Rare Metal Materials and Engineering
Volume 46, Issue 8, August 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(8): 2080-2086.

ARTICLE

Characterization on Solid Phase Diffusion Reaction Behavior and Diffusion Reaction Kinetic of Ti/Al

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Abstract: The solid phase diffusion reaction behavior between Ti and Al was characterized from 520 ℃ to 630 ℃ for different annealing time with titanium and aluminum being superfluous. When the samples are annealed up to 46 h, only intermetallic $TiAl_3$ phase forms and grows at the Ti/Al interface. It can be found that the growth rate of $TiAl_3$ towards $TiAl_3$/Al interface is more rapid than that towards Ti/$TiAl_3$ interface. Additionally, the solid-state diffusion reaction kinetic equation of $TiAl_3$ was successfully established in the present work. The reaction activation energy of Ti/Al is calculated to be 170.1 kJ·mol^{-1} and dynamic index n is 0.5. Hence, the growth of $TiAl_3$ is controlled by normal parabolic law with annealing time. Ti/Al powder compact was employed as experiment material to identify the proposed reaction kinetic equation for the growth of $TiAl_3$. It is suggested that no extra aluminum is found in the specimen annealed at 590 ℃/4.5 h, while the aluminum is still found at 590 ℃/3.5 h, indicating that it is in a good agreement with the developed solid-phase diffusion reaction equation.

Key words: Ti/Al; kinetic equation; diffusion; intermetallic compound

Recently TiAl intermetallic compounds have become attractive and potential candidate materials for aerospace structural and engine applications due to their desired combination of low density, high specific strength and relatively good properties at elevated temperature[1-3]. However, they are quite difficult to process because of their low ductility at ambient temperature, which has been the major limitation for the practical utility of such kind of materials[4,5]. Traditionally, TiAl-based alloys are processed using an ingot metallurgy method of casting followed by hot isostatic pressing[6]. But this kind of approach will cause casting defects because of poor castability of materials. Compared with the traditional casting method, the powder sintering processing has been considered as the alternative and desired way to fabricate the TiAl intermetallic compound. It is well known that titanium powder and aluminum powder can be initially compressed into workpiece at ambient temperature, and then the TiAl intermetallic compound can be produced with reaction sintering processing, which effectively overcomes the disadvantage of poor workability of TiAl intermetallic compounds due to their low ductility. Using this method, the intermetallic layer is found to be formed and grown when the reactant materials of titanium and aluminum are both in solid state. In the previous addressed studies, most of the scientists paid attention to the fabrication of composites and microstructural evolution of TiAl-based alloys[7-10]. Whereas only a few researches focused on the mechanism and kinetics of the intermetallic layer growth during solid-phase reaction. For instance, Wang et al[11] suggested that the lamellar microstructure would be found after the reaction between titanium and aluminum phases. With the help of mechanical balling technique, the finer microstructure can be observed in TiAl. Tang et al[12] considered that the solid phase reaction is composed of several simple physical-chemical processes. Basically, the reaction between titanium and aluminum cannot be completed until each process is terminated, indicating that the procedure with lowest chemical reaction rate plays an essential role in the entire chemical process. Based on the ad-

Received date: August 11, 2016
Foundation item: National Natural Science Foundation of China (51405110); Fundamental Research Funds for the Central Universities (HIT. NSRIF. 2014006); Specialized Research Fund for the Doctoral Program of Higher Education (20132302120002); China Postdoctoral Science Foundation (2014M551234)
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dressed study work, it can be found that the reported research results of diffusion reaction kinetic of Ti/Al are still limited. More importantly, the kinetic exponents and activation energies vary extensively among various investigations.

Therefore, in the present work, the diffusion couple of titanium and aluminum was prepared by embedding pure titanium and pure aluminum into steel sheath with whorls. The annealing experiments at various temperatures and time were carried out to characterize the solid-phase diffusion reaction behavior and to reveal the underlying mechanism. Moreover, the diffusion reaction kinetic equation of Ti/Al was successfully developed.

1 Experiment

In the present work, the pure titanium and aluminum (99.9% purity) were selected as the experimental materials. In order to analyze the chemical composition of the material, EDS was conducted for the as-received materials, as shown in Tables 1 and 2. The experimental specimens from the pure titanium and aluminum materials were cut by electric-discharge machining into cylinder with Φ20 mm×1.5 mm and Φ22 mm×16 mm, respectively. After grinding and polishing on the silicon carbide papers, the oxidized surface was removed by chemical etching in a solution of 15%NaOH and 10%HF at room temperature, followed by alcohol cleaning, water flushing and drying. Subsequently, the experimental specimens whose smooth surfaces were touched and put into steel sheath with whorls were compressed by the CSS-WEW 1000 hydraulic testing machine. Finally, the annealing treatment experiments were performed in a vacuum radiation heating furnace (10^{-1} MPa). All the specimens were annealed at 520, 560, 590 and 630 ℃. The diffusion time varied from 6 h to 46 h with the interval of 10 h. When verifying the diffusion reaction kinetic equation, the experimental materials were selected as the Ti/Al powder compactions. The thickness of the reaction layers at Ti/Al interfaces was measured from scanning electron microscope (SEM) images of the cross-sections. An SEM equipped with energy dispersive X-ray spectrometer (EDS) and an X-ray diffractometer (XRD) using Cu Kα radiation were used to identify the formation of intermetallic compounds during annealing treatments.

2 Results and Discussion

2.1 Solid phase diffusion reaction of Ti/Al

After the annealing experiments conducted at various temperatures of 520, 560, 590 and 630 ℃, it can be found from the cross section of the specimens that the titanium and aluminum are not consumed, which present the similar circumstance for different annealing temperatures and time. Fig.1 shows the BSE images of the Ti/Al interface reaction layers at 560 ℃ with various heating time. It can be observed that the annealed samples can be divided into three regions, including a dark region, a gray region and a white region. It can be known from the principle of BSE that different colors in the picture present the variation of atomic number, which means the color becomes lighter with the increasing atomic number. Because the atomic number of titanium (22) is larger than that of aluminum (13), it can be deduced that the composition of the dark, gray and white regions on each micrograph corresponds to Al, $TiAl_3$ and Ti, respectively. In addition, the thicknesses of the dark layer and the white layer decrease, while the thickness of the reaction layer increases with the increasing annealing time. It can be found that the thickest reaction layer is about 20 μm at 560 °C/46 h, whose thickness is still considered on the order of a micrometer.

Fig.2 shows the concentration profiles of the reaction layer at 560 ℃/46 h. From Fig.2a, it can be revealed that the element ratio of titanium to aluminum is 1:3, and thus the reaction product can be preliminary considered as the $TiAl_3$. Based on the BSE image of the reaction layer, the chemical component analysis was carried out in order to present the variation of reactants and the products. From Fig.2b, it can be obviously seen that the content of aluminum is 100 at% in the dark region while the content of titanium is almost 0 at% in the dark region. From the dark region to the gray region, the contents of aluminum and titanium present the sharp decrease and increase tendency, respectively. In the gray region, the contents of aluminum and titanium are steady, suggesting that no composition gradient can be noticed. The content of aluminum is almost 75 at%, while the content of titanium is 25 at% in the reaction layer. From the gray region to the white region, the contents of aluminum and titanium exhibit more obvious decrease and increase tendency, respectively. The content of aluminum is almost 0 at% and the content of titanium is 100 at% within the white region, which means only titanium is observed in this layer at 560 ℃/46 h.

After the annealing treatment at 630 ℃/46 h, the superfluous aluminum layer is removed in the NaOH solution. Fig.3 shows the X-ray diffraction pattern of the specimen annealed at 630 ℃/46 h without aluminum layer. It can be seen that $TiAl_3$ is the only compound observed after reactive diffusion between Ti and Al for time up to 46 h, which is similar to the research result addressed by Luo[13] and Shimozaki[14]. Therefore, it can be suggested that only one kind of intermetallic has been produced from titanium and aluminum.

Table 1 Chemical composition of pure titanium (wt%)

O	Si	C	Ti
0.18	0.63	0.11	≥99

Table 2 Chemical composition of pure aluminum (wt%)

O	Si	C	Al
0.21	0.096	0.081	≥99

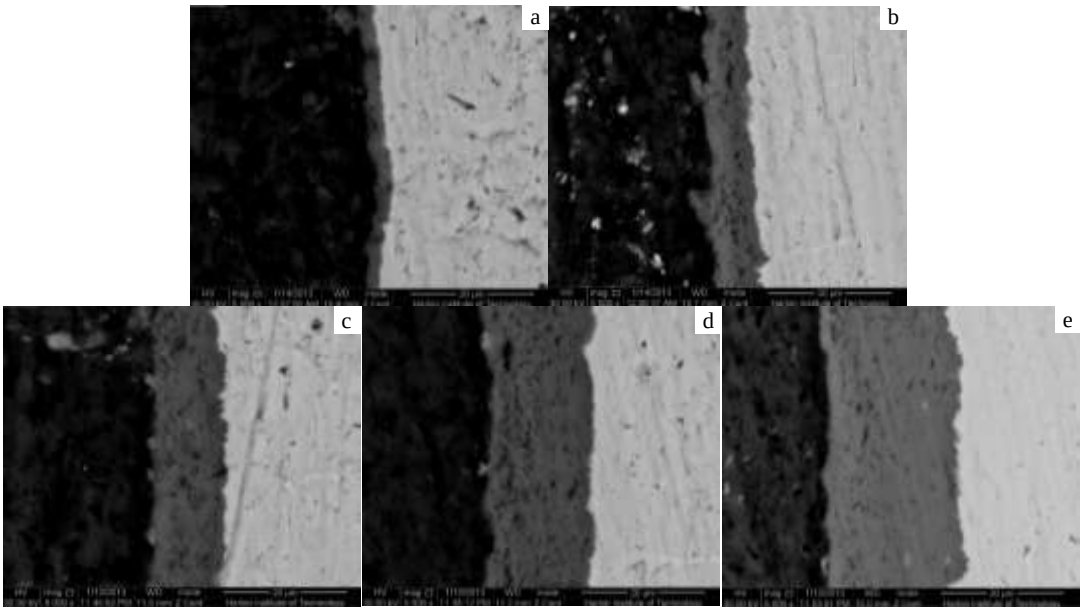

Fig.1 BSE images of Ti/Al interface region at 560 ℃ with different heating time: (a) 6 h, (b) 16 h, (c) 26 h, (d) 36 h, and (e) 46 h

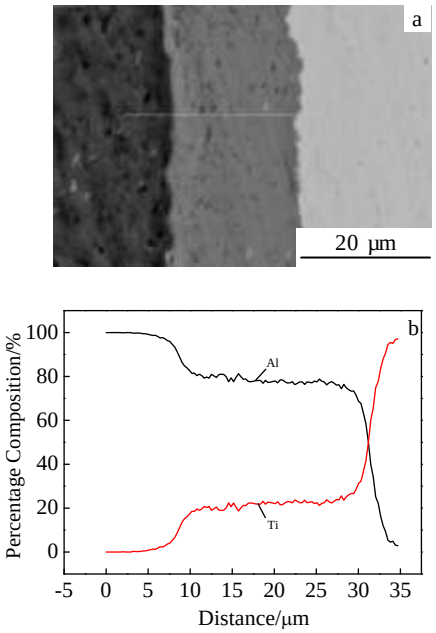

Fig.2 BSE image (a) and concentration profile (b) of the reaction layer at 560 ℃/46 h

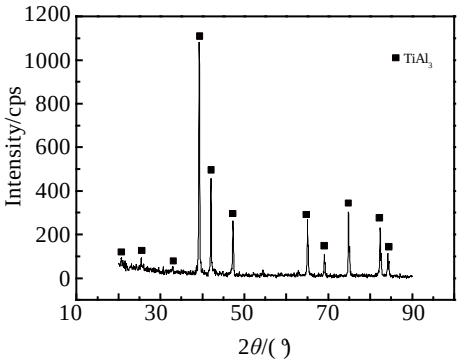

Fig.3 XRD pattern of the specimen diffusion treated at 630 ℃/46 h without aluminum layer

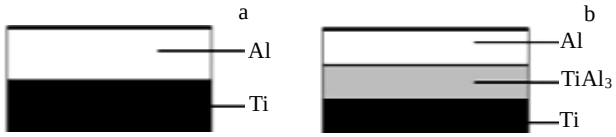

Fig.4 Schematic diagrams of diffusion of titanium and aluminum: (a) initial state and (b) annealing state

Fig.4 shows the schematic diagram of diffusion of titanium and aluminum. At the beginning of diffusion reaction in the Ti/Al diffusion couples at low temperature, inter-diffusion occurs between titanium atom and aluminum atom, which means the solid solution of Ti(Al) is formed in titanium layer and the solid solution of Al(Ti) is formed in aluminum layer. The crystal nucleus of $TiAl_3$ are found at Ti/Al interface when both of Ti(Al) and Al(Ti) are the supersaturated solid solutions, as shown in Fig.4. According to the binary phase diagram of titanium-aluminum, when aluminum is superfluous, it is easy to form intermetallic compound $TiAl_3$. Also, based on the calculation by Liu[15],

if Gibbs free energy is less than zero, the chemical reaction regarding the reactants of titanium and aluminum can be available to produce $TiAl_3$ particles. With the increasing reaction time, the $TiAl_3$ particles will form the continuous $TiAl_3$ layer, which is considered as the initial $TiAl_3$ reaction layer. After the formation of $TiAl_3$ reaction layer, the $Ti/TiAl_3$ and $TiAl_3/Al$ interfaces thus form. The driving force of nucleation is attributed to the concentration gradient. Fig.5 shows the Ti/Al binary phase diagram. It can be known that the equilibrium concentration of titanium atom in the aluminum layer can reach the peak value of 0.12 at%. The concentration of aluminum in $TiAl_3$ varies from 74.78 at% to 75.36 at% (0.58 at% concentration gradient). While the concentration of aluminum in the $TiAl_3$ layer can reach about 12 at%. Thus titanium or aluminum has concentration gradient in different phases, which provides the driving force for the inter diffusion of Ti/Al. With the help of driving force, titanium is able to diffuse through aluminum layer to form solid solution of Al(Ti). When the concentration of titanium is more than the maximum equilibrium concentration of 0.12 at% in the aluminum layer, the intermetallic $TiAl_3$ precipitates from supersaturated solid solution of Al(Ti) at the interface of $TiAl_3$/Al. In the meanwhile, the concentration of titanium in the aluminum layer decreases below the equilibrium concentration, and the concentration of titanium in $TiAl_3$ decreases back to the equilibrium concentration of $C_{\theta/Al}$, which results in the further diffusion of titanium atom into aluminum layer and vice versa for the diffusion of aluminum atom through titanium layer. Such kind of diffusion process further promotes the formation of new supersaturated solid solution with the increasing reaction time, which is beneficial to the nucleation and growth of $TiAl_3$ towards the titanium layer and aluminum layer.

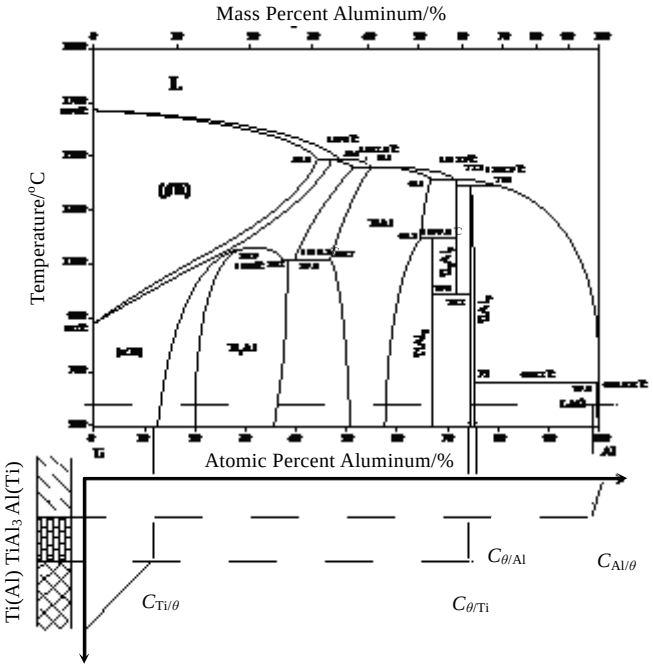

Fig.5 Concentration gradient schematic diagram based on the Ti/Al binary phase diagram

2.2 Solid-phase diffusion reaction kinetic of Ti/Al

It is universally acknowledged that at a given temperature the dependence of the thickness of an inter-diffusion layer on the diffusion time can be presented by the following empirical relationship[13]:

$$y=Kt^n \quad (1)$$

Eq. (1) can be written in the logarithmic form as follows:

$$\ln y=n\ln t+\ln K \quad (2)$$

where, y is the thickness of reaction layer (m), t is the diffusion time (s), K is the rate constant and n is the kinetic exponent.

When n is equal to 0.5, the growth of reaction layer is controlled by parabolic growth; when n is 1, the growth of reaction layer is dominated by linear growth. Usually, the value of K can be assumed to follow an Arrhenius type as presented in Eq. (3):

$$K=K_0\exp(-E/RT) \quad (3)$$

where, K_0 is the pre-exponential factor (m s^{-n}), R is the gas constant (8.31 J mol^{-1} K^{-1}), E is activation energy for growth (J mol^{-1}), and T is absolute temperature in Kelvin. The reaction kinetic equation can be established with substitution of E and K_0 into Eq. (1), which is described as Eq. (4):

$$y=K_0\exp(-E/RT)t^n \quad (4)$$

The measured value of thickness of reaction layer at various temperatures and time are listed in Table 3. The variation of thickness in logarithm scale ($\ln y$) with annealing time in logarithm scale ($\ln t$) at various annealing temperatures of the specimens is shown in Fig.6. It can be detected that four desired fitting straight lines are presented based on the linear regression analysis, whose slope is 0.508, 0.668, 0.503 and 0.496 corresponding to the temperatures of 520, 560, 590 and 630 ℃, respectively. With the consideration of the experimental error, the kinetic exponent can be determined as the value of 0.5, suggesting the growth of $TiAl_3$ follows the parabolic law with the reaction time at the annealing temperatures from 520 ℃ to 630 ℃.

The activation energy can be obtained from plots of $\ln K$ versus the $1/T$. Such kinds of plots are depicted in Fig.7. From this figure, it can be noted that the relationship between $\ln K$ and $1/T$ is presented as Eq. (5).

$$\ln K = 7.16 - 20473.7\frac{1}{T} \quad (5)$$

Compared with Eqs. (4) and (5), it can be noted that the value of E/R is 20473.7, and thus the estimated value for the activation energy (E) is obtained to be approximately 170.1 kJ·mol^{-1}. This finding is in accordance with the result reported by Loo et al[16], in which the reaction activation energy is calculated to be 180 kJ·mol^{-1} for the $TiAl_3$ produced in the Ti/Al diffusion couples. As a result, the diffusion reaction

Table 3 Experimental data of reaction layer ($TiAl_3$) thickness at different temperatures and time

T/℃	t/h	t/s	ln$t$	Thickness of reaction layer, y/×10^{-6}m	ln$y$
520	6	21600	9.98	1.04	–13.76
	16	57600	10.96	1.55	–13.38
	26	93600	11.45	2.17	–13.04
	36	129600	11.77	2.46	–12.92
	46	165600	12.02	3.01	–12.71
560	6	21600	9.98	3.88	–12.46
	16	57600	10.96	7.06	–11.86
	26	93600	11.45	9.43	–11.57
	36	129600	11.77	12.65	–11.28
	46	165600	12.02	15.43	–11.08
590	6	21600	9.98	7.77	–11.76
	16	57600	10.96	15.53	–11.07
	26	93600	11.45	18.64	–10.89
	36	129600	11.77	20.58	–10.80
	46	165600	12.02	21.74	–10.74
630	6	21600	9.98	24.35	–10.62
	16	57600	10.96	39.77	–10.13
	26	93600	11.45	50.69	–9.89
	36	129600	11.77	59.65	–9.73
	46	165600	12.02	67.43	–9.61

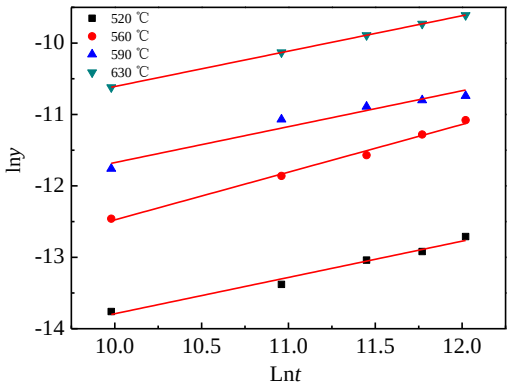

Fig.6 Relationship between the thickness of reaction layer and annealing time at different annealing temperatures

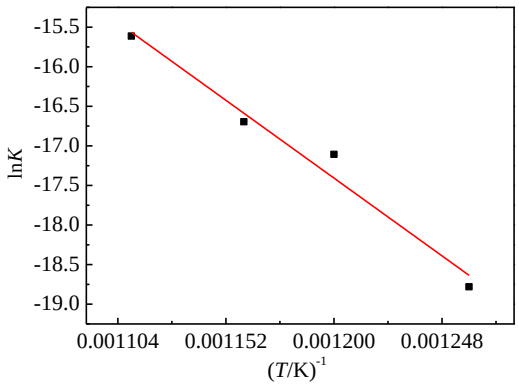

Fig.7 Relationship of ln$K$ and 1/T

kinetic equation of titanium and aluminum at the solid phase is presented as:

$$y = 1.2869\times10^{3}\exp(-170.1\times10^{3}/RT)t^{1/2} \quad (6)$$

From this equation it can be inferred that the thickness of reaction layer $TiAl_3$ increases with the increasing reaction time and annealing temperature, which is in accordance with the result addressed by Tardy et al[17]. In order to verify the accuracy of the established diffusion reaction kinetic equation, the comparison of the predicted and measured values of thickness of reaction layer at different annealing temperatures and time is shown in Fig.8. It can be seen that the predicted value is in an excellent agreement with the experimental data at 520, 590 and 630 ℃. When the specimens were annealed at 560 ℃ with different time, the predicted value is a little higher than the measured value, and the deviation is more obvious with the increasing reaction time. This is because that the increasing number of Kirkendall voids is produced with the increasing reaction time, which is not taken into account when developing the diffusion reaction kinetic equations. Although the error between the predicted and measured values exists, the accuracy of the proposed equation in the present work can still be accepted.

More importantly, the established diffusion reaction kinetic equation and the reactants are also verified by the solid-phase diffusion reaction sintering experiment of Ti/Al composite powder compaction. In the present work, the Ti/Al composite powder was compressed followed by the annealing experiments with various processing parameters. According to Eq. (6), it is known that it takes 4.5 h to exactly consume aluminum at 590 ℃. Thus the aluminum will be superfluous, when the specimens are annealed at 590 ℃/3.5 h. Fig.9 and Fig.10 show the BSE image and X-ray diffraction pattern of the specimens annealed at 590 ℃/3.5 h and 590 ℃/4.5 h, respectively. In Fig.9a, the microstructure contains titanium, aluminum, $TiAl_3$ and

v o i d s c o r r e - equation.

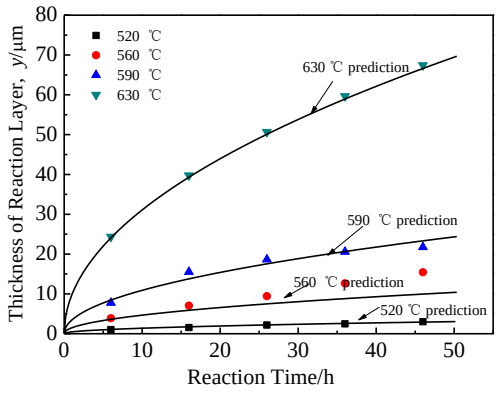

Fig.8 Comparison of predicted and measured thickness values of reaction layer at various annealing temperatures and time

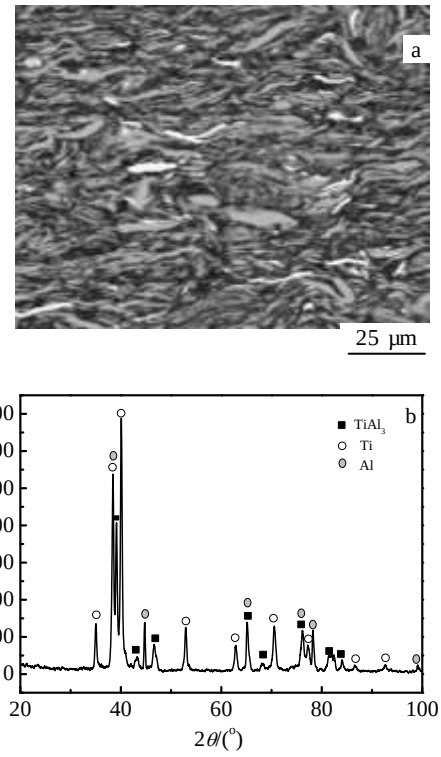

Fig.9 BSE image (a) and XRD pattern (b) of the specimen annealed at 590 ℃/3.5 h

sponding to different colors in the image. It can be known from Fig.9b that the diffusion reaction products are exactly $TiAl_3$ with superfluous aluminum, suggesting that the aluminum is not consumed completely at 590 ℃ and less than 4.5 h. While it is observed from Fig.10a that $TiAl_3$ is more than that in the specimen annealed at 590 ℃/3.5 h, and no aluminum is found based on the XRD result, which is in accordance with the predicted value from the established

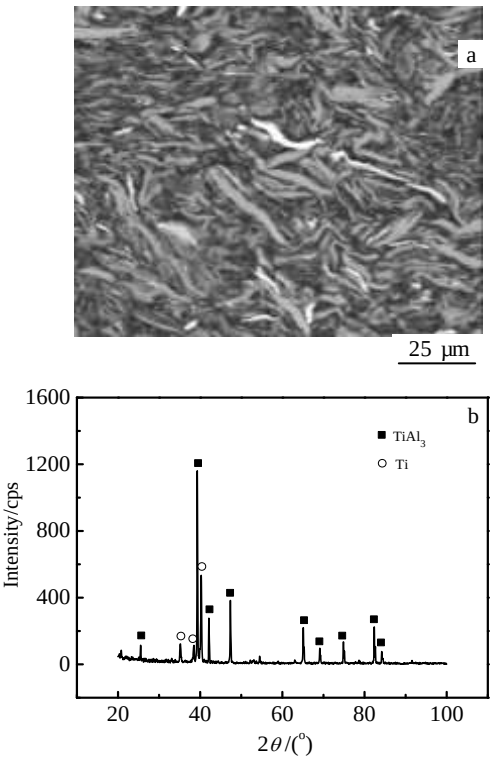

Fig.10 BSE image (a) and XRD pattern (b) of the specimen annealed at 590 ℃/4.5 h

3 Conclusions

1) $TiAl_3$ is the only observed intermetallic phase in the Ti/Al diffusion couple during solid-phase diffusion reaction at 520～630 ℃. At the same temperature, the diffusion coefficient of titanium in $TiAl_3$ phase is larger than that of aluminum. The growth rate of $TiAl_3$ towards $TiAl_3$/Al interface is more rapid than that towards the Ti/$TiAl_3$ interface.

2) The diffusion reaction kinetic equation is successfully developed, which is beneficial to presenting the relationship of the amount of reaction product and annealing temperature and time. The reaction activation energy is calculated to be 170.1 kJ·mol^{-1}, and the kinetic exponent is determined as the value of 0.5, suggesting the growth of $TiAl_3$ follows the parabolic law with the reaction time at the annealing temperature from 520 ℃ to 630 ℃.

3) The aluminum is not consumed completely at 590 ℃/3.5 h, while no extra aluminum is found in the specimen annealed at 590 ℃/4.5 h, which is in a good agreement with the developed solid-phase diffusion reaction equation in the present work.

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Ti/Al 固相扩散反应行为及其动力学研究

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摘 要：研究了 Ti/Al 热处理温度为 520～630 ℃之间不同温度条件下的固相扩散反应，实验选用 Ti/Al 粉末压坯作为研究 $TiAl_3$ 金属间化合物反应动力学模型的原始材料，当热处理时间达到 46 h 条件下，$TiAl_3$ 金属间化合物相在 Ti/Al 界面生成，实验结果显示 $TiAl_3$ 相沿 $TiAl_3$/Al 界面的生长速率明显优于沿 Ti/$TiAl_3$ 界面的生长速率。此外，建立了 $TiAl_3$ 固相扩散反应动力学方程，Ti/Al 固相扩散反应激活能和动力学指数分别为 170.1 kJ·mol^{-1} 和 0.5。通过对不同热处理条件下试样进行成分分析得到，在热处理工艺为 590 ℃/4.5 h 条件下，铝完全消耗，而 590 ℃/3.5 h 条件下仍有多余的铝剩余，该实验结果与所建立的固相反应扩散动力学模型相一致，表明该模型能够很好地预测 Ti/Al 材料固相反应的进行状态。

关键词：Ti/Al；动力学方程；扩散反应；金属间化合物

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