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The Preparation of TiAl-Based Intermetallics from Elemental Powders through a Two-Step Pressureless Sintering Process

J.B. Yang and W.S. Hwang

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Pressureless sintering is not considered feasible for the preparation of TiAl-based intermetallics from elemental powders due to the Kirkendall effect. When the compacts are sintered without pressure, swelling and surface cracking occur in the billets. Porous billets are obtained, which cannot be further used. Nevertheless, pressureless sintering is still worth investigating because of lower cost and easier operation. In this study, a two-step pressureless sintering process was developed to prepare the TiAl-based intermetallic preforms. The first step was to eliminate the aluminum particles in the billets through a solid-state sintering procedure to prevent the aluminum from melting and to suppress the formation of the Kirkendall pores by sintering with a constrained mold. The second step was to make the billets homogenized and densified by a high-temperature sintering procedure. Results show that the billets sintered with constrained molds are dense and crack free after the first step. Then, the billets are densified in the second step. Therefore, the application of constrained molds makes pressureless sintering feasible in the preparation of the TiAl-based intermetallics from the elemental powders. The microstructure is fully transformed from the aluminum and titanium compacts to the TiAl-based intermetallics after this two-step pressureless sintering process.

Keywords constrained, duplex, lamellar, Kirkendall effect, pressureless

1. Introduction

Elemental powder metallurgy (EPM) is one of the processes used to prepare TiAl-based intermetallics, which use elemental titanium and aluminum powders as the starting materials. However, the difference in diffusivities between titanium and aluminum is so large that the Kirkendall effect occurs during the sintering process (Ref 1-5). When the sintering procedure is conducted without pressure, swelling and cracking form in the sintered billets due to the formation of the Kirkendall pores (Ref 4, 5). Eventually, loose and brittle billets are obtained. If sintering temperatures above the melting point of aluminum are used for quick diffusion, that is liquid-phase sintering, aluminum is melted and flows out due to gravity. As a result, cavities are left in the billets (Ref 5), and this makes the billets even more loose. Therefore, the conventional EPM process has to be conducted by the pressurized sintering.

In general, the hot isostatic pressure (HIP) process, which is conducted through liquid-phase sintering, can suppress the Kirkendall pores and prepare dense TiAl-based intermetallics (Ref 1, 4, 6). However, the green compacts for HIP have to be canned to prevent overflowing of aluminum melt (Ref 3, 7). With HIP, the sintered billets are deformed into an irregular shape due to the squeezing of the aluminum melt under high pressure (Ref 4, 8). A significant amount of machining is needed to reach the desired shape. However, it is difficult for TiAl-based intermetallics to be machined due to poor machinability. Therefore, the near desired shape of the sintered billets is desired for subsequent machining.

Although pressureless sintering is not considered feasible in EPM, the dense TiAl-based intermetallics can still be prepared through pressureless sintering by heavy working on green compacts. It has been reported that large extrusion ratio or high-degree deformation on the green compacts can reduce the porosity ratio of the billets sintered without pressure due to the refinement of the elemental aluminum regions in the green compacts (Ref 2, 3, 5). When the elemental aluminum diffuses, pores are formed in the original elemental aluminum regions. Thus, the finer the elemental aluminum regions are, the smaller are the formed Kirkendall pores. However, although this procedure may be suitable for making raw materials such as plate, rod, and wire, it is not feasible to make the shaped powder metallurgy (PM) parts through the conventional PM process because the green compacts are made by compacting the mixture of powders in a conventional PM process. The elemental aluminum regions in the shaped compacts cannot be refined by large deformation such as extrusion or rolling. Therefore, to prepare the PM parts of TiAl-based intermetallics from the elemental powders through the conventional pressureless PM process, it is necessary to suppress the formation of the Kirkendall pores in the billets during sintering. Moreover, aluminum has to be fully diffused in the solid state, which means that the sintering temperature is below the melting point of aluminum, 665 °C. However, the intermediate $TiAl_3$ is formed and is stable during the low-temperature solid-state diffusion. Therefore, the higher-temperature sintering should be followed for quick diffusion to form the final TiAl-based intermetallics.

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In this study, a modified PM process was developed to prepare the TiAl-based intermetallic billets with the desired shape from elemental powders, which can reduce subsequent machining. This process includes two pressureless sintering steps, which are low- and high-temperature sintering. During low-temperature sintering, the compact is confined with a constrained mold and sintered in solid state. Then the sintered billet is further sintered through high-temperature sintering. The effects of process variables, such as compacting pressure, application of the constrained mold, sintering temperature, and sintering time on the densities of the specimen, as well as phase transformation during these two pressureless sintering steps, are investigated.

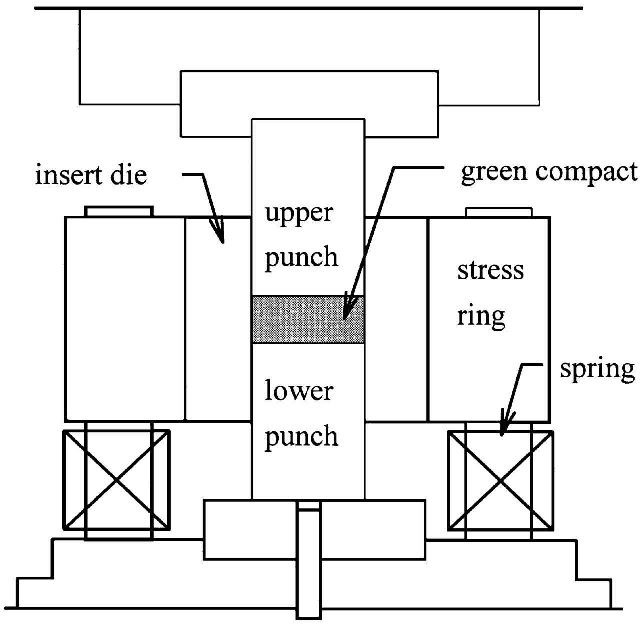


Fig. 1 A schematic illustration of the floating die for compaction

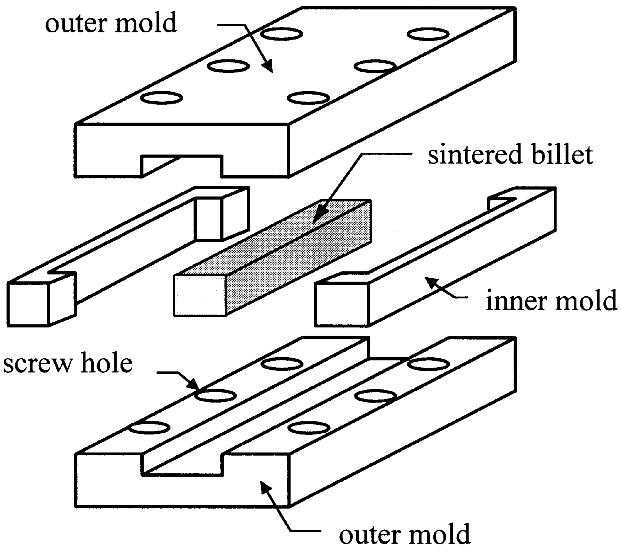


Fig. 2 A sketch of the constrained mold for the low-temperature sintering step. The billet is constrained by the inner molds and put in the outer molds. Then, the outer molds are tightened by screws

2. Experimental Procedures

The Ti-48at.%Al powder mixture was prepared with elemental titanium and aluminum powders. The powders obtained from CERAK Co. were approximately 99.5% pure and the particle sizes of the aluminum and titanium powders were 149 μm and ~44 to 149 μm, respectively. Each mixture was blended for two hours in a ball mixer. The mixture was pressed under the pressure of 250, 500, 750, and 1000 MPa at room temperature in a floating die to form the green compacts. The application of a floating die was expected to exert a biaxial pressing and to produce green compacts with uniform density. Figure 1 shows the design of the floating die. The dimensions of the green compact were 49.5 mm in length, 11.5 mm in width, and ~14.1 to 15.8 mm in height. The compacts had various heights due to different compacting pressures. The compacts were grounded to ~14.1 mm high.

The green compacts were then placed in a constrained mold. The design of the constrained mold fully enclosed the compact. The dimensions of the mold cavity were slightly larger than those of the billet by 0.1 mm on each side. The billet was first constrained by the inner molds and put in the outer molds. Then, the outer molds were tightened by screws. Figure 2 shows a sketch of the constrained mold. The die material was AISI 4340 and was heat-treated to ~35 to 40 HRC. The compacts were coated with boron nitride before they were put into the constrained molds for sintering under argon atmosphere. The purpose of the mold application was to confine the billets to suppress swelling during sintering and to minimize formation of Kirkendall pores.

The sintering process was then conducted without pressure in two steps, as shown in Fig. 3. The first step was low-temperature sintering, which was conducted at 645 °C for 15 h. During this step, the aluminum was eliminated in solid state. The compacts were also sintered with and without the constrained molds to investigate the effects of the constrained molds on the density of the billets. Then the billets were taken out of the constrained molds to be sintered in the second step, high-temperature sintering, which was conducted at 1250 °C for 6 h. The purposes of the second step were to homogenize the sintered billets and densify them by quick diffusion at high temperature. Phase determination was then performed by x-ray diffraction (XRD) analysis, and microstructural observation was conducted using an optical microscope and a scanning electron microscope (SEM). The etchant used was Keller's reagent.

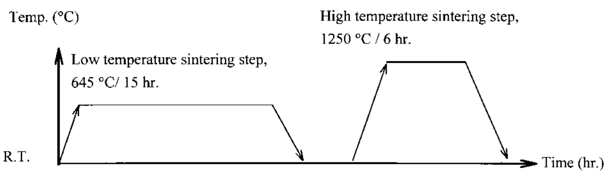


Fig. 3 Procedures for the two-step sintering process employed in this study

3. Results and Discussion

3.1 *The Effect of Compacting Pressure on the Density of Green Compact*

The mixture of elemental titanium and aluminum powders was placed in a floating die and compacted under pressure of 250, 500, 750, and 1000 MPa at room temperature. Figure 4 shows the effect of compacting pressure on the densities of green compacts. The density of the green compact increased as the pressure increased. When the pressure was >750 MPa, there was no significant change in the densities of the green compacts. When the pressure was 1000 MPa, the density of the green compact reached 3.59 g/cm^3. Because the theoretical density of the elemental powders mixture of Ti-48at.%Al was 3.63 g/cm^3, the density of the green compact reached 99% relative density. The microstructures in Fig. 5 show that there is no significant porosity in the cross sections of the billet even in the central area. Figure 5 shows that biaxial pressing can be obtained by using the floating die. When the compacting pressure was up to 1000 MPa, the billet of uniform density was almost completely densified. It then demonstrated that besides extrusion (Ref 1, 2) and hot pressing (Ref 3), compacting is a feasible way to prepare fully dense green compacts.

3.2 *The Effect of Using the Constrained Mold on the Density and Microstructure of the Billet during the Low-Temperature Sintering Step*

The green compacts were then sintered with and without the constrained molds through the low-temperature sintering step at 645 °C for 15 h. Figure 6 shows the densities of the billets sintered with and without the constrained molds with green compacts obtained under various compacting pressures. The densities of the billets sintered without the constrained molds were drastically lower than those of the original green compacts due to the Kirkendall effect. Contrary to that, the densities of the billets sintered with the constrained molds were only slightly lower than those of the starting green compacts and approximately two times higher than densities of billets sintered without constrained molds. The appearance of the green compact and the sintered billets in Fig. 7 also shows these differences. The billet sintered without the constrained molds swelled and had cracks on the surface (Ref 4). However, the billet sintered with the constrained mold swelled only slightly and had no apparent cracks on the surface. It is then obvious that the application of the constrained molds during sintering drastically suppresses the swelling of the billets, produces crack free billets, and minimizes the formation of the Kirkendall pores. Moreover, the original shapes of the sintered billets can be retained. Basically, the densities of the billets sintered with or without the molds in this stage are controlled by the extent of the Kirkendall effect. The phenomena are shown in Fig. 8, as density decreases with increased sintering time. This can be attributed to the existence of aluminum in the billets. The more aluminum is diffused, the more Kirkendall pores are formed and the looser is the billet.

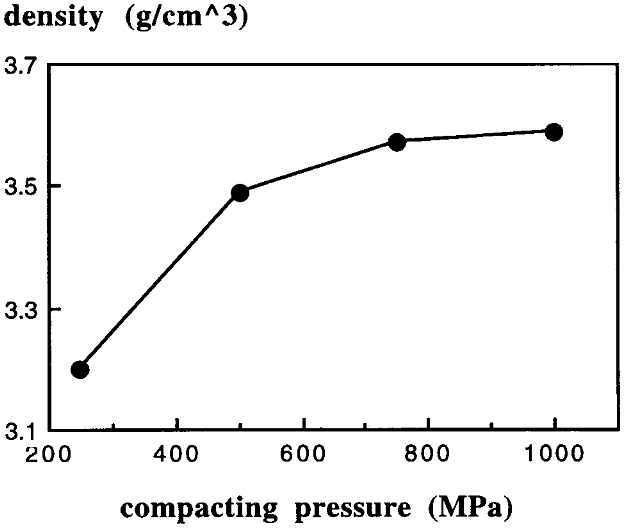
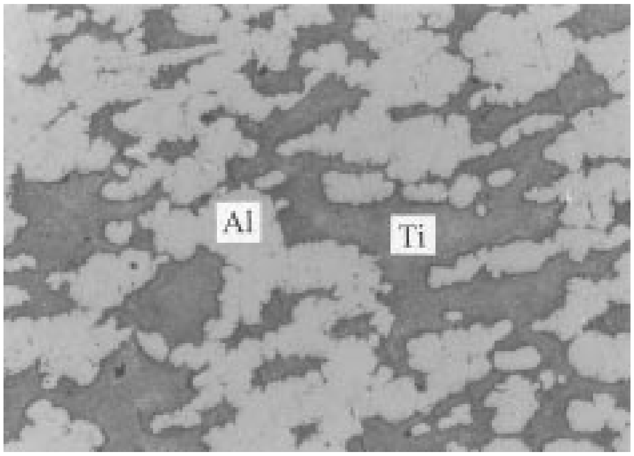
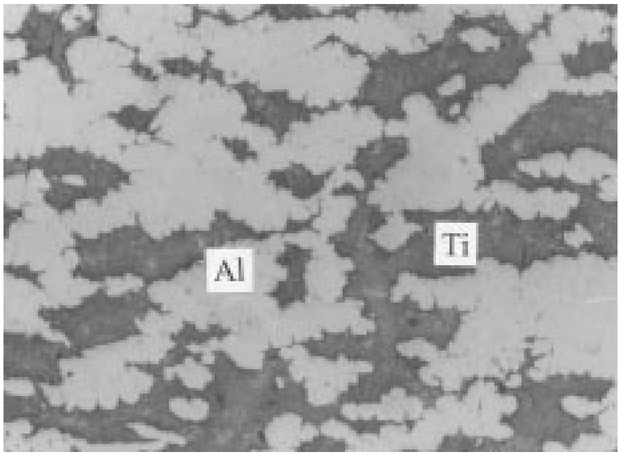


Fig. 4 Effect of compacting pressure on the densities of the green compacts



(a)



(b)

Fig. 5 Microstructure of the green compact. (a) Near surface (b) Central section

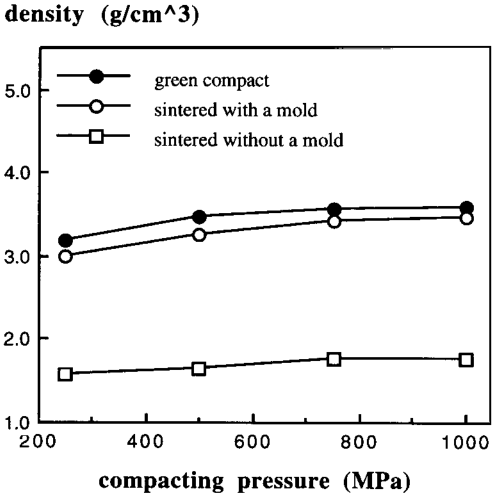


Fig. 6 Densities of the billets sintered from the green compacts obtained under various compacting pressure with and without constrained molds

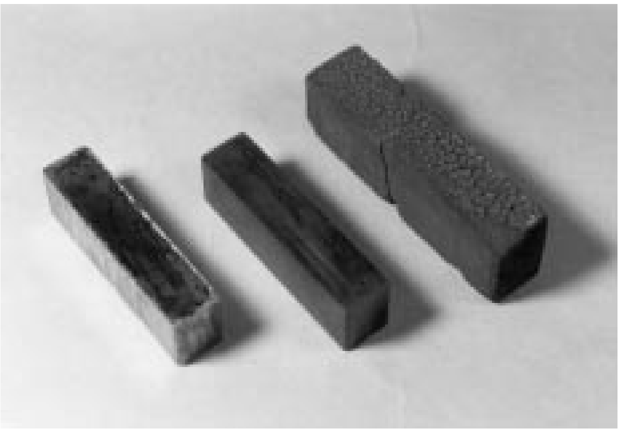


Fig. 7 Appearances of the green compact (left) and billets sintered with the constrained molds (middle) and without the constrained molds (right)

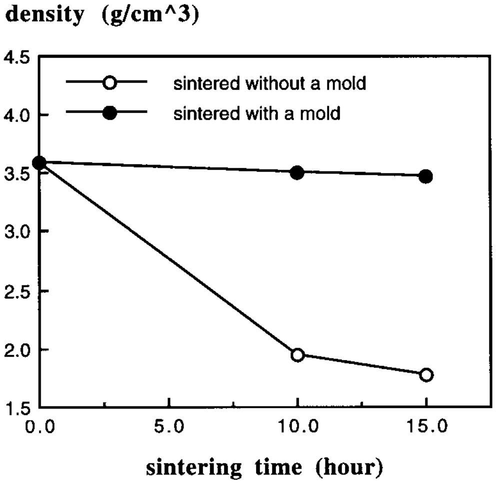


Fig. 8 Variation of billet density with time during the low-temperature sintering stage. The billet was originally prepared under the compact pressure of 1000 MPa

Figure 9(a) shows the microstructure of the billet sintered with the constrained molds for 10 h during the low-temperature sintering stage. Large amounts of titanium particles remain and are enclosed by $TiAl_3$ layers, which are the intermediate phases formed due to the interdiffusion between titanium and aluminum (Ref 2, 9-11). Small amounts of remaining aluminum can be observed, and pores are formed near the remaining aluminum particles. This demonstrates that aluminum diffuses faster

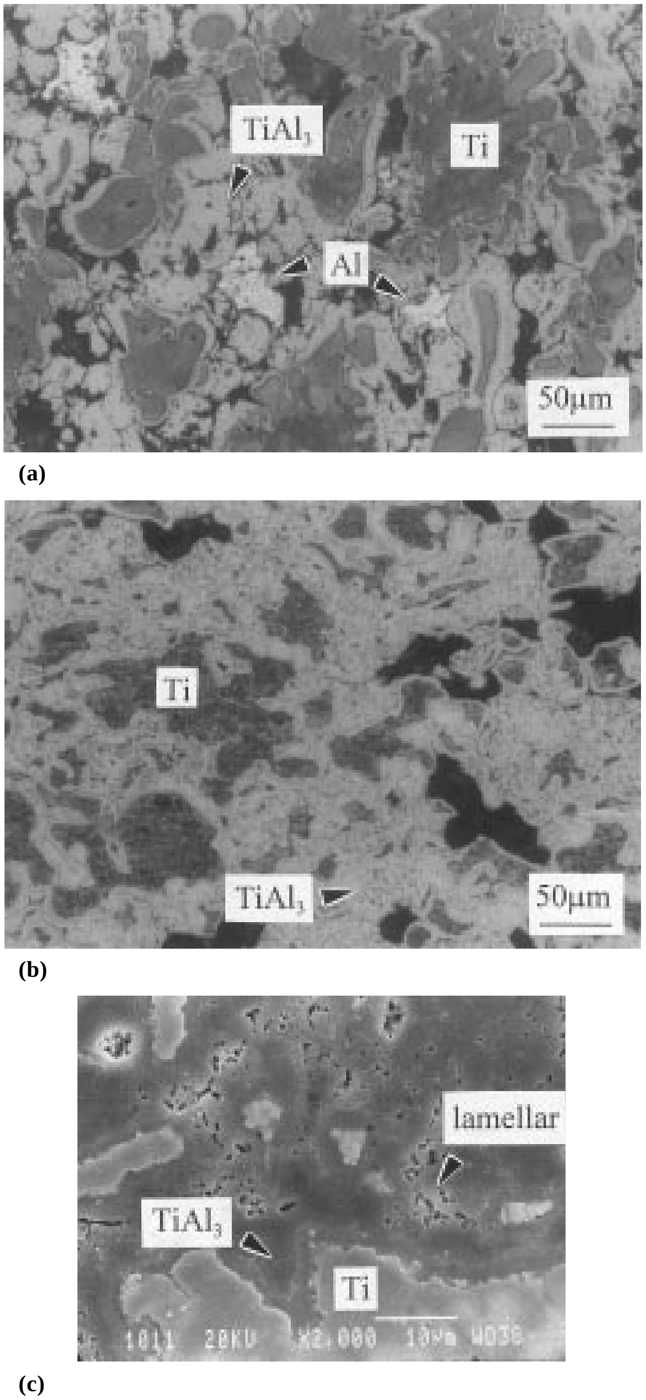


Fig. 9 Microstructure of the billet sintered with the constrained molds during the low-temperature sintering stage. (a) 645 °C/10 h. (b) 645 °C/15 h. (c) Scanning electron microscopy of (b)

than titanium and that the Kirkendall pores are formed in the original elemental aluminum regions after aluminum diffuses to the titanium regions. When this diffusion process is finished after 15 h, no significant amount of aluminum can be observed in the microstructure. The original elemental titanium powder particles become small, isolated particles, and $TiAl_3$ layers grow wider, as seen in Fig. 9(b). However, Fig. 9(c) shows that some precipitates are observed in the $TiAl_3$ layers. The XRD analysis of the sintered billet, as shown in Fig. 10(b), shows that TiAl and Ti_3Al are formed in this stage, rather than titanium and $TiAl_3$. Aluminum is completely eliminated. It has been reported that the mixture of the TiAl and Ti_3Al phases will precipitate in the $TiAl_3$ layers when the microstructure of titanium particles enclosed by $TiAl_3$ layers is heated from 630 to 1250 °C (Ref 11). Then the precipitates develop into the ($\gamma + \alpha_2$) lamellar ring structures in the further sintering. Therefore, the precipitates are the mixture of γ-TiAl and α_2-Ti_3Al, which is probably the precursory phase of the ($\gamma + \alpha_2$) lamellar structure. However, the microstructure of the billets sintered without the constrained molds after the low-temperature sintering stage shows that the aluminum particles remain, as shown in Fig. 11. Without the constrained molds, the aluminum particles still remain even after the billet is sintered for 44 h (Fig. 12). It takes a long time to fully eliminate the aluminum particles in this low-temperature sintering without constrained molds. Therefore, the application of constrained molds in this step can enhance the diffusion of aluminum and dramatically shorten the sintering time for eliminating aluminum particles.

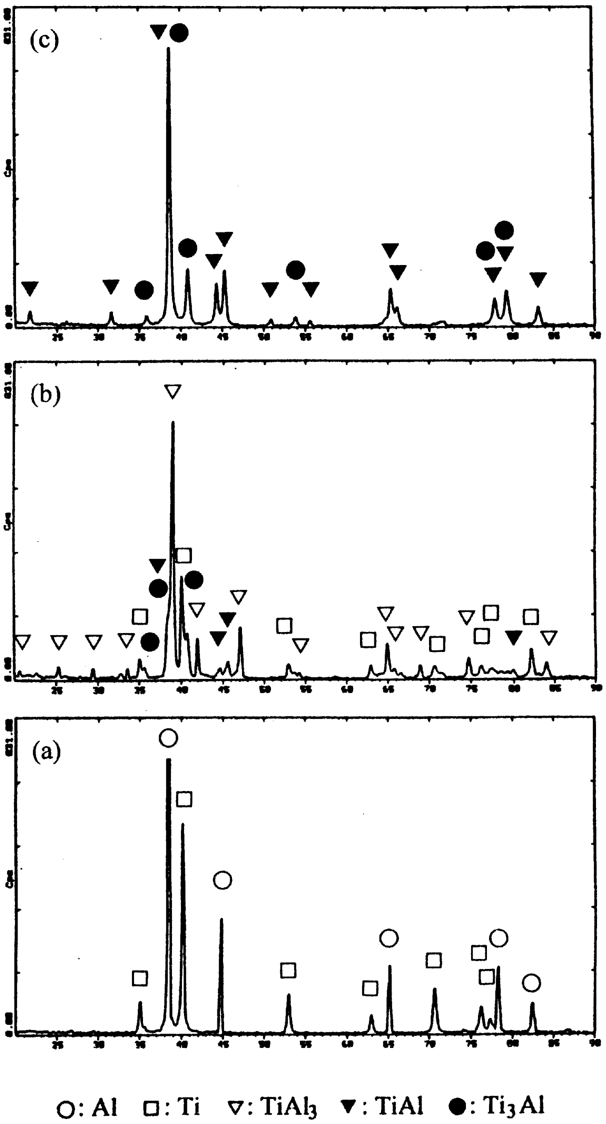


Fig. 10 X-ray diffraction analysis for (a) green compact, (b) billet sintered with the constrained molds during the low-temperature sintering stage at 645 °C for 15 h, and (c) billet sintered with the constrained molds during the high temperature sintering stage at 1250 °C for 6 h

3.3 The Variation of Density and Evolution of Microstructure for the Billet Sintered in the High-Temperature Sintering Step

The billets compacted at <1000 MPa and sintered with the constrained molds through the low-temperature sintering step were taken out of the constrained molds and sintered without

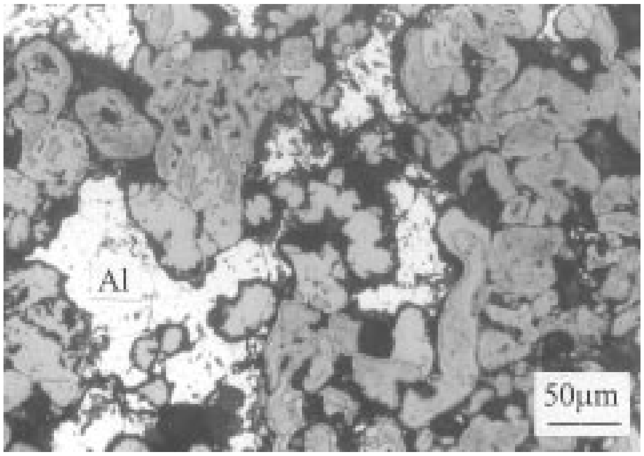


Fig. 11 Microstructure of the billets sintered without the constrained molds after the low-temperature sintering step

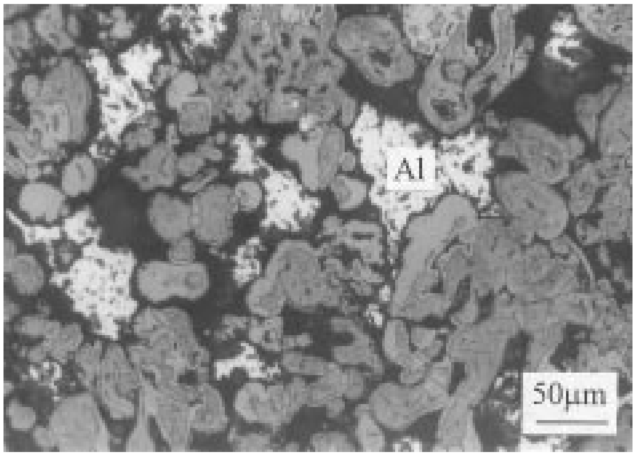


Fig. 12 Microstructure of the billets sintered without the constrained molds at 645 °C for 44 h

pressure at 1250 °C for 6 h. Figure 13 shows the variations of density and porosity ratio of the billets during this sintering step. The density increased slightly during the first two hours and then rapidly increased as sintering proceeded. Opposite the density change, the porosity ratio decreased as sintering time increased. This is because a large amount of titanium remained in the billets in the beginning of this stage and the titanium density was higher than that of the titanium aluminides. Therefore, density of the billet increased only slightly after the first two hours in spite of the fact that porosity decreased significantly. After sintering for six hours, the density of the sintered billet reached 3.52 g/cm^3. This is ~92.6% of the relative full density, which is determined by the average of the reported densities (Ref 12). The decrease of porosity ratio shows that the sintering behavior during this step follows the densification theory of the conventional powder metallurgy. Figure 14 also shows the densification phenomena of the billet after this step by porosity decrease in the microstructure. Muramatsu et al. (Ref 13) have used Ti + $TiAl_3$ powder mixture to prepare TiAl-based intermetallics by using the conventional pressureless sintering process. The densities of the specimen also increase as sintering time and temperature increases. It shows that the sintering behavior of the billet without the existence of elemental aluminum will obey the densification theory of conventional PM due to the absence of the Kirkendall effect.

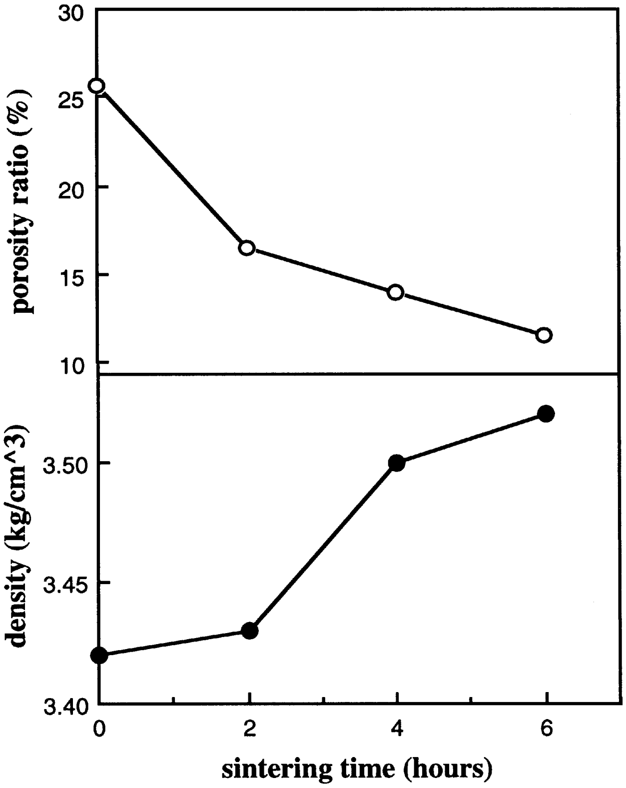
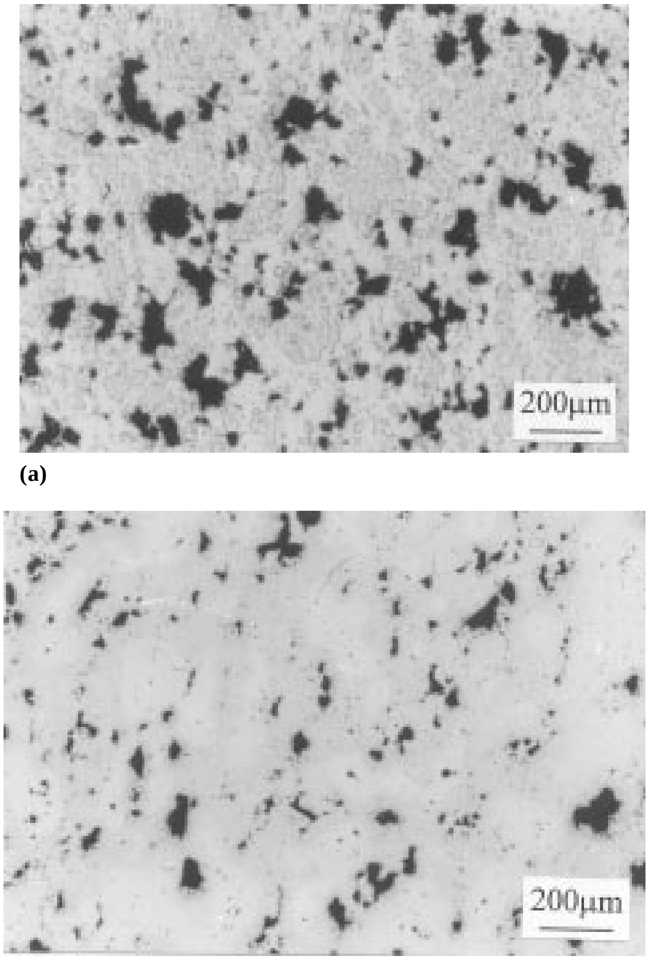


Fig. 13 Variations of densities and porosity ratio for the billets during the high-temperature sintering step. (The billets are initially compacted under 1000 MPa and then sintered with the constrained molds through the low-temperature sintering step.)

The XRD analysis in Fig. 10(c) shows that only TiAl and Ti_3Al exist after the high-temperature sintering step. The $TiAl_3$ intermediate phase is eliminated due to the quick interdiffusion between titanium and aluminum. It shows that the sintering at 1250 °C for 6 h can homogenize the billets. Figure 15(a) shows that there are two regions in the microstructure including the dark matrix and the white colonies. The dark matrix is the (γ-TiAl + α_2-Ti_3Al) lamellar phase, as shown by the SEM photograph in Fig. 15(b). The white colonies analyzed by energy-dispersive x-ray analysis (EDXA) are the γ-TiAl phases. Therefore, the microstructure of the γ-TiAl + (γ + α_2) lamellar phase, which is the so-called duplex structures (Ref 1, 2), is obtained after the high-temperaure sintering step. The microstructure transformation procedures during sintering from the compacts of titanium and aluminum to TiAl-based intermetallics have been studied and reported by the authors (Ref 11). The $TiAl_3$ intermediate phases formed first and then disappeared. Finally, the microstructure of a γ-TiAl + α_2-Ti_3Al + lamellar ring was formed. If longer sintering time is used, as in this study, the α_2-Ti_3Al phase transforms to (γ + α_2) lamellar



(b)

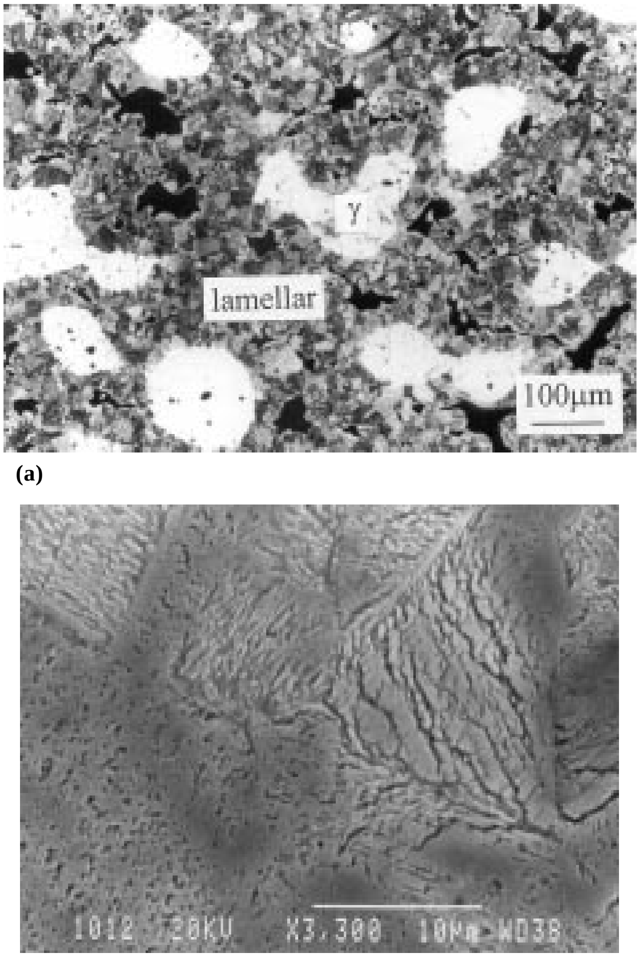
Fig. 14 Porosities in the microstructures of the billets. (a) After sintering with the constrained molds in the low-temperature sintering step. (b) After the high-temperature sintering step for 6 h. (The billets were initially compacted under 1000 MPa.)

phase due to titanium diffusing out of the α_2-Ti_3Al phase into the surroundings. Finally, the intermetallics of γ-TiAl + (γ + α_2) lamellar phase are obtained. Figure 16 shows a schematic illustration of the transformation procedures, which explain the phase transformations for the processing steps observed in this study.

4. Conclusions

A two-step sintering procedure is proposed in this study to make pressureless sintering feasible in preparing TiAl-based intermetallics from elemental aluminum and titanium powders. The density of the billet can be retained by using the constrained molds in the low-temperature sintering step and then increased in the high-temperature sintering step. The shape of the billet can also be retained after the sintering procedures, and the subsequent machining of the billet can be reduced. If denser billets are needed, a densified process such as HIP, HP (hot pressing), or the high-temperature sintering for longer time can be used afterward to densify the billets. The conclusions of this study can be summarized as follows:

- Green compact of nearly full densification can be obtained by pressing on elemental powders mixture of Ti-48at.%Al with a floating die under pressure of 1000 MPa
- Application of the constrained molds in the low-temperature sintering step can suppress swelling of the billets and formation of the Kirkendall pores in the billets, which causes density drop and cracking. Also, low-temperature sintering prevents the aluminum from melting so that crackless and dense billets can be prepared for subsequent high-temperature sintering.
- Application of the constrained molds during the low-temperature sintering step can eliminate the elemental aluminum in the green compact and dramatically shorten the required sintering time. There is no elemental aluminum retained after sintering with the constrained molds at 645 °C for 15 h, while a significant amount of the elemental aluminum still remains after sintering at 645 °C for 44 h without the constrained molds.
- The density of the billet during the low-temperature sintering step is still affected by the Kirkendall effect despite the application of the constrained molds. However, the billet can be densified during the high-temperature sintering step following the densification theory of the conventional powder metallurgy.
- The microstructure shows that after the low-temperature sintering with constrained molds, certain elemental titanium particles remain and are surrounded by $TiAl_3$ layers. A small amount of lamellar phase precipitates in the layers. After the high-temperature sintering, intermetallics with γ-TiAl colonies and lamellar phases are formed. The microstructure also shows that the designed sintering procedures can attain the goal of homogenization.



(a)

(b)

Fig. 15 Microstructure of the billet after the high-temperature sintering step with (a) optical micrograph and (b) scanning electron micrograph, which shows the lamellar phases. (The billets were initially compacted under 1000 MPa and then sintered with the constrained molds through the low-temperature sintering step.)

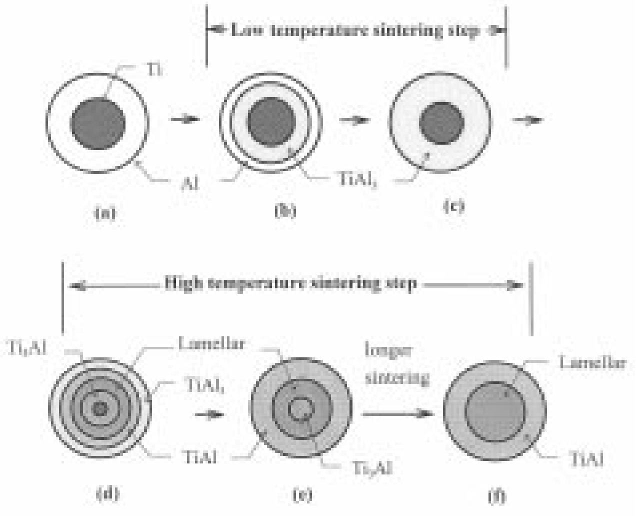


Fig. 16 A schematic illustration of the phase-transformation procedures observed in this study. (a) The compacts. (b) to (e) The phase transformation (Ref 11). (f) After longer sintering in this study

Acknowledgments

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References

1. G.-X. Wang and M. Dahms, An Overview: TiAl-Based Alloys Prepared by Elemental Powder Metallurgy, *PMI*, Vol 24 (No. 4), 1992, p 219-225
2. G.-X. Wang and M. Dahms, Synthesizing Gamma-TiAl Alloys by Reactive Powder Process, *JOM*, Vol 45 (No. 5), 1993, p 52-56
3. K. Shibue, Suppression of Pores for TiAl Intermetallic Compound Prepared by Reactive Sintering, *Sumitomo Light Met. Tech. Rep.*, Vol 32 (No. 2), 1991, p 95-101
4. P. L. Sullivan, HIP Processing of Ti-Al Intermetallic Using Blended Elemental Powder, *J. Mater. Process. Tech.*, Vol 38, 1993, p 1-13
5. G.-X. Wang and M. Dahms, An Effective Method for Reducing Porosity in the Titanium Aluminide Alloy $Ti_{52}Al_{48}$ Prepared by Elemental Powder Metallurgy, Scr. Metall. Mater., Vol 26 (No. 9), 1992, p 1469-1474
6. M. Dahms, F. Schmelzer, J. Seeger, and B. Wildhagen, Microstructure and Mechanical Properties of γ Base Titanium Aluminide Produced from Extruded Elemental Powders, *Mater. Sci. Technol.*, Vol 8 (No. 4), 1992, p 359-362
7. M. Dahms, Titanium Aluminide Foil by Elemental Powder Processing, *MSE*, Vol A, 151, 1992, p L27-L29
8. A. Jakob and M. Speidel, Development of Foil Metallurgy Technique for Production of TiAl, *MST*, Vol 10 (No. 10), 1994, p 845-847
9. F.J.J. van Loo and G.D. Rieck, Diffusion in the Titanium-Aluminum System-I. Interdiffusion between Solid Al and Ti or Ti-Al Alloys, *Acta Metall.*, Vol 21 (No. 1), 1973, p 61-71
10. M. Dahms, Formation of Titanium Aluminides by Heat Treatment of Extruded Elemental Powders, *MSE*, Vol A, 110, 1989, p L5-L8
11. J.B. Yang, K.W. Teoh, and W.S. Hwang, Solid-State Hot Pressing of Elemental Aluminum and Titanium Powders to Form TiAl ($\gamma + \alpha_2$) Intermetallic Microstructure, *J. Mater. Eng. Perform.*, Vol 5 (No. 5), Oct 1996, p 583-588
12. Y.W. Kim, Intermetallic Alloy Based on Gamma Titanium Aluminide, *JOM*, No. 7, 1989, p 24-30
13. Y. Muramatsu, T. Ohkoshi, and H. Suga, Production of Highly Densified TiAl by Die Compacting-Sintering Method, *J. Jpn. Inst. Met.*, Vol 57 (No. 8), 1993, p 944-951