Solid-State Hot Pressing of Elemental Aluminum and Titanium Powders to Form TiAl ($\gamma + \alpha_2$) Intermetallic Microstructure

J.B. Yang, K.W. Teoh, and W.S. Hwang

The elemental powder metallurgy (EPM) process is used to prepare TiAl-base intermetallics. An EPM process conducted by two-stage solid-state hot pressing was employed to prepare TiAl-base intermetallics and to investigate the resulting microstructural changes. The results showed that the $TiAl_3$ phase forms in the first stage. During the temperature increase to the second sintering stage, lamellar phases start to precipitate in the $TiAl_3$ matrix. Further, the $TiAl_3$ phase transforms to TiAl, and Ti_3Al layers develop in the remaining titanium particles. Meanwhile, the lamellar phases grow into ring-type structures between the TiAl matrix and the Ti_3Al layers. After the second stage, the remaining titanium particles are fully reacted, and a microstructure of Ti_3Al phases enclosed by fine-grained lamellar rings in the TiAl matrix is developed.

Keywords
APM, EPM, Kirkendall effect

1. Introduction

THE EXCELLENT high-temperature properties of TiAl-base intermetallics make these materials potential alternatives to superalloys for aerospace engine and structural parts applications. Because of their poor workability, powder metallurgy is an effective forming approach for TiAl intermetallics. This process can be conducted in two ways: elemental powder metallurgy (EPM) and alloy powder metallurgy (APM). Elemental powders are cheaper and have better formability than alloy powders. Therefore, EPM has been widely studied for the preparation of TiAl intermetallics (Ref 1-7). In general, the fabrication steps of EPM include mixing of pure aluminum and titanium powders, compacting and extruding the mixture, and sintering either with pressure by using hot isostatic pressing (HIP) (Ref 2-4) or without pressure (Ref 5, 6). Because of the large difference in diffusivity between titanium and aluminum, pores are formed during pressureless sintering due to the Kirkendall effect (Ref 1-4). Hot isostatic pressing is also employed after pressureless sintering to eliminate the Kirkendall pores and to prepare the dense TiAl intermetallics (Ref 2, 3).

During sintering in an EPM process, interdiffusion between aluminum and titanium occurs and some intermediate phases are formed. When the heating cycle is completed, the final TiAl-base intermetallic is obtained. Depending on the annealing temperature, the microstructures of TiAl-base intermetallics can be divided into four groups (Ref 1, 2, 8). A dual phase is formed by annealing below the eutectoid temperature. A partially lamellar structure or a duplex structure is formed when annealing is between the eutectoid temperature and the α-transus temperature, depending on the annealing time. A fully lamellar structure is formed when the annealing temperature is above the α-transus temperature.

Diffusion experiments were conducted by van Loo and Rieck (Ref 9, 10) with Ti-Al and Ti-$TiAl_3$ diffusion couples annealed at 516 to 642 °C and at 870 °C, respectively. The annealing was undertaken to investigate the microstructural changes resulting from interdiffusion between aluminum and titanium. Only $TiAl_3$ was formed within the first diffusion couple (Ref 9), and some intermediate phases such as $TiAl_2$, γ-TiAl, and α_2-Ti_3Al were found within the second diffusion couple (Ref 10). Based on these results, it was proposed that $TiAl_3$ formed first at the interface between titanium and aluminum for the reaction sequence during the EPM process from the Ti+Al powder compact to the final ($\gamma + \alpha_2$)-type TiAl intermetallics. After further diffusion, aluminum was consumed and intermediate phases (e.g., $TiAl_2$, TiAl, and Ti_3Al) developed between titanium and $TiAl_3$. Finally, ($\gamma + \alpha_2$)-type TiAl intermetallics were obtained (Ref 2). However, a differential scanning calorimetry (DSC) test conducted by Rawers et al. (Ref 11), with a heating rate of 10 °K/min from room temperature to 1200 °C, showed that the intermediate phases developed during heating.

In this study, an EPM process conducted by solid-state hot pressing was used to prepare ($\gamma + \alpha_2$)-type TiAl intermetallics and to investigate the microstructural evolution.

2. Experimental Procedures

The Ti-48 at.% Al powder mixture was prepared with pure titanium and aluminum powders. The powders had a purity of approximately 99.5%, and the particle sizes were 149 μm and 44 to 149 μm, respectively. Each mixture was blended for 2 h in a ball mixer. The powder mixture was pressed to form a green compact under a pressure of 12.5 kg/mm^2 at room temperature. Then, the compact was hot pressed in a protective argon atmosphere to form a sintered billet (25 mm diam and 10 mm high). During hot pressing occurred a continuous two-stage sintering process that included a solid-state diffusion stage and a densification stage. In the solid-state diffusion stage, the material was sintered at 630 °C for 22 h under a pressure of 45 MPa during

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the first 5 h. Then the temperature was raised to 1250 °C at 20.6 °C/min. For the densification stage, the material was sintered at 1250 °C for 2 h under a pressure of 45 MPa.

The sintering procedure is illustrated in Fig. 1. The idea was to eliminate the elemental aluminum in the first solid-state stage and to densify the specimen in the second stage. The purpose of applying pressure in the initial 5 h of the first stage was to break the surface oxide layer of powder particles by deformation and to maintain good contact between particles (Ref 3). This could be achieved because aluminum particles are very soft at 630 °C. Phase determination was performed by x-ray diffraction (XRD) analysis, and microstructural observation was conducted using an optical microscope and a scanning electron microscope (SEM).

3. Results and Discussion

To study the microstructural evolution, several specimens were prepared for observation. They represented sintering times of 5 and 22 h during the solid-state diffusion stage, temperatures of 950, 1100, and 1250 °C during the heating cycle, and the condition after the densification stage.

3.1 *Phase Transformation during the Solid-State Diffusion Stage*

Figure 2 shows the microstructure after sintering at 630 °C and under 45 MPa for 5 h. The elemental aluminum is largely deformed and kept in good contact with the titanium particles. Diffusion layers of $TiAl_3$ develop between aluminum and titanium particles (Ref 1-4). During pressureless sintering at 630 °C, the diffusion layers grow wider. Pores resulting from the Kirkendall effect form and grow increasingly larger. At the end of the solid-state diffusion stage, some titanium particles remain, which are enclosed by $TiAl_3$ diffusion layers, and pores are present in the microstructure (Fig. 3). No significant amount of aluminum can be observed optically. X-ray diffraction analysis during this stage shows that aluminum gradually disappears and that some titanium remains while $TiAl_3$ is formed (Fig. 4a to c). Some elemental aluminum is still detected at the end of the solid-state diffusion stage.

3.2 *Phase Transformation during the Temperature Increase from 630 to 1250 °C*

Figure 5 shows that the pores previously formed in the solid-state diffusion stage are pressed into particle boundaries and

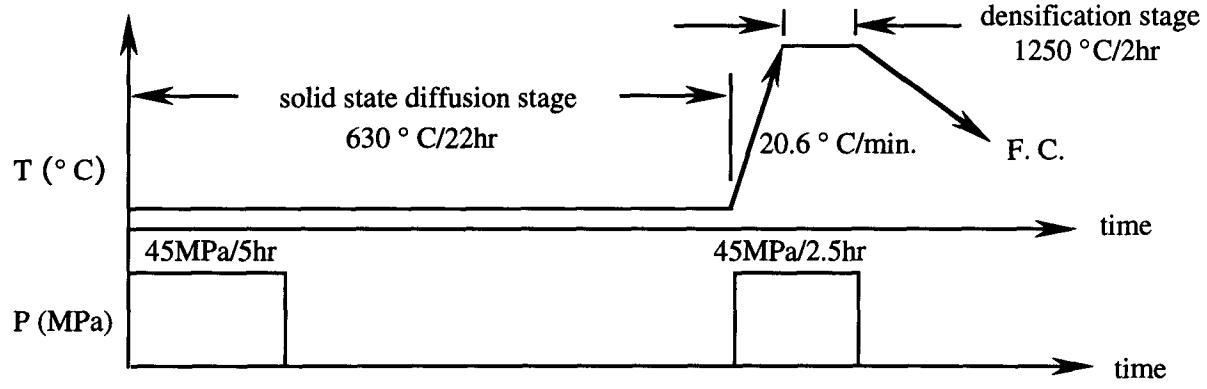


Fig. 1 Solid-state hot pressing procedure

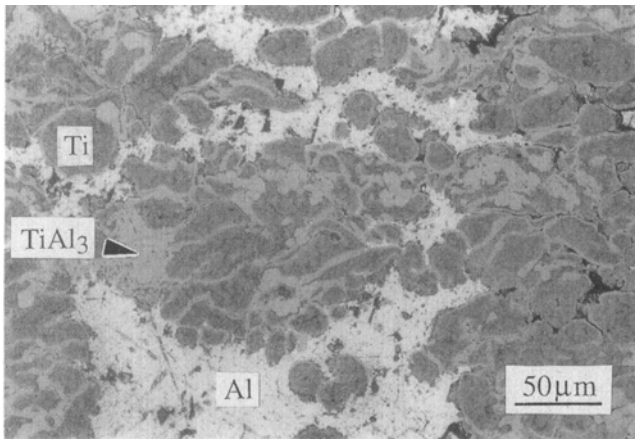


Fig. 2 Microstructure of green compact after the first 5 h of the solid-state diffusion stage

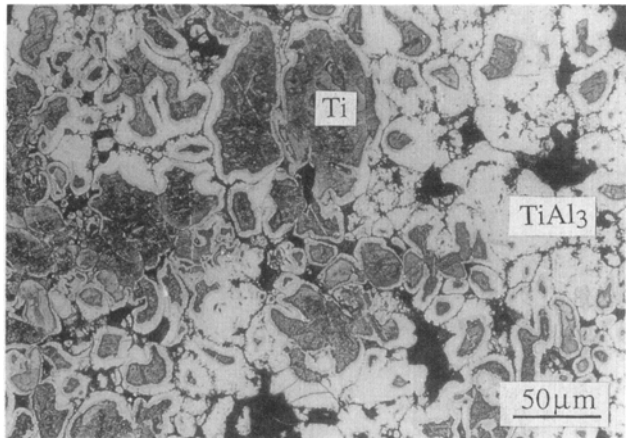


Fig. 3 Microstructure of green compact at the end of the solid-state diffusion stage

that some titanium particles still remain when temperature is raised to 950 °C. Meanwhile, some precipitates are formed in the $TiAl_3$ matrix, which is the previous diffusion layer. X-ray diffraction analysis shows that Ti_3Al and TiAl start to form at this temperature (Fig. 4d). The formation of these two phases was also detected by Rawers et al. (Ref 11) during DSC testing at approximately 675 and 725 °C.

Figure 6 shows that the precipitates grow and appear lamellar in shape around the particle boundaries, which form a triangular junction due to the impingement of the $TiAl_3$ matrix when the temperature is raised to 1100 °C. The remaining titanium particles become smaller, and diffusion layers develop due to a higher mobility of titanium at this temperature. Therefore, the precipitates observed at 950 °C can be considered precursors of the lamellar phase, which is a mixture of γ-TiAl and α_2-Ti_3Al. Because the eutectoid temperature is around 1125 °C (Ref 1, 2), the heatings at 950 and 1100 °C are within the $(\gamma + \alpha_2)$ two-phase region. Therefore, the lamellar phase will develop when interdiffusion occurs between titanium in the remaining particles and aluminum in $TiAl_3$ matrix. X-ray diffraction analysis shows that TiAl and Ti_3Al quickly form and that titanium and $TiAl_3$ decrease in this period (Fig. 4e). The diffusion layer analyzed by the energy-dispersive x-ray technique exhibits as a titanium-rich phase. It can be considered to be a Ti_3Al phase resulting from quick diffusion of titanium from the remaining titanium particles.

When the temperature is raised to 1250 °C, which is above the eutectoid temperature, the remaining titanium particles are fully reacted and the lamellar phase develops into a ring-type structure (Fig. 7), instead of the dispersed precipitates previously formed around the particle boundaries. X-ray diffraction analysis shows that TiAl and Ti_3Al increase continuously, whereas $TiAl_3$ almost disappears and no titanium can be detected (Fig. 4f). Other than the lamellar phase ring, two distinct areas can be distinguished by x-ray image analysis. One is a titanium rich area enclosed by the lamellar phase ring; the other is an aluminum-rich area that includes the particle boundary. This can be seen in Fig. 7(c). The former is considered to be the Ti_3Al phase, which evolves from the growth of Ti_3Al diffusion layer. The latter is the TiAl phase, which develops from the $TiAl_3$ matrix. These phase transformations are also carried out by the interdiffusion between aluminum and titanium.

There is a reason behind the development of the lamellar phase ring. When the ring area around the remaining titanium particle has a composition corresponding to that of the eutectoid phase, the eutectoid reaction where α transforms to $\alpha_2 + \gamma$ will occur after cooling. Although it was reported that $TiAl_2$ phase formed after extensive annealing at 870 °C (Ref 10), no significant amount of $TiAl_2$ is present during the temperature increase. Because the XRD pattern of $TiAl_2$ is similar to that of TiAl except for the (011) peak of $TiAl_2$, this peak can be used to confirm the formation of $TiAl_2$. No significant intensity of the peak is observed from the XRD data during the temperature increase.

3.3 *Phase Transformation after the Densification Stage*

The microstructure after the densification stage is shown in Fig. 8. The particle boundaries are almost completely eliminated. Some micropores are left, all of which are no larger than 10 μm. The lamellar phase rings grow, and the lamellar grains develop to a size of 20 to 30 μm. The orientation of the lamellar phase is random. The grains in the matrix and in the rings can be observed by optical microscope only under polarized light (Ref 5). X-ray diffraction analysis for this case shows that only the TiAl and Ti_3Al phases are present (Fig. 4g). X-ray image analysis also shows two areas separated by the fine-grained la-

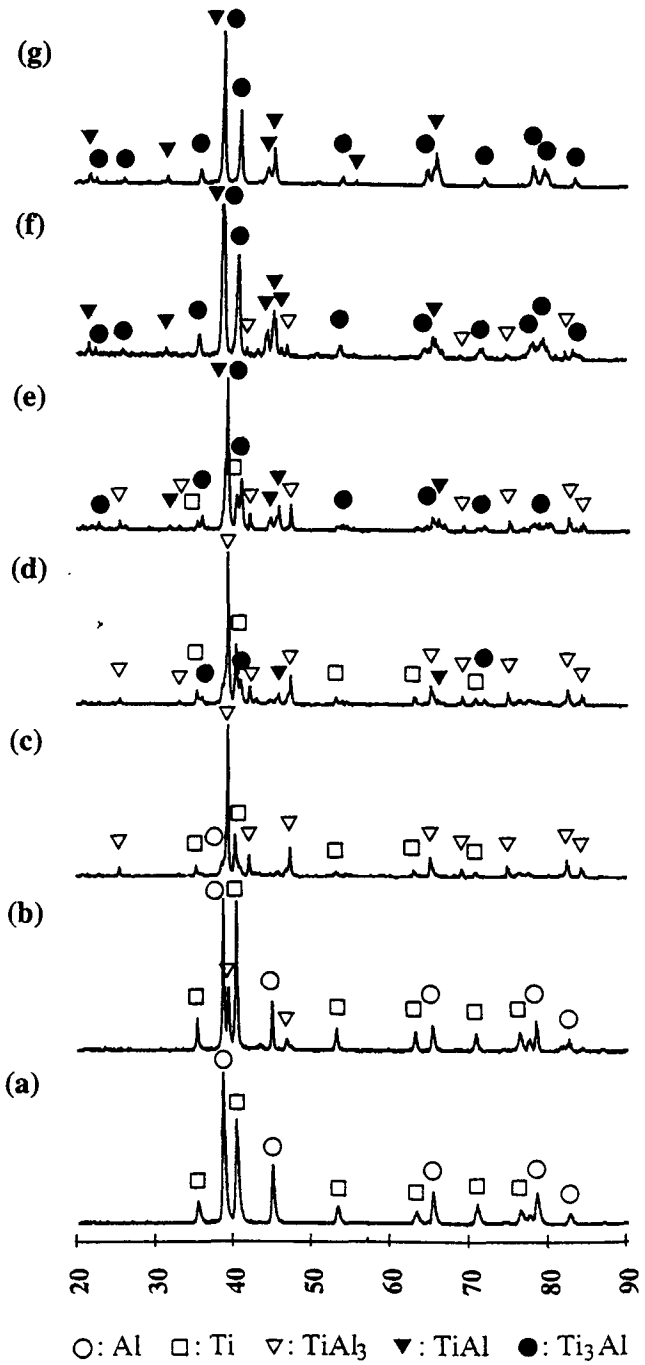
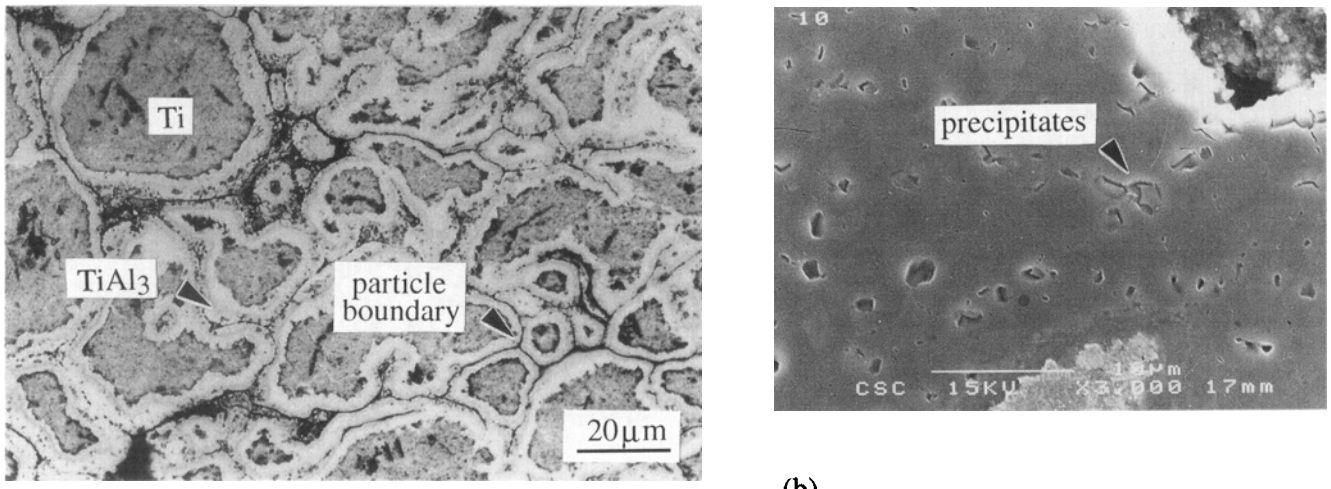
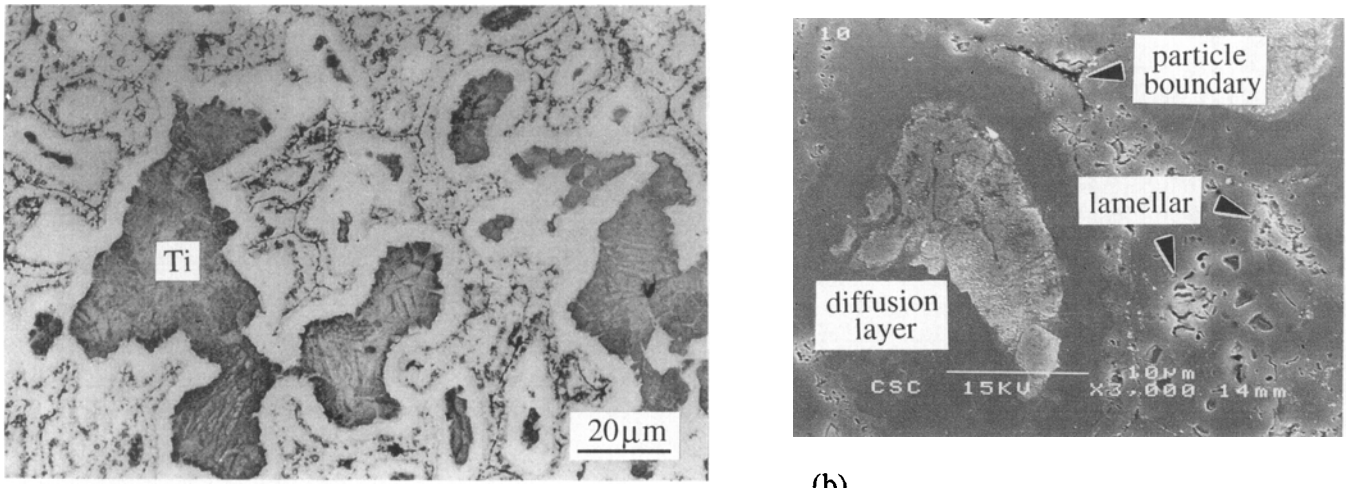


Fig. 4 X-ray diffraction analysis through the solid-state hot pressing procedure. (a) As compacted. (b) 630 °C/5 h. (c) 630 °C/22 h. (d) Heating to 950 °C. (e) Heating to 1100 °C. (f) Heating to 1250 °C. (g) 1250 °C/2 h



(a) (b)

Fig. 5 Microstructure formed when the temperature is increased to 950 °C. (a) Optical micrograph. (b) SEM micrograph



(a) (b)

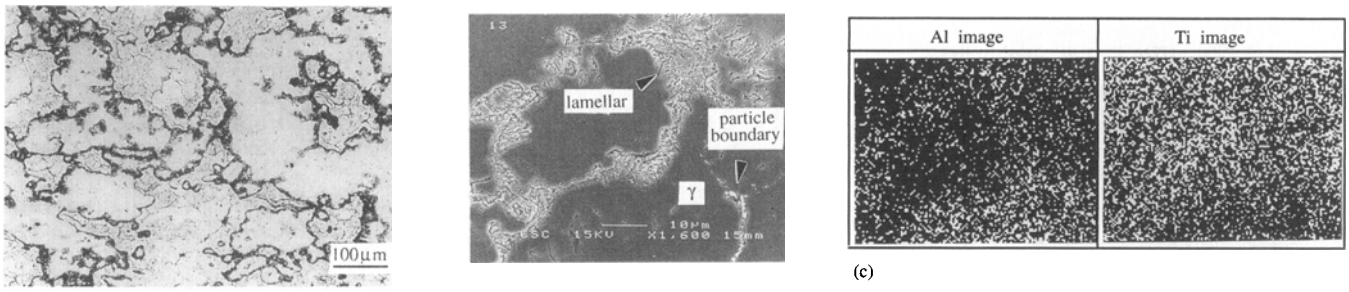
Fig. 6 Microstructure formed when the temperature is increased to 1100 °C. (a) Optical micrograph. (b) SEM micrograph

mellar ring. One is rich in titanium and can be identified as Ti_3Al. The other is rich in aluminum and can be identified as TiAl. These are shown in Fig. 9.

4. Conclusions

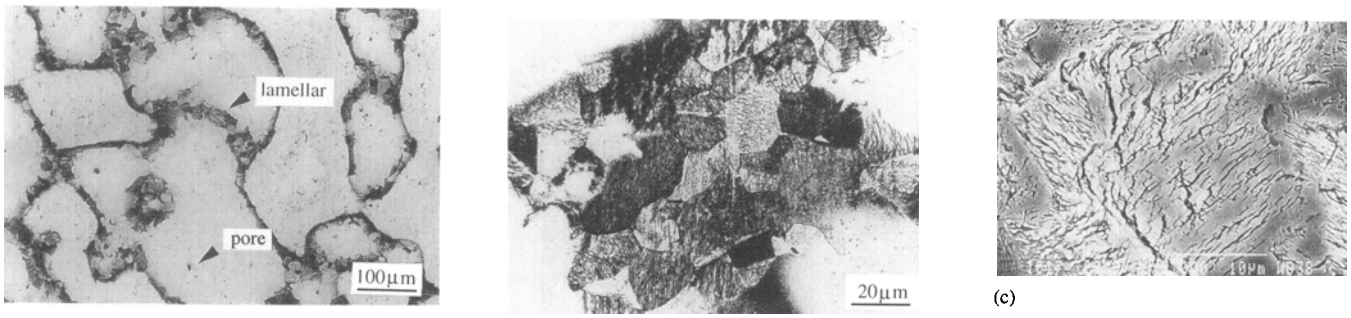
This study demonstrated that the dense $(\gamma + \alpha_2)$-type TiAl intermetallics can be prepared from elemental powders via a two-stage solid-state hot pressing process. The microstructural changes that occur during hot pressing, which is different from the previous liquid phase sintering, can be summarized:

- A diffusion layer of $TiAl_3$ forms between the titanium and aluminum particles during the solid-state diffusion stage. Heating for 22 h at 630 °C is necessary to eliminate most of the elemental aluminum in the green compact.
- During the temperature increase from 630 to 1250 °C, $(\gamma + \alpha_2)$ lamellar phases first precipitate in $TiAl_3$ matrix. The remaining titanium particles then gradually disappear, accompanied by the development of Ti_3Al diffusion layers in the vicinity. Meanwhile, the lamellar precipitates develop as a ring-type structure. Finally, the area of the previously remaining titanium particles transforms to Ti_3Al enclosed by the fine-grained lamellar rings. The original $TiAl_3$ matrix transforms to TiAl.
- After the conclusion of the densification stage, which is annealing at 1250 °C for 2 h under a pressure of 45 MPa, particle boundaries are eliminated and micropores no larger than 10 μm are formed. The dense TiAl-base intermetallic is obtained, with Ti_3Al enclosed by a fine-grained $(\gamma + \alpha_2)$ lamellar ring in the TiAl matrix.



(a) (b) (c)

Fig. 7 Microstructure formed when the temperature is increased to 1250 °C. (a) Optical micrograph. (b) SEM micrograph. (c) X-ray image analysis of (b)



(a) (b) (c)

Fig. 8 Microstructure formed after the densification stage (1250 °C/2 h). (a) Optical micrograph. (b) Grains in the lamellar ring. (c) SEM micrograph of the lamellar phase

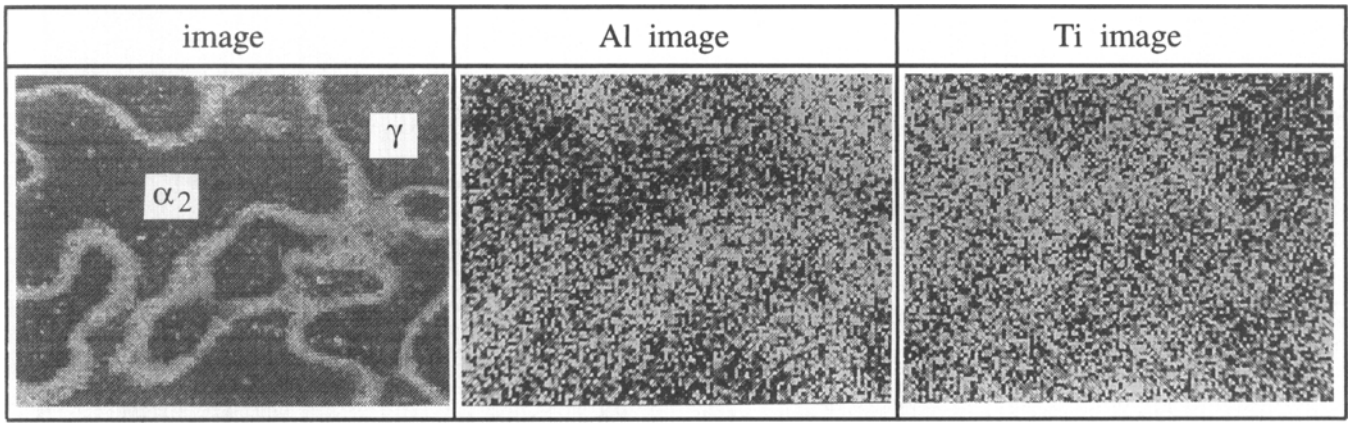


Fig. 9 X-ray image analysis after the densification stage (1250 °C/2 h)

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