

Microstructure evolution of Al–Ti liquid–solid interface

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Abstract: Al–Ti diffusion couples were made by embedded technology and treated at the temperature between the melting points of Al and Ti. The microstructure evolution and growth mechanism of the Al–Ti DRZ were investigated. The result shows that the DRZ, the mixture of TiAl_3 and Al, grows layer by layer along their chemical equilibrium zone. In the course, the growth interface moves toward the aluminum side. TiAl_3 is the only new phase which forms earliest in the course of heat-treatment. The growth mechanism of the DRZ changes after the phase transition of titanium. Before the phase transition of titanium, the growth of the DRZ is controlled by the dissolution speed of the titanium to the molten aluminum, while after the phase transition of titanium, the growth is controlled by the chemical reaction speed of Al and Ti atoms, and consequently, its growth rate is greatly increased.

Key words: Al–Ti liquid–solid interface; diffusion-reaction zone; microstructure evolution; growth mechanism

1 Introduction

The Al–Ti composites, which can maximize the potentials of aluminum and titanium, have been widely applied to the aerospace and automotive industry [1,2].

However, it is difficult to achieve reliable connection of aluminum and titanium by means of conventional welding method due to the very differences between physical and chemical properties of the two materials. Therefore, diffusion bonding becomes concerns of many researchers [3–18]. In the diffusion bonding course of dissimilar metals, a new intermetallic phase zone named DRZ tends to form by the diffusion and reaction of the heterogeneous atoms. The nature of the DRZ greatly influences and even determines the properties of the composites. Hence, it is important theoretically and practically to study the microstructure evolution, the formation mechanism and the growth pattern of the DRZ and then to predict and control its structures and properties.

At present, most of the studies are focused on the process parameters for the optimal performance [4–12], and Al–Ti solid–solid diffusion [13–18], while fewer researchers have centered on Al–Ti liquid–solid diffusion, and the diffusion and reaction process in the Al–Ti liquid–solid interface and the growth of the DRZ

are still poorly investigated.

Compared with solid–solid diffusion, liquid–solid diffusion has a broader prospect of engineering applications due to its faster diffusion speed and shorter joint forming time. In this work, Al–Ti diffusion couples were prepared by embedded technology, and the samples were treated at different temperatures which are between the melting points of Al and Ti to form Al–Ti DRZ. The microstructure evolution and growth mechanism of the DRZ in the Al–Ti liquid–solid interface have been investigated to provide experimental and theoretical basis for the preparation of the Al–Ti composites.

2 Experimental

A $\phi 4.8$ mm hole was drilled in the middle of an aluminum block with dimensions of 10 mm×10 mm×10 mm, and then oxide films on the surface of the aluminum block and the inner hole were removed with a file and sandpapers. A titanium wire with 5 mm in diameter was filed to a taper pin in accordance with the size of the hole in the aluminum block, sanded smooth, and then fitted into the hole of the aluminum block tightly to form a sample. The sample was placed into a small ceramic crucible. The crucible with the sample was placed into a vacuum furnace, and then was heated to the temperature between the melting points of aluminum and

titanium. The titanium wire was surrounded by the molten aluminum to form a liquid–solid diffusion couple. To avoid the molten aluminum sticking on the ceramic crucible, the Al_2O_3 powders must be paved in the bottom of the crucible before the diffusion couple is put into it.

To study the evolution and growth behavior of the microstructure of the Al–Ti liquid–solid interface, the diffusion couples were treated at different temperatures between the melting points of aluminum and titanium. For practical industrial applications, the heat treatment temperature should not be too high but ensure that the liquid aluminum has a good wettability to the solid titanium. On one hand it can save energy; on the other hand, it is not easy to control the growth of the DRZ at a too high temperature. Therefore, in this experiment the diffusion couples were treated at 700, 750, 800, 850, and 900 °C and held for 5, 20, 30, and 60 min at each temperature.

After the diffusion couples were treated, ground and polished, the bonding situations and microstructures were observed under optical microscope and scanning electron microscope. Point analysis and line analysis of electron probe were adopted to test the composition of different points and distribution of different elements in the DRZ, and then the phases of the DRZ were determined in combination with Al–Ti binary phase diagram.

3 Results

Figure 1 shows the metallographic images of Al–Ti diffusion couples which were treated at 700 °C. At 700

°C for 5 min, a few gray particles scatter in the Al–Ti interface but there is no evident DRZ. At 700 °C for 20 min, there is a clear DRZ composed of aluminum, sparsely-dispersed gray particles, and plenty of holes. At 700 °C for 30 min, the concentrated degree of the gray particles increases and the pores reduce. At 700 °C for 60 min, the concentrated degree of the gray particles further increases and the holes disappear, and a compact DRZ is formed which is composed of aluminum and the gray particles; the DRZ bonds closely with both the aluminum and the titanium. Precipitates appear neither in the aluminum nor in the titanium outside the DRZ.

Figure 2 shows metallographic images of Al–Ti diffusion couples which were treated at 750 °C for different time. At 750 °C for 5 min, there is a clear DRZ in the Al–Ti interface which is still composed of aluminum and gray particles. The microstructures of the DRZs at 750 °C for 20, 30, and 60 min are similar to those at 750 °C for 5 min, while the thicknesses of the DRZs increase with the extension of holding time. The sizes of gray particles in the DRZs are not very uniform. Some small particles can be seen among the larger ones. Still no new precipitates emerge in the aluminum and the titanium outside the DRZs.

Figures 3–5 show metallographic images of Al–Ti diffusion couples which were treated at 800, 850, 900 °C, respectively. These images show that the DRZs of these samples are composed of aluminum and gray particles, whose microstructures are the same as those treated at 750 °C. At the same temperature, the thicknesses of the DRZs increase with the extension of holding time. The sizes of gray particles in the DRZs are not very uniform,

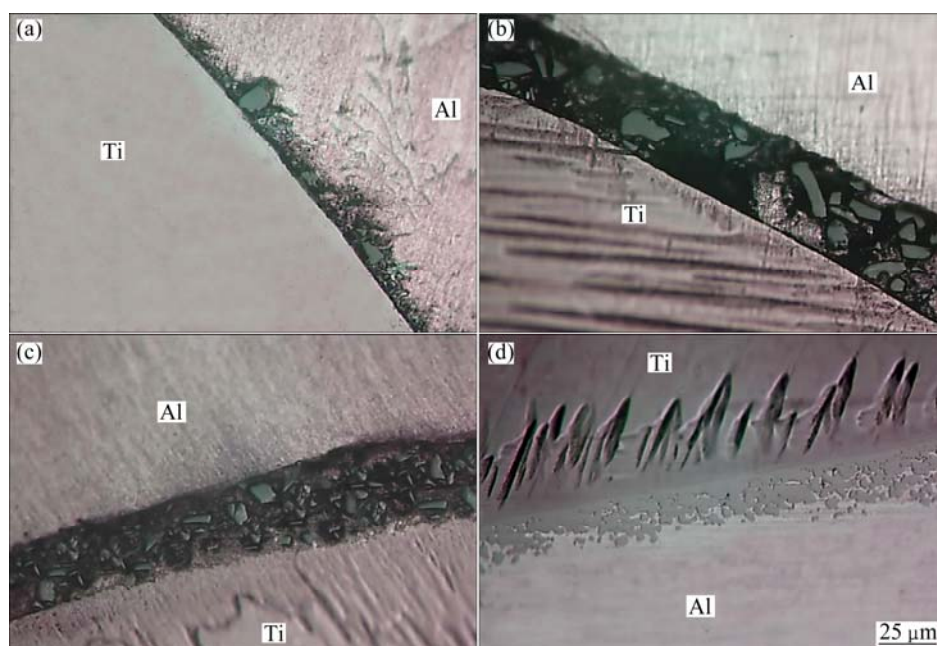


Fig. 1 Metallographic images of Al–Ti DRZ after being treated at 700 °C for different time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 60 min

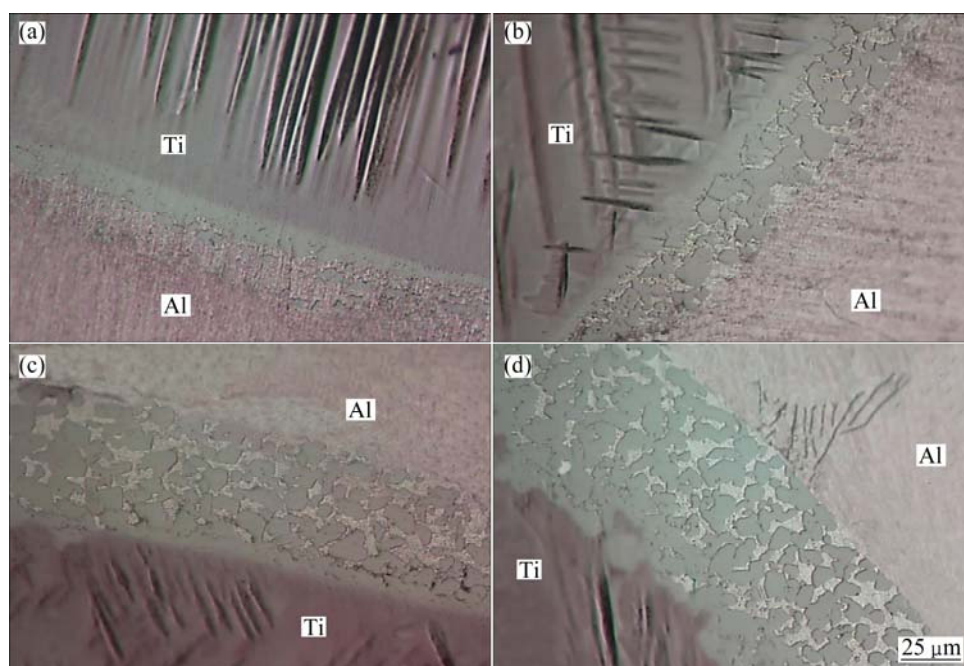


Fig. 2 Metallographic images of Al–Ti DRZ after being treated at 750 °C for different time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 60 min

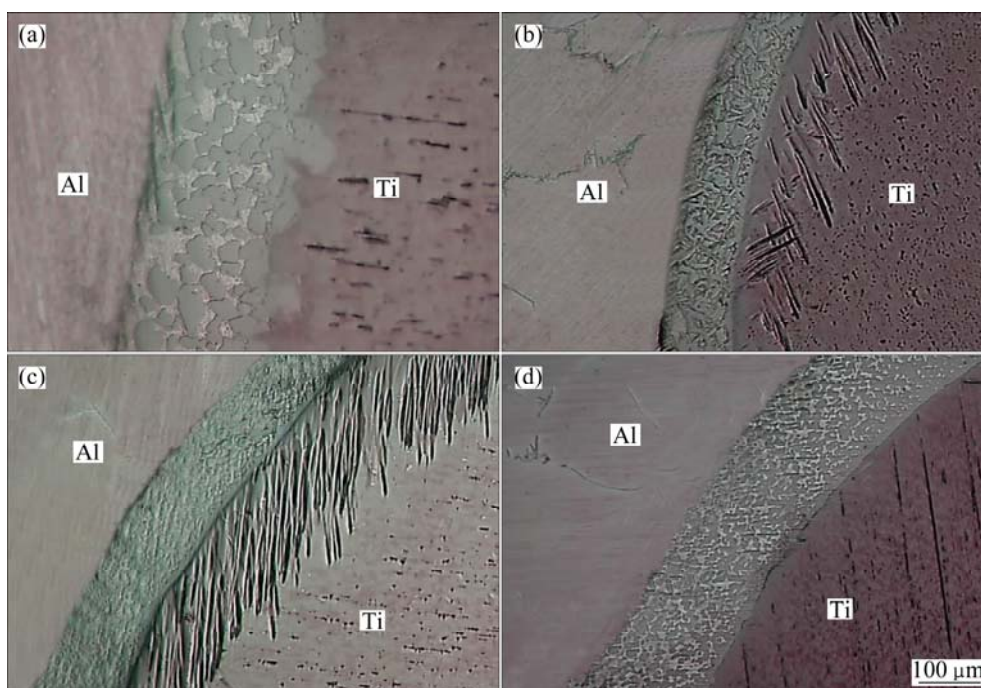


Fig. 3 Metallographic images of Al–Ti DRZ after being treated at 800 °C for different time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 60 min

with some small particles scattering among the larger ones. When the samples are treated at 800 and 850 °C, still no new precipitates emerge in the aluminum and the titanium outside the DRZs. However, when the sample is treated at 900 °C, long rod-like precipitates appear in the aluminum and no new precipitates appear in the titanium (Fig. 6). Moreover, compared with those treated at 850 °C, the DRZ at 900 °C exhibits rapid growth process. In

Al–Ti binary phase diagram (Fig. 7) [19], allotropic transformation of Ti occurs at 882 °C from close packed hexagonal (CPH) α -Ti to body-centered cubic (BCC) β -Ti, which should be the root reason for the sudden variation of experimental phenomena.

To further study the microstructure of the DRZ in the Al–Ti liquid–solid interface, the sample treated at 800 °C for 60 min was investigated by electron

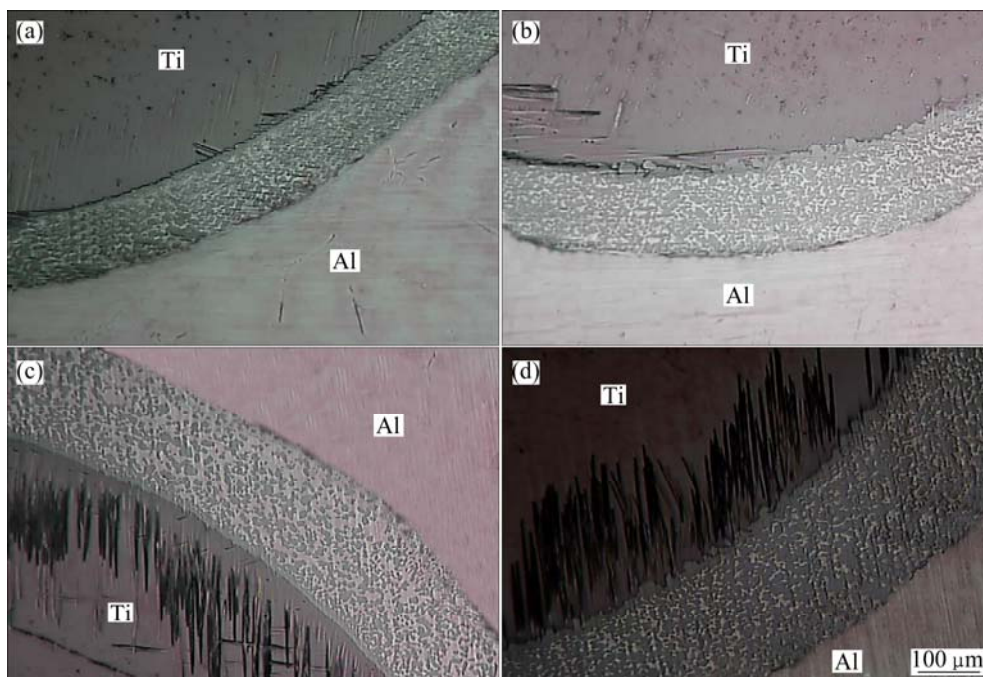


Fig. 4 Metallographic images of Al-Ti DRZ after being treated at 850 °C for different time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 60 min

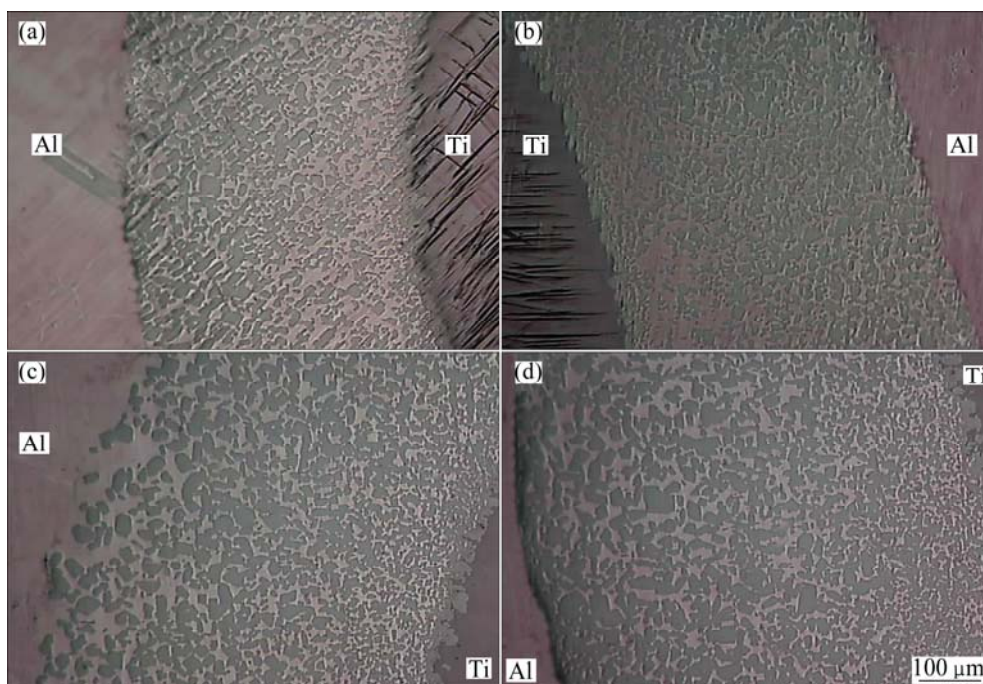


Fig. 5 Metallographic images of Al-Ti DRZ after being treated at 900 °C for different time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 60 min

microprobe spectroscopy. The point positions are shown in Fig. 8(a), and the line scanning curves are shown in Fig. 8(b), and the point analysis results are shown in Table 1.

From the curves of line scanning spectrum, the compositions of Ti and Al vary sharply in the interface between the DRZ and Ti, which indicates the formation

of intermetallic compound. In the DRZ, the spectra of Ti and Al wave dramatically rather than stabilize in a line, which indicates that the DRZ is not a single intermetallic compound layer. Moreover, Ti peak appears when the scanning line crosses the gray particle while Al spectral line varies in the opposite direction. Al peak appears while Ti spectrum intensity is near to zero when the



Fig. 6 Metallographic images of Al substrates after being treated at 900 °C for different time: (a) 5 min; (b) 20 min; (c) 30 min; (d) 60 min

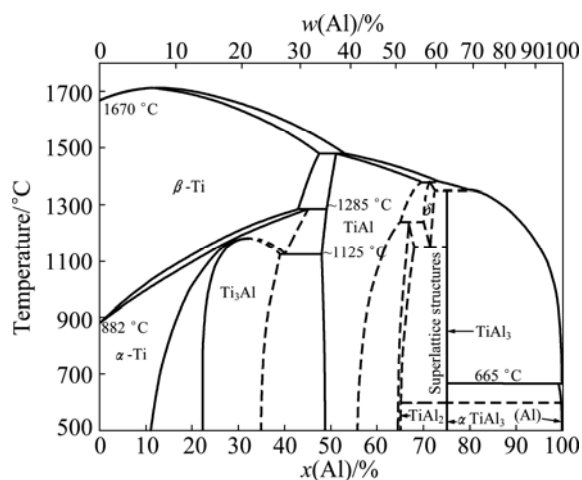


Fig. 7 Al–Ti binary phase diagram

scanning line crosses the black phase. Therefore, it can be concluded that the DRZ is composed of the particle phase and Al solid solution which contains small quantities of Ti. The Al spectrum intensity is near to zero in titanium and the Ti spectrum intensity is near to zero in aluminum, which indicates that neither Al atoms nor Ti atoms diffuse to the other side across the DRZ.

Point spectrum data (Table 1) demonstrate that the contents of Al atoms in points 1, 2, 3, 4, 5 and 6, are 100%, 76.09%, 98.98%, 74.48%, 73.72% and 0 separately. According to Al–Ti binary phase diagram [19], the phases at points 1, 2, 3, 4, 5, and 6 are Al, TiAl_3 , (Al), TiAl_3 , TiAl_3 and Ti, respectively. The DRZ

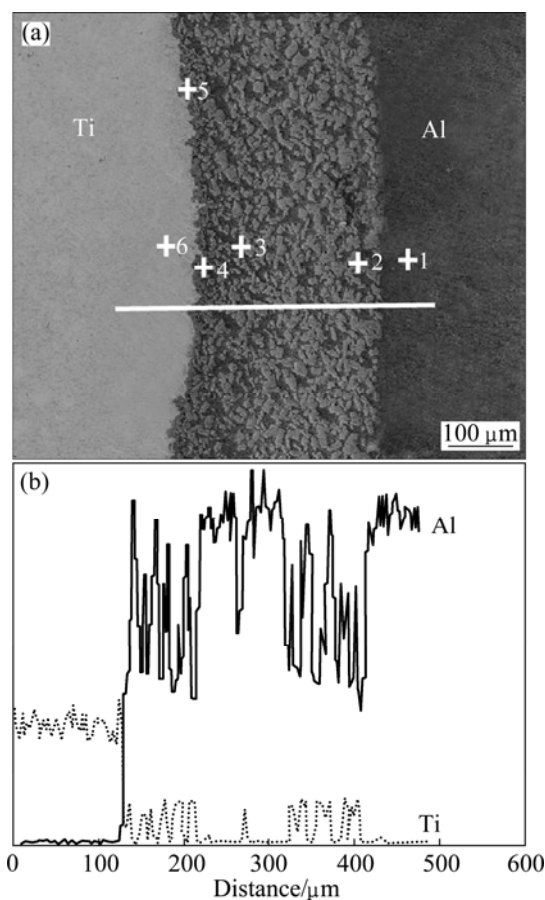


Fig. 8 Line and points for composition analysis of Al–Ti after treatment by EDX: (a) Line and fixed-point locations; (b) EDX spectrum

Table 1 Composition of points in Fig. 8(a) for Al–Ti after treatment at 800 °C for 60 min by EDX

Point	$x(\text{Al})/\%$	$x(\text{Ti})/\%$	Phase
1	100	0	Al
2	76.09	23.91	TiAl ₃
3	98.98	1.02	(Al)
4	74.48	25.52	TiAl ₃
5	73.92	26.08	TiAl ₃
6	100	0	Ti

is composed of TiAl₃ particles and Al solid solution containing a small amount of Ti.

Additionally, long rod-like precipitates in aluminum were investigated through EDS. The contents of Al and Ti atoms are 74.36% and 25.64% respectively, which indicates that the phase is TiAl₃ according to Al–Ti binary phase diagram [19].

Therefore, under the conditions of this experiment, after treatment at temperatures below 900 °C, the microstructure of Al–Ti diffusion couple is Al/(TiAl₃+Al)/Ti. After the treatment at 900 °C, there are long rod-like TiAl₃ precipitates in the aluminum outside the DRZ. TiAl₃ is the only new-formed intermetallic compound in heat treatment process.

4 Discussion

The experiment shows that no evident DRZ was observed when the sample was treated at 700 °C for 5 min, and only a few TiAl₃ particles scattered in some spots. It can be inferred that interdiffusion abilities of Al and Ti are very weak and the effect on the DRZ can be ignored before Al melts.

After Al melts, molten aluminum spreads rapidly under the capillary pressure. Ti contacting molten aluminum begins to dissolve and diffuse to the molten aluminum. Because the solubility of Ti in such conditions is extremely low (about 1% in molten aluminum at 900 °C) [19], Ti atoms saturate soon after they diffuse to molten aluminum, then oversaturated Ti atoms react with Al atoms to form solid TiAl₃. In Al–Ti phase diagram [19], there is coexistence area of solid TiAl₃ and molten aluminum (Fig. 7), so TiAl₃ could nucleate in oversaturated molten aluminum and grow up with the dissolving and diffusing of Ti atoms until TiAl₃ and molten aluminum reach their chemical equilibrium. Therefore, the microstructure of the DRZ in the Al–Ti liquid–solid interface is a mixture structure of Al and gray particles of TiAl₃.

Due to limited dissolution speed of Ti to molten aluminum at 700 °C, few Ti atoms dissolve and diffuse to molten aluminum when the sample is treated for 5 min,

so only few TiAl₃ particles scatter in some spots in the DRZ. When the samples are treated for 20 or 30 min, still few Ti atoms dissolve to molten aluminum, which results in few TiAl₃ particles scattering in the DRZ, and TiAl₃ and molten aluminum do not reach their chemical equilibrium, so there are many holes in the DRZ for the shrinkage of aluminum in the solidification process. When the samples are treated for 60 min, adequate Ti atoms dissolved in the Al–Ti interface to form TiAl₃, which coexists with molten Al to chemical equilibrium, and they form mixed structure after cooling.

When the samples are treated at or above 750 °C, due to the increase of the dissolution speed of Ti to molten aluminum, adequate Ti atoms diffuse into the DRZ and enough TiAl₃ forms to reach the chemical equilibrium with the molten aluminum even for 5 min, which forms compact mixture structure of TiAl₃ and Al after cooling. With the extension of holding time, Ti will continue to decompose, diffuse and react, which gives rise to increasing of the thickness of the DRZ.

In the process of cooling, the secondary TiAl₃ nuclei precipitate from the molten aluminum in the DRZ for the lower solubility of Ti atoms until the temperature lowers to 665 °C. Yet the solubility of Ti atoms in molten aluminum in the experiment is approximate to that at room temperature, so there are few TiAl₃ precipitates during this period. Cooling to 665 °C, a portion of TiAl₃ and molten aluminum in the DRZ make peritectic reaction to form solid solution of aluminum. With the temperature going down, tertiary TiAl₃ nuclei precipitate for the decreasing of solubility of Ti atoms in Al solid solution, which causes nonuniformity of sizes of TiAl₃ particles in the DRZ. Some small-size TiAl₃ particles should be the secondary TiAl₃ and tertiary TiAl₃ in cooling process.

According to the structure evolution of Al–Ti liquid–solid interface, the growth of Al–Ti DRZ should be decided by three factors such as the dissolution speed of titanium to molten aluminum, the diffusion speed of Ti atoms into the molten aluminum and the chemical reaction speed of Ti atoms and Al atoms to form TiAl₃. The growth speed of DRZ is determined by the lowest speed of the above-mentioned three factors.

It is found that the growth speed of the DRZ varies dramatically at 900 °C due to the allotropic transformation of solid Ti from CPH α -Ti to BCC β -Ti. Allotropic transformation of titanium directly affects the dissolution speed of Ti to molten aluminum. Thus it can be concluded that the growth speed of the DRZ before the allotropic transformation of titanium is determined by the dissolution speed of Ti to molten aluminum. In other words, the dissolution speed of titanium to molten aluminum is slower than the diffusion speed of Ti atoms in molten aluminum and chemical reaction speed of Ti

atoms and Al atoms. Therefore, no extra Ti atoms diffuse forward during the chemical reaction until the chemical reaction zone reaches the equilibrium between TiAl_3 and molten aluminum, and chemical reaction stops at this moment, which enables post-dissolved Ti atoms to diffuse forward across the zone. When the next neighbor area saturates, Al atoms and Ti atoms are involved in chemical reaction until TiAl_3 and molten aluminum reach chemical equilibrium, then post-dissolved Ti atoms continue to diffuse forward, so this process moves in cycles. By this way, the DRZ gets thicker, and the growth interface moves towards the aluminum side. Therefore, the DRZ grows layer by layer which is composed of mixed phase of TiAl_3 and aluminum with chemical equilibrium, and no extra Ti atoms diffuse into the aluminum outside the DRZ all along. Thus when samples are treated below phase transformation temperature of Ti, no precipitates are observed in the aluminum outside the DRZ, and the growth speed of the DRZ is determined by the dissolution speed of Ti to molten aluminum.

When the sample was treated at 900 °C, the growth speed of the DRZ increases sharply and long rod-like TiAl_3 precipitates appear in the aluminum outside the DRZ, which indicates that part of Ti atoms are involved in chemical reaction and redundant parts continue to diffuse into the aluminum outside the DRZ. At this moment, the dissolution speed of Ti to molten aluminum increases rapidly for the allotropic transformation of Ti, which exceeds the chemical reaction speed between Al atoms and Ti atoms, that is, the growth of the DRZ is dominated by the chemical reaction speed. TiAl_3 nuclei separate out from the molten aluminum since solubility of Ti atoms decreases in the cooling process, and

long-distance diffusion ability of Ti atoms is strong due to the high precipitation temperature. When the temperature lowers to 750 °C, the solubility of Ti is similar to that at room temperature, which signifies the completion of precipitation process. Since the whole process of precipitation occurs at higher temperature, and Ti atoms keep their strong long-distance diffusion ability to ensure the growth of TiAl_3 to a certain direction, therefore, all TiAl_3 precipitates in the aluminum outside the DRZ are of long rod shape.

Therefore, the growth mechanism of the DRZ in Al–Ti liquid–solid interface varies after the phase transition of Ti, from being dominated by the dissolution speed of Ti to molten aluminum to being dominated by the chemical reaction speed of Al atoms and Ti atoms.

In the heat treatment conditions of this experiment, TiAl_3 is the firstly formed phase. In Ref. [20], it has been proved that among all Ti–Al compounds, TiAl_3 , TiAl and Ti_3Al could be directly formed by the reaction between Ti and Al, while TiAl_2 and Ti_2Al_5 could be formed only through a series of intermediate reactions, in which TiAl is the intermediate product. The relationship between Gibbs energy of formation of Ti–Al compounds and temperature was also calculated in Ref. [20], and energy of formation of TiAl_3 is the lowest among all Ti–Al compounds, therefore, TiAl_3 is formed first. In the conditions of this experiment, there is sufficient molten aluminum to supply Al atoms for the nucleation and the growth of TiAl_3 , so TiAl_3 is the only new-formed phase. Only when the holding time is longer than the time that molten aluminum is totally consumed, the other new phases could be formed.

To sum up, the microstructure evolution process of Al–Ti liquid–solid interface is shown in Fig. 9.

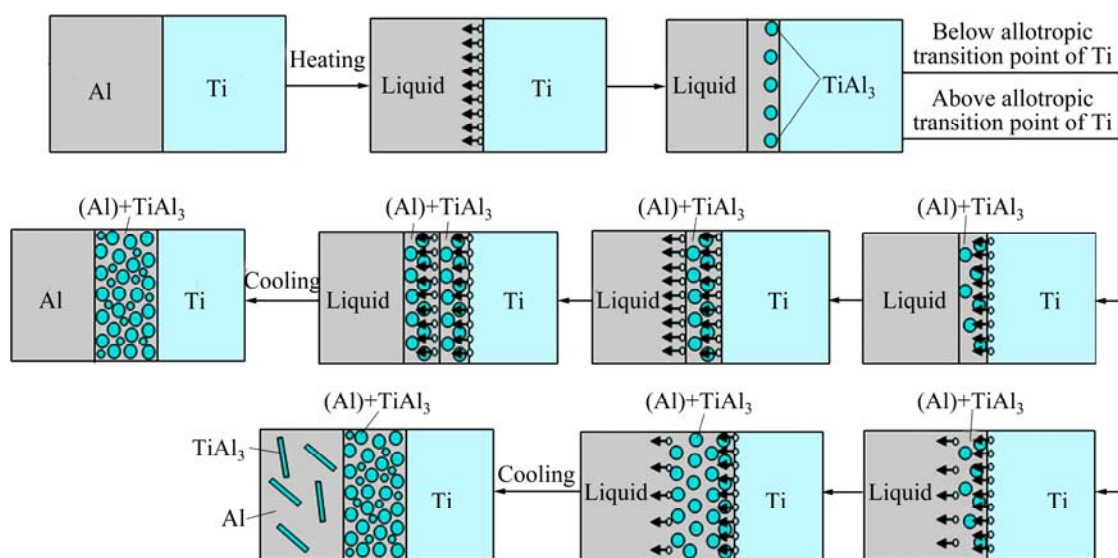


Fig. 9 Schematic of microstructure evolution in Al–Ti liquid–solid interface

5 Conclusions

1) When the molten aluminum has not been completely consumed, the DRZ is the mixture of TiAl_3 and Al, and grows layer by layer where TiAl_3 and molten aluminum reach their chemical equilibrium. TiAl_3 is primarily formed and is the only new phase.

2) The growth mechanism of the DRZ differs before and after the allotropic transformation of Ti. Before the allotropic transformation of Ti, it is dominated by dissolution speed of Ti into molten aluminum; while after the allotropic transformation of Ti, it is dominated by chemical reaction speed of Al atoms and Ti atoms, and the growth speed increases greatly.

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Al–Ti 液固界面的组织结构演变

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摘要: 采用镶嵌式扩散偶技术制备 Al–Ti 扩散偶, 在 Al 熔点以上, Ti 熔点以下进行扩散热处理, 研究 Al–Ti 液–固界面扩散反应层的组织结构演变及生长机制。实验结果表明, 热处理后的扩散反应层为 TiAl_3 颗粒和铝的混合组织, 以 TiAl_3 和液相铝的平衡化学位共存区逐层生长, 生长界面朝铝基一侧移动; TiAl_3 相是热处理过程中最先出现也是唯一出现的新生相; 钛相变前后, 扩散反应层的生长机制发生了改变。相变前, 由钛向液相铝中的溶解速度控制; 相变后, 转变为 Al、Ti 原子的化学反应速度控制, 生长速度大幅度加快。

关键词: Al–Ti 液固界面; 扩散反应层; 组织演变; 生长机制

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