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Mechanism of non-isothermal reaction between elemental powders Ti and Al①

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Abstract: The mechanism of the reaction between elemental Ti and Al powders in continuous heating was studied through DSC and XRD phase analyses. Results show that, only one exothermic peak appeared on DSC curves for blended elemental Ti and Al powder compacts; and the onset temperature increased with increasing heating rate. After heating to 1 200 ℃, the main phases of the heating products were Ti_3Al and TiAl phases. By kinetic calculation, the apparent activation energy for the exothermic reaction was determined as 340±20 kJ/mol. Based on these results, it is suggested that the reaction between elemental Ti and Al powders be a complex one. During this reaction, $TiAl_3$ is formed first, finally Ti_3Al and TiAl. The rate and intensity of the reaction are inherently dependent on the composition and morphology of raw materials, as well as the heating rate.

Key words: TiAl-based alloy; reaction mechanism; kinetic activation energy **Document code: A**

1 INTRODUCTION

Elemental powder metallurgy (EPM) has drawn great attention in the preparation of TiAl-based alloys for its advantages of cost-saving and convenience in operation[1~5]. Currently, the mechanical properties of EPM TiAl-based alloy are almost as high as those of the forged TiAl-based alloy[6~8]. One of the most important aspect in the study of EPM TiAl-based alloy is the reaction mechanism between elemental Ti and Al powders. The research work in this field can be divided into two groups: 1) study the diffusion process between Ti-Al diffusion couple[9,10]; 2) study the reaction between Ti, Al blended powders in continuous heating through DTA (differential temperature analysis) or DSC (differential scanning calorimeter)[1,7].

Van Loo[9] found that when Ti-Al diffusion couple was held in the temperature range of 520 ~ 620 ℃, $TiAl_3$ was the only reaction product. Leitner *et al*[1] found that in the DSC curve of the blended elemental Ti-49Al (mole fraction, %) powders, there were two exothermic peaks. One began at a temperature of 520~ 620 ℃, and the other began at a temperature of 660~ 680 ℃. They thought that the first peak was related to the solid reaction, and the other was related to the melting of Al. These two studies show that the exothermic reaction between solid Ti and Al precede the melting of Al. However, Lee[7] found that in the DTA curve of blended elemental Ti-Al-Mn-Mo powders, there appeared an endothermic peak at first, i. e. the melting of Al, and then an exothermic peak. It indicated that the exothermic reaction between Ti and Al followed the melting of Al. Meanwhile, the reaction products are also different in the Ti-Al diffusion couple and the blended elemental powders. The former was only $TiAl_3$ single phase, while the later were Ti_3Al, TiAl and small amount of $TiAl_3$ phases.

This work aims at studying the reaction mechanism between Ti, Al powders in detail, in order to improve the understanding of this aspect.

2 EXPERIMENTAL

2.1 DSC test

Elemental Ti, Al powders were mixed in a proportion of Ti-48Al (mole fraction, %), and cold pressed at a pressure of 400 MPa. The particle size distribution of the raw material powders is shown in Fig. 1, and their oxygen contents are all $2\,400 \times 10^{-6}$. DSC tests were conducted in Perkin-Elmer thermal analysis system under Ar atmosphere at heating rates of 5 ℃/min, 30 ℃/min, 40 ℃/min and 50 ℃/min. The temperature range of the samples heated at rates of 5 ℃/min and 40 ℃/min was from room temperature to 1 200 ℃, and those of the samples heated at 30 ℃/min and 50 ℃/min were from room temperature to 1400 ℃ and 1300 ℃ respectively.

2.2 Kinetic calculation

The variation of the reaction rate constant k can

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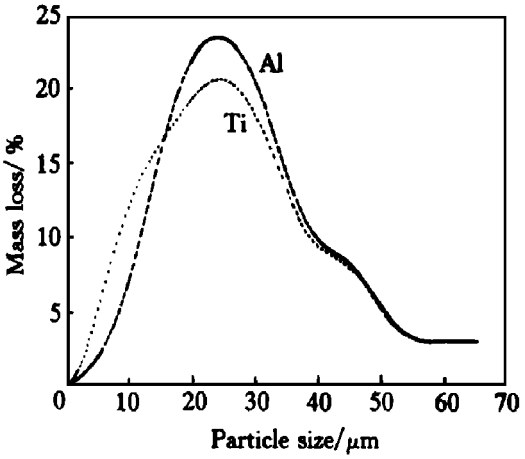

Fig. 1 Particle size distribution of raw powders

be described by Arrhenius equation:

$$k = A \cdot \exp(-E/RT) \quad (1)$$

where A is frequency factor; E is reaction activation energy; R is gas constant, 8.314 J·mol^{-1}·K^{-1}; T is absolute temperature.

The most important data above is the reaction activation energy. It represents the minimal energy that is necessary for the molecular with an average energy to be activated. Eqn. (1) indicates the smaller the reaction activation energy is, the faster the reaction rate will be. Through Kissinger method[11], the reaction activation energy can be calculated from DTA or DSC curves, as shown in Eqn. (2). Firstly, several DSC curves were obtained at different heating rates β, and their peak temperature T_p was also determined. After calculation, the $\ln(\beta/T_p^2) \sim 1/T_p$ relationship curve can be established. According to Eqn. (2), the slope of the curve and then the value of E can be obtained.

$$\frac{d\left[\ln\frac{\beta}{T_p^2}\right]}{d\left[\frac{1}{T_p}\right]} = -\frac{E}{R} \quad (2)$$

2.3 X-ray diffraction analysis

After DSC tests, the samples heated at rates of 5 ℃/min and 40 ℃/min were analyzed by X-ray diffraction in a Riguchu 3014 type diffraction machine. The operation conditions were: CuK α, scanning rate 2°/min. Chung[12,13] had suggested a set of quantitative X-ray diffraction analysis method —— Matrix-flushing method. When a binary system is studied, the contents of the two phases can be calculated by Eqn. (3).

$$X_i = \frac{1}{1 + \frac{K_i}{K_j} \cdot \frac{I_j}{I_i}} \quad (i, j = 1, 2) \quad (3)$$

where X_i is the mass fraction of phase i; I_i and I_j are the intensities of selected diffraction peaks of the two phases respectively; K_i and K_j are the reference intensities of the two constitution phases, and will be constant for a same phase. Therefore, the bigger the value of I_i/I_j is, the higher the content of phase i will be. In this study, the sample mainly consists of TiAl and Ti_3Al phases, so it can be considered as a pseudo-binary system, and the value of I_i/I_j is used to qualitatively judge the content of TiAl. As the most intense peak of TiAl (111) overlaps with the (002) peak of Ti_3Al, (200) peak is selected for TiAl phase and (201) peak is selected for Ti_3Al.

3 RESULT

3.1 DSC result

The DSC curves of the blended Ti-48Al powders at different heating rates are shown in Fig. 2. All the curves have only one exothermic peak, and the onset temperature and the peak temperature are retarded as the heating rate increases, as listed in Table 1. The onset temperature for the sample heated at the rate of 50 ℃/min is nearly similar to that for 40 ℃/min, but its peak temperature has still been retarded. In this study, the onset temperature was determined by the intersection of the tangent of the base line and the line from the peak point with the maximum slope.

Table 1 Onset temperature and the peak temperature of samples (℃)

Temperature/ ℃	Heating rate/ (℃·min^{-1})			
	5	30	40	50
Onset	645.72	651.71	662.44	660.89
Peak	655.61	678.47	694.43	704.13

3.2 Kinetic calculation

The $\ln(\beta/T_p^2) \sim 1/T_p$ relationship curve is shown in Fig. 3, from which the reaction activation energy is calculated as 340 ± 20 kJ/mol.

3.3 X-ray diffraction analysis result

Fig. 4 shows the X-ray diffraction patterns of the samples heated at rates of 5 ℃/min and 40 ℃/min. Both the samples consist of Ti_3Al (α_2) and TiAl (γ) phases. In the sample heated at 5 ℃/min exists small amount of α-Ti, no apparent $TiAl_3$ phase can be detected possibly due to its low content. Through qualitative analysis, it was found that the content of TiAl in the sample heated at 40 ℃/min was a bit lower than that of 5 ℃/min, because the value of I_i/I_j for the former is 1.92, while the later 2.02.

4 DISCUSSION

4.1 Onset temperature for the reaction

The DSC curve in this study is a little different from those in Leitner's[1] and Lee's[7]. There is only one exothermic peak, which initiates at 645~ 662 ℃, no peak indicating the melting of Al has been

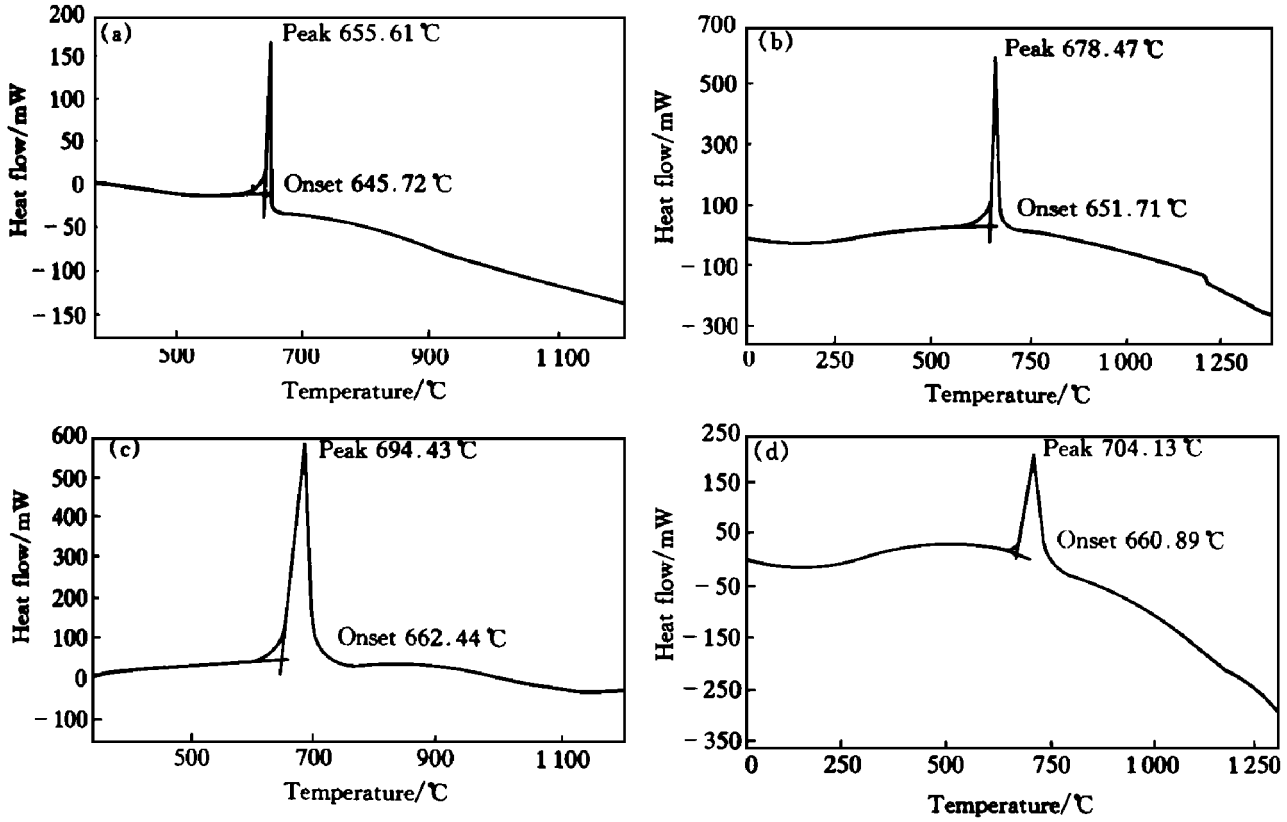

Fig. 2 DSC curves of Ti-48Al powder compact at various heating rates
(a) —5 ℃/min; (b) —30 ℃/min; (c) —40 ℃/min; (d) —50 ℃/min

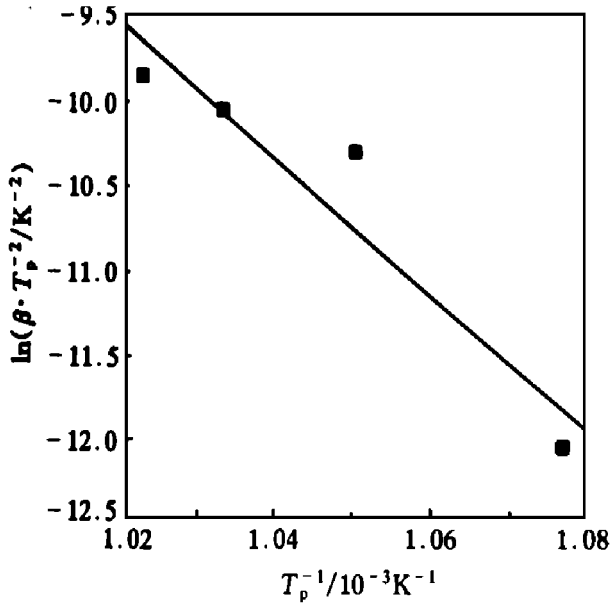

Fig. 3 Kinetic calculation curve of Fig. 2

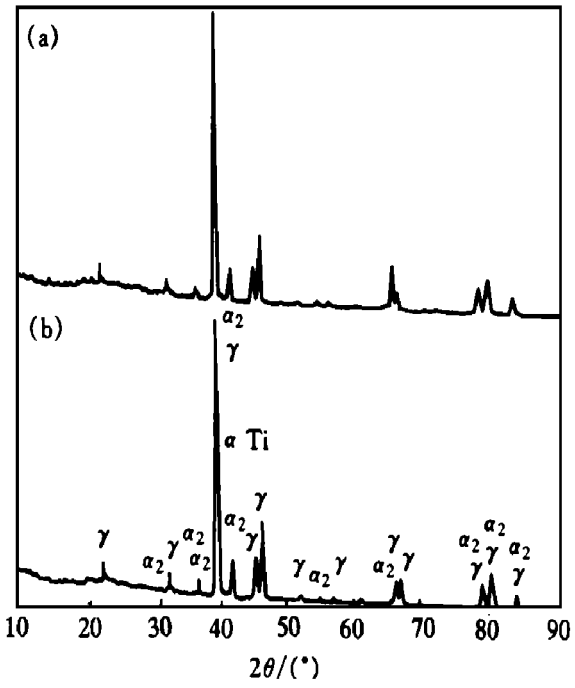

Fig. 4 XRD patterns of specimens after DSC analyses
(a) —5 ℃/min; (b) —40 ℃/min

detected. However, through detailed analyzing, it has been found that these results are consistent.

1) In Lee's DTA curves[7], the base line had risen before the endothermic peak. It indicates that the exothermic reaction had begun slowly before the melting of Al. The onset temperature was retarded possibly due to the addition of alloy powders (Mo, Mn powders). The existence of these alloy powders can retard the reaction for the same reason that restricting agent is always added to the SHS process to control the reaction. When the heat sent out by the Ti-Al reaction was insufficient to compensate for the heat absorbed by the melting of Al, an endothermic peak would appear. The particle size of Al in this study is close to that of Lee's, so the melting point of Al should be the same. However, the reaction of Ti-Al powders in this study was more intense than that of Lee's due to the absence of other alloy powders. As the heat sent out had exceeded that absorbed by

the melting of Al, an exothermic peak appeared.

2) Reference [1] had not provided the particle size of the raw powders, but the two exothermic peaks in its DSC curves can be considered as a big exothermic peak interrupted by the melting of Al. That is to say, the exothermic reaction began before the melting of Al, but the reaction rate was slow and the heat sent out was consumed by the melting of Al, so the total heat was dropped. On the other hand, the activity of Al increased quickly as Al melted, and the reaction between Ti-Al elements was also promoted. When the heat sent out covered the melting of Al, a second exothermic peak appeared.

In conclusion, the exothermic reaction of Ti-Al elements precedes the melting of Al. The onset temperature and the intensity of the reaction are largely dependent on the composition, particle size of the raw material and heating rate. When the reaction rate is slow and the exothermic heat can not compensate for the melting of Al, an endothermic will appear.

4.2 Reaction product

In the diffusion reaction of Ti-Al diffusion couple, $TiAl_3$ was found to be the only products, while multi-phase products of TiAl, Ti_3Al and $TiAl_3$ were found in the reaction of Ti-Al powders. Kattner[15] had listed the standard Gibbs formation energy for the above three phases, as drawn in Fig. 5. It can be seen that the standard Gibbs formation energy for $TiAl_3$ is the lowest, so it will be the first formation phase. Although TiAl and Ti_3Al phases were obtained in this work after heating to 1 200 ℃, other studies after quenching at the reaction peak point had also shown the same results[7, 14]. It indicates that the reaction products of Ti-Al powders are TiAl and Ti_3Al phases. In addition, the reaction activation energy obtained in this study are much higher than that of $TiAl_3$ (200 ± 20 kJ/mol)[1]. These contradictions can be analyzed as follows.

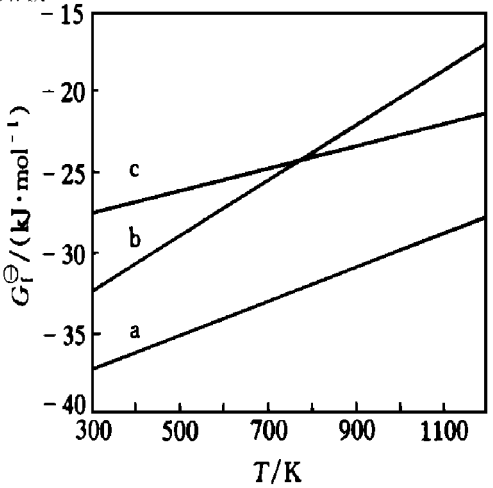

Fig. 5 $\Delta G_f^\ominus$-T relationship of Ti-Al intermetallics[15]
a—$TiAl_3$; b—TiAl; c—Ti_3Al

The prerequisite for the calculation of reaction activation energy from DSC curves is that the reaction should be an one-order reaction, i.e. the reaction can be completed through one time of molecular collision. For complex reaction, the calculated activation energy is an apparent one. As $TiAl_2$ has not been found in this study and $TiAl_3$ is a well-accepted intermediate phase, it is deduced that the reaction between Ti-Al powders is possibly a complex one, as shown below.

$$Ti + 3Al \rightarrow TiAl_3 \quad (4)$$

$$4Ti + TiAl_3 \rightarrow Ti_3Al + 2TiAl \quad (5)$$

According to Kattner's data[15], $\Delta G_f^\ominus$ for reaction (5) can be drawn in Fig. 6. It is found that $\Delta G_f^\ominus < 0$ and the reaction can proceed.

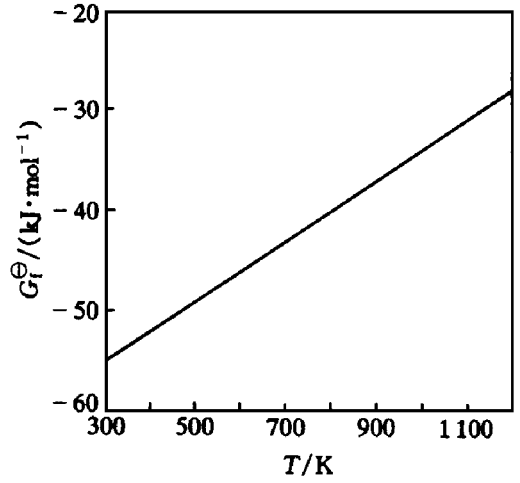

Fig. 6 $\Delta G_f^\ominus$-T relationship of reaction (5)

The final problem is the difference between the reaction product of Ti-Al diffusion couple and Ti-Al powders. It is related to the content of Al element in the raw material. The initial reaction between Ti, Al elements is through the diffusion of Al in the reaction interface. In Ti-Al diffusion couple, the reaction temperature was below the melting point of Al and the amount of Al was high enough. Element Al diffused continuously through the grain boundaries of $TiAl_3$ to the reaction interface, and reaction (4) proceeded constantly, therefore $TiAl_3$ was the only product. In the reaction of Ti-Al powders, the activity of Al powder was far higher than that of Al block, reaction (4) proceeded very fast. As the amount of Al was limited, Al powders was consumed soon and reaction (5) began. Al in $TiAl_3$ is a very active element[16], it diffuses through grain boundaries to Ti particle to form Ti_3Al phase, and TiAl phase forms in the $TiAl_3$ matrix[16~18]. Therefore, the reaction product of Ti-Al powders consists of TiAl and Ti_3Al phases. The proceeding of reaction (5) is influenced by reaction onset temperature, which is influenced by heating rate. The faster the heating rate, the higher the onset temperature, the higher the activity of Al and the more complete the reaction (5). Therefore, in the sample heated at 5 ℃/min there is still small

amount of α-Ti, while in the sample heated at 40 ℃/min there isn't. However, the content of TiAl and Ti_3Al phases will be rearranged according to phase equilibrium through elements diffusion. Long times of heating will favor the formation of TiAl phase, so the content of TiAl phase decreases with increasing heating rate.

5 CONCLUSIONS

1) The reaction between elemental Ti, Al powders is a complex one. $TiAl_3$ is formed first, and finally Ti_3Al and TiAl. The onset temperature for this reaction is ahead of the melting point of Al, and is retarded with increasing heating rate.

2) The reaction rate and intensity are largely dependent on the composition, morphology of the raw powders and heating conditions as well. All these factors also influence the shape of DSC (DTA) curves of Ti-Al elements and the final product during continuous heating.

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