y-axis and $-1/RT_{0\,cr}$ on x-axis, Eq. (11) gives a straight line with a slope of E. Such

a plot provides a feasible approach to the estimation the E for self-heating process during TA experiment.

Application of Semenov theory of spontaneous ignition in self-heating activation energy evaluation

The geometric sizes and corresponding heating conditions are listed in Table 1. Figure 2a, b, c and d illustrate the DSC curves of various samples heated at 10, 20, 30 and 40 K min^{-1}, respectively. On each DSC curve, there is an endothermic peak at about 928 K, which is due to melting of aluminum phase. On heating to higher temperatures, a strong exothermic peak is observed at about 1073 K representing the TE reaction of Ti+3Al→TiAl$_3$. Figure 3 shows the reaction product of this non-isothermal DSC experiment was measured by XRD and identified as mono-phase TiAl$_3$ compound.
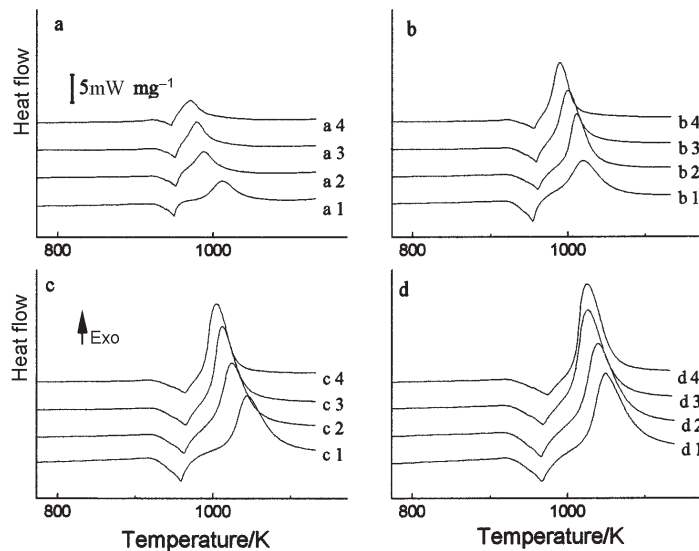

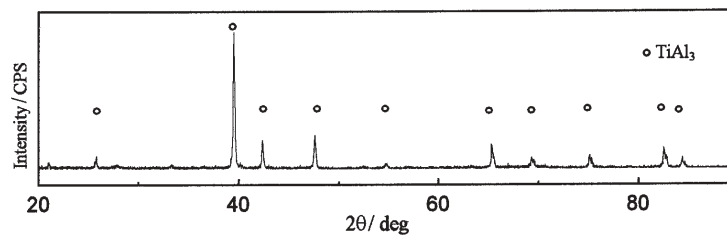**Fig. 2** DSC curves for Ti–75 at% Al samples in different sizes

Fig. 3 X-ray diffraction patterns of product of Ti–75 at% Al sample using non-isothermal DSC

$T_{0\,cr}$ was evaluated by locating the onset of $d^3H/dt^3=0$ on DSC curve, as presented in Fig. 4. $T_{0\,cr}$s of samples of different geometric and experimental condition were shown in Table 1. Figure 5, the dependence of $T_{0\,cr}$ on sample size, indicates that $T_{0\,cr}$

Table 1 Experimental parameters and results of cylindrical Ti–75 at% Al samples at different sizes

Groups	Sample No.	Heating rates/ K min^{-1}	Geometric sizes/ mm	$T_{0\,cr}$S/ K	Number of DSC curves in Fig. 2
N1	N1-1	10	φ5×0.80	1000	a 1
	N1-2	10	φ5×1.27	979	a 2
	N1-3	10	φ5×1.66	970	a 3
	N1-4	10	φ5×2.44	963	a 4
N2	N2-1	20	φ5×0.80	1017	b 1
	N2-2	20	φ5×1.26	1004	b 2
	N2-3	20	φ5×1.68	991.5	b 3
	N2-4	20	φ5×2.46	981	b 4
N3	N3-1	30	φ5×0.94	1033	c 1
	N3-2	30	φ5×1.28	1015	c 2
	N3-3	30	φ5×1.68	1004	c 3
	N3-4	30	φ5×2.50	994	c 4
N4	N4-1	40	φ5×0.80	1036	d 1
	N4-2	40	φ5×1.25	1027	d 2
	N4-3	40	φ5×1.65	1015	d 3
	N4-4	40	φ5×2.60	994	d 4

decreases with the increasing sample height at the same heating condition. Figure 6 is the $2\ln T_{0\,cr}+\ln(1/r+1/h) \sim -1/RT_{0\,cr}$ plot for the TE synthesis of Ti+3Al→TiAl$_3$ under present experimental condition. The average linear fitted slope is 169±15 kJ mol^{-1}, which closes to with the activation energy of the interdiffusion between Ti and Al through TiAl$_3$ layer, listed in Table 2.

Table 2 Activation energies for the reactions and interdiffusions in Ti–Al system

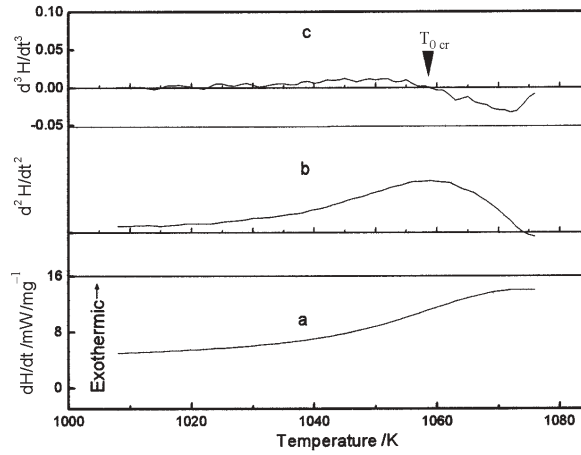| Reactions or interdiffusion couples	Diffusion-barrier layer	E_a/kJ mol^{-1}	Ref.
Ti(s)+3Al(l)→TiAl$_3$	–	97	[26]
Ti–Al	TiAl$_3$	180	[27]
TiAl–Al	TiAl$_3$	95	[27]
Ti–TiAl	Ti$_3$Al	273	[28]
Ti$_3$Al–TiAl$_2$	TiAl	235	[28]
TiAl–TiAl$_3$	TiAl$_2$	240	[28]
Ti–TiAl$_3$	Ti$_3$Al+TiAl+TiAl$_2$	206	[28]

Fig. 4 Typical curves of (a) the leading edge of the exothermic peak of the DSC at a linear heating rate for Ti–75 at% Al system and (b) its first, (c) second order derivatives
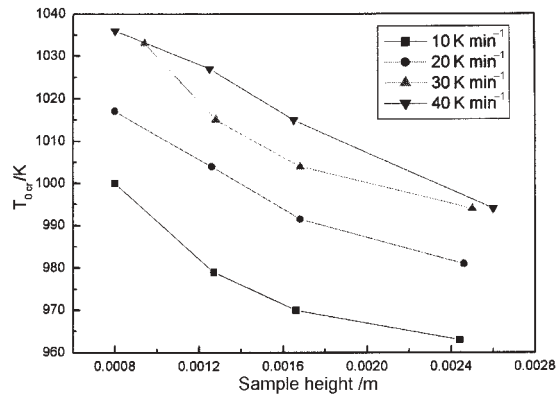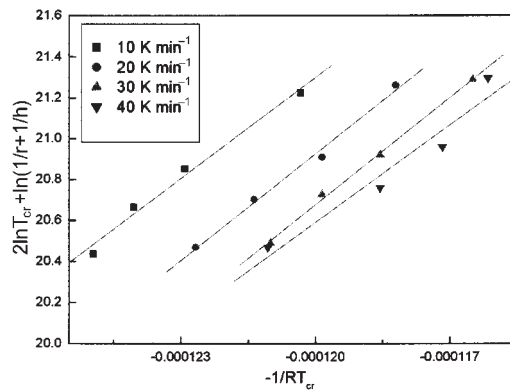

Fig. 5 The dependence of $T_{0\,cr}$ on sample size

Fig. 6 $2\ln T_{0\,cr}+\ln(1/r+1/h)$ ● − $-1/RT_{0\,cr}$ plot of Ti–75 at% Al samples in different geometric sizes

Friedman method for evaluation of self-heating activation energy

Methodological consideration

For the thermokinetic analysis of solid-state reactions, the following formula has widely been applied [16]

$$\frac{d\alpha}{dt} = K(T)f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (12)$$

where α, A, E, R, T and $f(\alpha)$ are the extent of conversion, apparent pre-exponential factor, apparent activation energy, gas constant, temperature and kinetic model function, respectively.

Taking logarithms of Eq. (12), we obtain

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln[Af(\alpha)] \qquad (13)$$

Thus E can be estimated from the slope of the plot of $\ln(d\alpha/dt)$ *vs*. $1/T$ at a given α under different heating rates. This method for calculation of E was originally proposed by Friedman [26]. Friedman method belongs to model-free approaches that allow to evaluate Arrhenius parameters without knowing the reaction model. The best known model-free approaches are the isoconversional methods (Friedman [26] and Ozawa–Flynn–Wall methods [27, 28]). These methods yield E as a function α. Knowledge of the dependence of E on α assists in both detecting multiple processes and drawing certain mechanistic conclusions [29, 30]. Furthermore, the isoconversional methods yield similar dependences of E on α for both isothermal and non-isothermal experiments [30–32]. In the light of the results of the ICTA Kinetic Project: computational aspects of kinetic analysis [33–37], various isoconversional methods applied to the same set of non-isothermal data have produced consistent dependences of E on α by different participators.

For the convenience of processing TA data, kinetic analysis of conventional TA data has been carried out by assuming constant rate of variation of the sample temperature [16]. In a CS reaction, however, such an assumption is practically not justified owing to the effect of self-heating during reaction [38]. Recently, one of the most important findings of the extended interpretation of the Friedman method is that the Friedman method is applicable to TA data in which the programmed temperature conditions have been distorted by self-heating and/or self-cooling effects because Eq. (2) is not limited by an assumption of constant heating rate [38].

Evaluation of activation energy of self-heating process by Friedman method

Figure 7 shows the non-isothermal DSC curves of the CS reaction of Ti+3Al→TiAl$_3$ in the Ti–75 at% Al powder mixture at the heating rates of 8, 10, 15 K min^{-1}. There is an endothermic peak at 928 K, corresponds to the melting of aluminum, in each curve. On heating to higher temperature, a strong exothermic peak is observed, which

represents the formation of $TiAl_3$. The results of XRD identification indicate that all samples transformed into mono-phase of $TiAl_3$ during experiments.
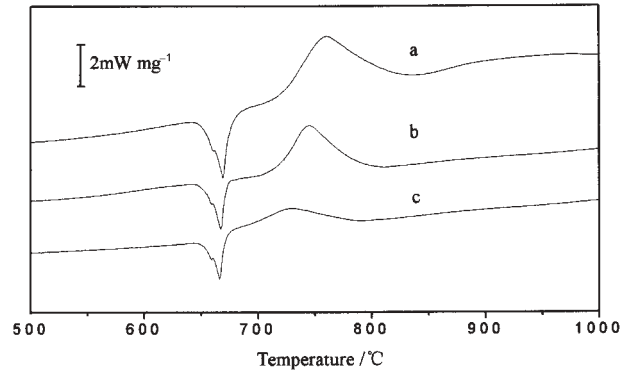

Fig. 7 DSC curves of TE reaction of $Ti+3Al \rightarrow TiAl_3$ at the heating rate of a – 8, b – 10, c – 15 K min^{-1}

In order to explore the inherent complexity of CS synthesis reaction without the uncertainty caused by self-heating effect, Friedman method has been applied to the DSC data of $Ti+3Al \rightarrow TiAl_3$ at the heating rate of 8, 10, 15 K min^{-1}, as shown in Fig. 8. The conversion dependence of E on α for $Ti+3Al \rightarrow TiAl_3$ is displayed in Fig. 9, where lg$A$ is estimated assuming a first order reaction. Obviously, there are three different stages in the dependence curve in Fig. 9: ascending, flat and descending stages. According to these characteristics, we identified that there are at least three processes in the duration of reaction. The possible processes are illustrated in Fig. 10. The obtained dependence begins at the approximate E of 109 kJ mol^{-1} for the process #1. The ascending stage of the dependence indicates that process #2 with higher E of 175 kJ mol^{-1} makes a growing contribution to the heat release detected by
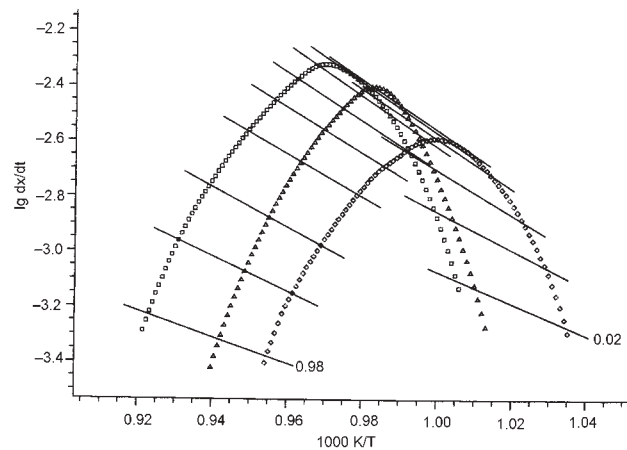

Fig. 8 Friedman plot for the DSC data of the reaction of $Ti+3Al \rightarrow TiAl_3$ at the heating rate of 8, 10 and 15 K min^{-1}

DSC apparatus. As the dependence reached the maximum, its shape becomes flat from α=0.2 to 0.5 because overall heat release is merely governed by the process #2 in this stage. Having finished this flat stage, the descending stage occurs because of the relatively increasing contribution of the process #3 with the E of 89 kJ mol^{-1}, which is estimated from the minimum value of E at the end of the reaction. It should be emphasized that the value of 109 and 89 kJ mol^{-1} among above-mentioned three E are both approximations, because there are no flat trend indicative of an exclusively-controlled process [39].
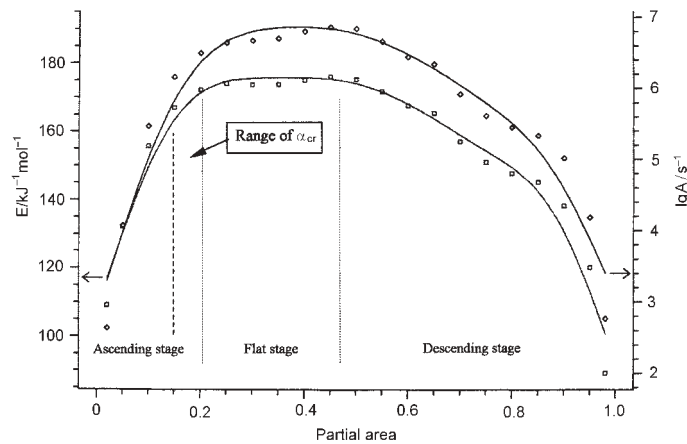

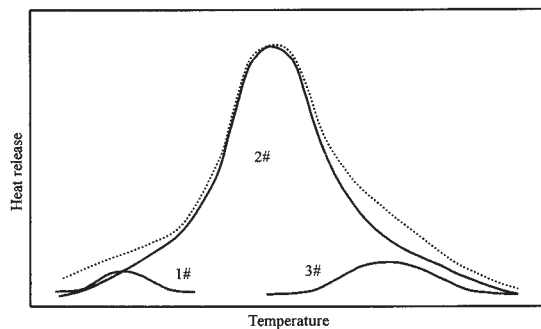**Fig. 9** Dependence of E_a and lg$A$ on α for the formation of TiAl$_3$ through TE synthesis

Fig. 10 A scheme of possible kinetic processes in the reaction of Ti+3Al→TiAl$_3$, the dotted line presenting the overall heat release

The collection of the activation energies for the reactions and interdiffusions in Ti–Al system are listed in Table 2. Compared with the values in Table 2, we find that the calculated E of 109, 175 and 89 kJ mol^{-1}, corresponding to process #1, #2 and #3, agree well with the values of activation energies for direct chemical reaction between Ti(s) and Al(l), interdiffusions between Ti and Al through TiAl$_3$-layer, as well as

interdiffusion between TiAl and Al through TiAl$_3$-layer, respectively. So we propose the following mechanism of the CS synthesis reaction of Ti+3Al→TiAl$_3$. During reaction, TiAl$_3$ is at first formed at the interface between Ti(s) and Al(l) by chemical reaction, which is identified as process #1. With the thickening of TiAl$_3$-layer, process #2, controlled by the interdiffusion between Ti and Al through TiAl$_3$-layer, is taking a more important role in the formation of TiAl$_3$. In the range of α from 0.2 to 0.5, it is the only process for the formation of TiAl$_3$. Further diffusion leads to occurrences of TiAl and other intermetallic compounds displayed in Ti–Al binary phase diagram. When α is beyond 0.5, the process #3, rate-controlled by the interdiffusion between TiAl and Al through TiAl$_3$-layer is activated and lasts to the end of the reaction. The similar reaction mechanism has been reported by Wang and Dahms in the investigations for the reactive sintering in Ti–Al powder mixture [40].

The α_{cr} representing α of the ignition of self-heating process was determined as that at $d^3H/dt^3=0$ in DSC curves, similar to the method illustrated in Fig. 4. Following such an approach, the average α_{cr} of DSC experiments at the heating rate ranging from 8 to 15 K min^{-1} is estimated about 0.15–0.2. Therefore, E of the self-heating process in the DSC experiments of Ti–75 at% Al samples can be evaluated about 170±5 kJ mol^{-1} according to E~α plot (Fig. 9).

Such a value agrees well with that obtained by both the linear fitting method developed from Semenov's theory of spontaneous ignition. Under present experimental conditions, the self-heating process occurred at the end of ascending stage in E~α plot (Fig. 9). The ascending stage of the dependence of E on α indicates that the process #2 rate-controlled by interdiffusion between Ti and Al through TiAl$_3$-layer with E of 175 kJ mol^{-1} makes an increasing contribution to the heat release, which might be responsible for self-heating. This result illustrates that such an interdiffusion might be the rate-controlling step of the self-heating process in DSC experiment of Ti–75 at% Al samples.

Conclusions

The activation energy of self-heating process during the non-isothermal DSC experiments of Ti–75 at% Al cylindrical samples in various sizes is evaluated 169 ±15 kJ mol^{-1} by linear fitting the $2\ln T_{0\,cr}+\ln(1/r+1/h)$ $vs.$ $-1/RT_{0\,cr}$ plot.

By estimating the corresponding E at α_{cr} on E~α curve plotted by Friedman method, the E of self-heating process in the non-isothermal DSC experiments of Ti–75 at% Al samples can be obtained about 170±5 kJ mol^{-1}.

The consistent kinetic results for the self-heating process in DSC can be obtained by above two approaches.

The possible rate-controlling step of the self-heating process is interpreted as the interdiffusion between Ti and Al through TiAl$_3$-layer with the value comparison between the calculated activation energies and experimental results collected from literature.

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References

1 A. G. Merzhanov, Chemistry of advanced materials, Ed. by C. N. R. Rao, Blackwell Scientific Publications, Oxford 1993 p. 19.

2 J. P. Lebrat and A. Varma, Combust. Sci. Tech., 88 (1992) 177.

3 Z. A. Munir and W. Lai, Combust. Sci. Tech., 88 (1992) 201.

4 M. J. Capaldi, A. Sadi and J. V. Wood, ISIJ International, 37 (1997) 188.

5 S. Yin, Combustion Synthesis, Metallurgy Press, Beijing 1999 p. 5.

6 J. Wong, E. M. Larson, J. B. Holt, P. A. Waide, B. Rupp and R. Frahm, Science, 249 (1990) 1406.

7 N. Akhtar, R. Janes and M. J. Parker, J. Mater. Sci., 31 (1996) 3053.

8 V. A. Knyazik, A. S. Shteinberg and V. I. Gorovenko, J. Thermal Anal., 40 (1993) 363.

9 X. Wang, H. Y. Sohn and M. E. Schlesinger, J. Mater. Sci. Eng., 186 A (1994) 151.

10 T. Wang, L.-Y. Xiang, M.-L. Zhu and J.-S. Zhang, Mater. Lett., accepted.

11 X. He, X. Xu, J. Han and J. V. Wood, J. Mater. Sci. Lett., 18 (1999) 1201.

12 S. D. Dumead, D. W. Readey, C. E. Semler and J. B. Holt, J. Am. Ceram. Soc., 72 (1989) 2318.

13 J. B. Holt, D. D. Kingman and G. M. Bianchini, Mater. Sci. Eng., 71 (1985) 321.

14 S. D. Dunmead and Z. A. Munir, J. Am. Ceram. Soc., 75 (1992) 180.

15 L. L. Wang and Z. A. Munir, Metall Mater Trans. B, 26B (1995) 595.

16 J. Šesták, Thermophysical Properties of Solids, Elsevier, Amsterdam 1994.

17 H. C. Yi, A. Patric and J. J. Moore, J. Mater. Sci., 27 (1992) 6797.

18 N. N. Semenov, On Some Problems of Chemical Kinetics and Reactivity, Ind. AN SSSR, Moscow 1958, p. 421.

19 R. Z. Hu, Z. Q. Yang and Y. J. Liang, Thermochim. Acta., 134 (1988) 429.

20 S. J. Chu, Thermal Analysis of Explosives, Science Press, Beijing 1994, p. 184.

21 C. G. Feng, Theory of Thermal Explosion, Science Press, Beijing 1988, p. 1.

22 A. G. Merzhanov and V. G. Abramov, Propell. Explos., 6 (1981) 130.

23 J. Mackowiak and L. L. Shreir, J. Less-Common Metals, 15 (1968) 341.

24 F. J. J. van Loo and G. D. Rieck, Acta Metal., 21 (1973) 61.

25 F. J. J. van Loo and G. D. Rieck, Acta Metal., 21(1973) 73.

26 H. Friedman, J. Polym. Sci., 6C (1963) 183.

27 T. Ozawa, Bull. Chem. Soc. Japan, 38 (1965) 1881.

28 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, 70A (1966) 487.

29 S. Vyazovkin, Int. Rev. Phys. Chem., 19 (2000) 45.

30 S. Vyazovkin, Int. J. Chem. Kinet., 28 (1996) 95.

31 S. Vyazovkin and C. A. Wight, Int. Rev. Phys. Chem., 17 (1998) 407.

32 S. Vyazovkin and C. A. Wight, J. Phys. Chem., A101 (1997) 8279.

33 M. E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham J. Opfermann, R. Stey, H. L. Anderson, A. Kemler, R. Keuleers, J. Janseens, H. O. Desseyn,

Chao-Rui Li, Tong B. Tang, B. Roduit, J. Malek and T. Mitsuhashi,Thermochim. Acta, 355 (2000) 125.
34 M. Maciejewski, Thermochim. Acta, 355 (2000) 145.
35 S. Vyazovkin, Thermochim. Acta, 355 (2000) 155.
36 A. K. Burnham, Thermochim. Acta, 355 (2000) 165.
37 B. Roduit, Thermochim. Acta, 355 (2000) 171.
38 N. Koga, Thermochim. Acta, 258 (1995) 145.
39 S. Vyazovkin, Thermochim. Acta, 236 (1994) 1.
40 G. Wang and M. Dahms, JOM, 45 (1993) 52.