

Pressure-Assisted Reactive Synthesis of Titanium Aluminides from Dense 50Al-50Ti Elemental Powder Blends

E. PARANSKY, E.Y. GUTMANAS, I. GOTMAN, and M. KOCZAK

In the present research, dense γ -TiAl based intermetallic samples were fabricated by reactive synthesis of fully dense elemental 50 at. pct Al-50 at. pct Ti powder blends. Two different processing routes were attempted: thermal explosion under pressure (combustion consolidation) and reactive hot pressing. In both approaches, relatively low processing or preheating temperatures (≤ 900 °C) were used. The entire procedure of thermal explosion under pressure could be performed in open air without noticeable oxidation damage to the final product. The application of a moderate external pressure (≤ 250 MPa) during synthesis was shown to be enough to accommodate the negative volume change associated with TiAl formation from the elemental components and, thereby, to ensure full density of the final product. Microstructure and phase composition of the materials obtained were characterized employing X-ray diffraction and scanning electron microscopy with energy dispersive analysis. It was found that at elevated temperatures (*e.g.*, 900 °C), the equiatomic 50Al-50Ti alloy lies beyond the homogeneity range of the γ -TiAl phase in the Ti-Al binary and contains, in addition to γ -TiAl, Al-rich Ti_3Al . Mechanical properties of the materials synthesized were evaluated in compression tests at different temperatures and by microhardness measurements. Due to its very fine microstructure, the Ti-Al material synthesized *via* reactive hot pressing exhibited superplastic behavior at temperatures as low as 800 °C.

I. INTRODUCTION

WITH the growing need for improved high performance materials for advanced engineering applications, intermetallic alloys have emerged as the most promising substitutes for conventional superalloys. Among all the intermetallics, titanium aluminide alloys based on γ -TiAl are receiving the most attention due to a very favorable combination of the low density and good mechanical properties coupled with the high melting temperature and excellent oxidation resistance. Ultimately, bringing these attractive intermetallic materials into use largely depends upon the availability of practical processing routes. Conventional casting of TiAl-base intermetallics is difficult due to their relatively high melting temperature and the extreme reactivity of Ti. More importantly, however, cast TiAl alloys are usually not suitable for subsequent forming as a result of inhomogeneities and segregations in the solidification microstructure combined with the lack of ductility.^[1] At the same time, powder metallurgy methods capable of providing near-net-shape parts seem to be a more attractive processing alternative. Over the past 2 decades, significant progress has been made in the area of powder processing of intermetallics. Rapid solidification techniques, such as

melt spinning, inert gas atomization, and mechanical alloying, have been extensively used to produce nickel-aluminum and titanium-aluminum intermetallic powders.^[2,3] These prealloyed powders are consolidated to full density employing hot pressing, hot extrusion, or hot isostatic pressing (HIP)^[4]—methods that usually require temperatures in excess of the material service temperature. Such temperatures can result in the undesirable TiAl grain growth and, more importantly, in the interaction between TiAl and reinforcement phases in the cases where TiAl acts as a matrix for a composite material. Thus, reactions between TiAl and high strength continuous SiC fibers (*e.g.*, SCS-6) at temperatures as low as 1100 °C have been shown to result in catastrophic deterioration of the fiber properties.^[5] In order to maintain a desirable microstructure (and, thereby, to obtain enhanced behavior in a compacted part), the time-temperature thermal exposure during consolidation should be minimized.

A different approach to the processing of intermetallics, in general, and of aluminides, in particular, is reactive synthesis from elemental powders. One of the important examples of this approach is self-propagating high temperature synthesis (SHS).^[6,7,8] The term SHS, or combustion synthesis, is used to describe processes in which initial reagents, when ignited, spontaneously transform into products, due to the exothermic heat of reaction. The SHS reaction can proceed as a layerwise or volumetric combustion, the latter usually referred to as “thermal explosion.” The technique is extremely attractive due to the self-generation of energy and short processing cycles, and it can be useful in producing both intermetallic powders and sintered bodies. Various SHS-related techniques developed for the synthesis of dense intermetallics, in general, and TiAl, in particular, have been recently discussed by Dunand in a review paper.^[9] Dense TiAl ($\rho \geq 95$ pct) was successfully synthesized from elemental powders^[10-15] or foils^[8,16,17] em-

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This article is based on a presentation made in the “In Situ Reactions for Synthesis of Composites, Ceramics, and Intermetallics” symposium, held February 12-16, 1995, at the TMS Annual Meeting in Las Vegas, Nevada, under the auspices of SMD and ASM-MSD (the ASM/TMS Composites and TMS Powder Materials Committees).

ploying pressure-assisted methods, such as reactive hot pressing (RHP), reactive hot isostatic pressing, and variations thereof. In most of these techniques, however, the reaction between Ti and Al does not seem to occur in a self-sustaining manner, and even when it does (*e.g.*, pseudo-HIP-SHS^[13]), the released exothermic heat is not fully utilized for the material consolidation. As a result, the advantages of SHS are, at least partially, lost and the synthesis-densification process again requires long exposures at high processing temperatures approaching those typical of the more conventional consolidation of TiAl from prealloyed powders.

It is interesting to note that the highest densities ($\rho \geq 98$ pct) reported for reactively synthesized TiAl were achieved when the mixture of reactants (Ti and Al) was a practically pore-free body produced by extrusion^[11] or compaction^[13] of powders. A similar approach, *i.e.*, full density high pressure consolidation (cold sintering)^[4,18,19] of micron/submicron elemental powder blends followed by postconsolidation synthesis treatment, was earlier used by the authors for the reactive processing of CoAl and NiAl intermetallics.^[20,21] For example, fully dense single-phase CoAl samples were synthesized by RHP (250 MPa) at a relatively low temperature of 800 °C.^[22] In this approach, short diffusion distances associated with the fine powders employed allowed synthesis to be completed over relatively short time periods, thus preventing the undesirable coarsening of microstructure. Grain size control is vital for the powder metallurgy oriented processing of intermetallic materials, since superplasticity is often observed in fine-grained intermetallics including TiAl,^[23,24] and it could be utilized for their full density consolidation.

In the present work, we report on the low temperature RHP synthesis of pore-free TiAl from fully dense fine elemental powder blends. Combustion consolidation, *i.e.*, pressure-assisted thermal explosion, was also conducted.

II. EXPERIMENTAL APPROACH AND RATIONALE

A. Materials and Sample Preparation

In the present research, Al powders with two different particle sizes, $\leq 1 \mu\text{m}$ (ultrafine) and $< 5 \mu\text{m}$, and Ti powders with two different particle sizes, $1 \mu\text{m}$ and $\leq 10 \mu\text{m}$, from CERAC* were used. A schematic of TiAl processing

*CERAC is a trademark of Cerac, Inc., Milwaukee, WI.

from the elemental Ti and Al powders is shown in Figure 1. As a first step, homogeneous powder mixtures with a composition corresponding to stoichiometric TiAl, 50 at. pct Al-50 at. pct Ti (36 wt pct Al-64 wt pct Ti), were prepared by high energy attrition milling. The milling time was 4 hours, and the grinding media-to-powder ratio was 2:1. The low grinding media-to-powder ratio employed prevented mechanical alloying; no peaks other than those of the starting components (Ti and Al) were present in X-ray diffraction (XRD) patterns of the blends even after 24 hours of milling. (It should be mentioned that when a high 10:1 grinding media-to-powder ratio was employed, mechanical alloying with the formation of TiAl₃ was observed (by XRD) in the Ti-Al blends after 2 hours of milling.) Two

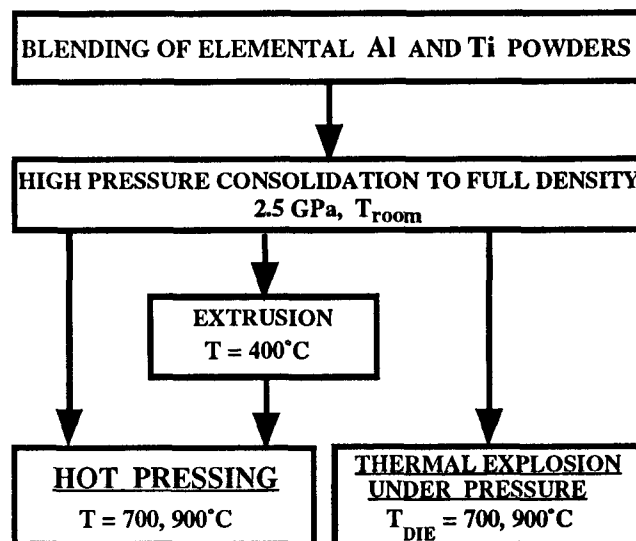


Fig. 1—Schematic of the approach to the processing of dense TiAl from elemental powder blends.

different types of blends were studied: an ultrafine (Al, $1 \mu\text{m}$ + Ti, $1 \mu\text{m}$) blend and a coarser (Al, $5 \mu\text{m}$ + Ti, $10 \mu\text{m}$) blend. The prepared blends were compacted to ~ 70 pct theoretical density and heat treated in vacuum at 350 °C in order to remove absorbed gases and hydrates from the Al powder surface.^[4,25] The green compacts were high pressure consolidated at room temperature (cold sintered) to full density at pressures up to 2.5 GPa, yielding samples $\sim 4 \times 4.5 \times 18$ mm. TEFLON** spray was used as a die lubricant

**TEFLON is a trademark of E.I. Du Pont de Nemours & Co., Inc., Wilmington, DE.

in the cold sintering operation. In addition, a number of cylindrical samples, 20 mm in diameter, were prepared from the (Al, $5 \mu\text{m}$ + Ti, $10 \mu\text{m}$) blend and extruded at 400 °C using an extrusion ratio of $R = 25:1$.

B. Synthesis of TiAl-Based Alloys

The synthesis of TiAl intermetallic was accomplished *via* two different processing routes: combustion consolidation (thermal explosion under pressure) and reactive hot pressing. In both routes, processing was conducted in an Instron testing machine and external pressure was applied in order to accommodate the negative volume change associated with the formation of TiAl from the elemental constituents ($\text{Ti} + \text{Al} \rightarrow \text{TiAl}$, $\Delta V = -7$ pct).

Preliminary experiments showed that, without application of external pressure, the ignition temperature of thermal explosion in cold-sintered Ti-Al powder blends was ~ 600 °C for the coarse (5- to $10\text{-}\mu\text{m}$) blend and ~ 550 °C for the fine ($1\text{-}\mu\text{m}$) blend. Thermal explosion under pressure was performed only for the samples cold sintered from the coarse (5- to $10\text{-}\mu\text{m}$) Ti-Al blend. Samples were placed in a pressure die preheated to 700 °C or 900 °C and rapidly loaded (crosshead speed 50 mm/min) to 150 MPa (Figure 2). (Rigid dies made of a Nimocast superalloy were used in this operation, as well as in the hot pressing synthesis.) To ensure that thermal explosion does not occur before the pressure is applied, the samples were thermally insulated by an $\sim 0.2\text{-mm}$ -thick coating of a BN spray. Since the

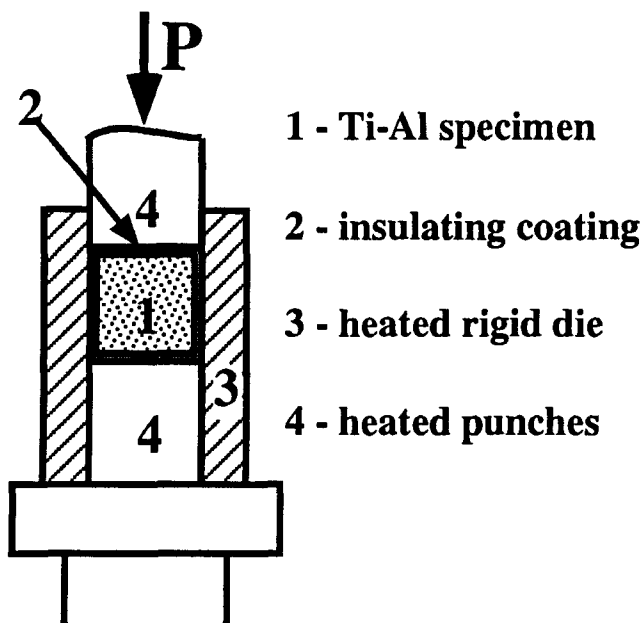


Fig. 2—Schematic of thermal explosion under pressure.

heating of the samples in this scheme was realized *via* heat transfer from the die walls and punches, the presence of the coating delayed the onset of thermal explosion until the sample had been fully loaded. After thermal explosion, the sample was held under pressure for 1 minute and then unloaded and taken out of the die. The entire procedure of thermal explosion under pressure was performed in open air.

The hot pressing synthesis of TiAl from both fine and coarse (extruded and unextruded) Ti-Al powder blends was performed at 700 °C, 250 MPa or 900 °C, 150 MPa. Cold sintered samples were placed into a cold die, loaded to the required pressure, slowly heated (~ 10 °C/min) with the die to the processing temperature, and held at this temperature for 1 hour. (This is in contrast to the thermal explosion synthesis where the samples were placed into a hot die.) The BN spray was used as a die lubricant in the hot pressing operation. Temperature during hot pressing was recorded by means of a sensitive 0.2-mm-diameter chromel-alumel thermocouple that had been pressed into the sample during cold sintering. In order to monitor phase evolution in Ti-Al samples during hot pressing synthesis, several interrupted hot press runs were also conducted. To achieve full conversion of the Ti + Al blend into TiAl, samples hot pressed at 900 °C were further annealed at 1100 °C for up to 10 hours in a vacuum furnace.

C. Microstructure Characterization

After processing, as-synthesized and heat-treated samples were mechanically polished. Phase composition of the material obtained was characterized employing XRD. A PHILIPS* NJ. PW-1820 diffractometer with a Cu X-ray tube

*PHILIPS is a trademark of N.V. Philips Gloelampenfabriken, Eindhoven, The Netherlands.

($\delta_{\text{Cu } K_{\alpha}} = 0.1542$ nm) was employed operating at 40 KV and 40 mA. Scanning was performed in a step mode with a 0.025 deg step and a 5-second exposure point in a 30 to 90 deg diffraction angle range. For two-phase samples, in-

tegrated peak intensities of different phases were calculated using a PHILIPS PW-1869 fitting procedure (based on a pseudo-Voigt function). The XRD intensities were converted into volume fractions using the direct comparison method.^[26] The estimated accuracy of calculated volume fractions was ± 4 pct.

Microstructures of the samples and chemical composition of different phases after synthesis and subsequent heat treatments were studied employing a scanning electron microscope (SEM) JSM-840 with an energy dispersive spectrometer (EDS) Link AN10000. Quantitative determination of porosity, as well as of volume fractions of different phases, was carried out with the help of a computer-aided image analysis system. Quantitative EDS analysis was based on K_{α} analytical lines from the spectra acquired at the 20 kV accelerating voltage. Cobalt was used as a standard, and ZAF correction was performed using a standard procedure from the Link software package.

D. Mechanical Testing

Mechanical properties of the samples after different heat treatments were evaluated by measuring their microhardness (Vickers, 200 g load). Yield stress in compression, σ_y , was measured as a function of temperature for the samples hot pressed at 900 °C. Polished rectangular samples ($4 \times 4 \times 10$ mm) were tested in compression at a strain rate of 1×10^{-4} s $^{-1}$. For selected samples, compression tests were conducted to fracture, and fracture surfaces were studied in an SEM. In addition, strain-rate change tests (from 1×10^{-4} to 1×10^{-3} s $^{-1}$) were performed at different temperatures to evaluate the strain-rate sensitivity coefficient, m , of the samples hot pressed at 900 °C. The term m , which is an exponent in the relationship between flow stress, σ , and strain rate, $\dot{\epsilon}$, at constant strain and temperature ($\sigma = C(\dot{\epsilon})^{m/\epsilon,T}$), was determined by measuring the change in flow stress brought about by a change in $\dot{\epsilon}$ ^[27] (Figure 3):

$$m = \frac{\log(\sigma_2/\sigma_1)}{\log(\dot{\epsilon}_2/\dot{\epsilon}_1)}$$

Enhanced strain-rate sensitivity ($m > 0.2$) is indicative of superplastic behavior.

III. RESULTS AND DISCUSSION

A. Thermal Explosion under Pressure

During combustion consolidation, thermal explosion occurred ~ 15 to 20 seconds after the pressure had been applied. Once the reactants were ignited, the pressure dropped by ~ 30 pct for several seconds and again increased to 100 pct (150 MPa). The pressure drop was, most probably, associated with the melting of Al and the practically instantaneous volume decrease during the “explosive” reaction of Ti aluminides formation from their elemental constituents. The temperature of the sample rapidly increased to ~ 1100 °C (when the pressure die had been preheated to 700 °C) or to above 1200 °C (when the die had been preheated to 900 °C). Such a temperature increase (≤ 400 °C), which is considerably lower than could be expected from the corresponding SHS adiabatic temperature (Ti + Al \rightarrow TiAl, $T_{ad} = 1381$ °C), must be a result of the very rapid

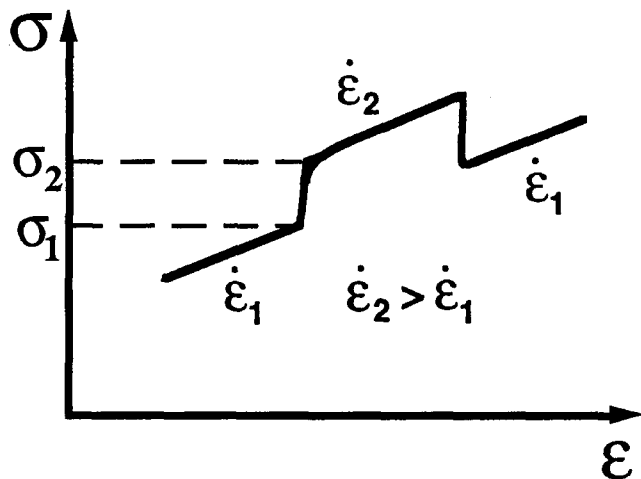


Fig. 3—Strain-rate change test to determine strain-rate sensitivity.

heat transfer from the sample into the highly conductive pressure die. For the same reason, the cooling of the sample from the combustion to the die temperature was very fast (<5 seconds). In spite of the fact that the SHS processing was performed in open air without any protective atmosphere, no oxidation damage was detected in the final product. This must be due to the 100 pct density of the starting powder blends as well as to the extremely short exposures at the relatively high combustion temperature. After combustion consolidation, the samples remained near fully dense, with less than 1 pct residual porosity observed in the final microstructure.

The XRD patterns in Figure 4 illustrate phase composition of the samples after thermal explosion under pressure. When the pressure die had been preheated to 700 °C, the material synthesized comprised TiAl, Ti₃Al, TiAl₂, and ~10 vol pct of unreacted Ti. Apparently, rapid heat transfer from the combustion zone hindered the self-sustaining reaction, thereby preventing full conversion of the Ti-Al blend into TiAl. When the preheating temperature was raised to 900 °C, no elemental Ti was detected in the sample after thermal explosion. Still, full conversion was not achieved, the phase composition of the material synthesized being ~60 vol pct TiAl + 40 vol pct Ti₃Al. According to the EDS analysis, the composition of Ti₃Al in this sample was 36.5 ± 1.5 at. pct Al, which corresponds to the Al-rich boundary of the Ti₃Al homogeneity range. The composition of the TiAl phase ranged from 50 to 65 at. pct Al, covering the whole high temperature homogeneity range of TiAl. It is worth mentioning that when different sections of the sample ($T_{\text{die}} = 900\text{ °C}$) were analyzed, XRD data showed that, compared to the middle region, outer layers had a lower TiAl/Ti₃Al ratio and, in addition, contained some TiAl₂. This implies that, during thermal explosion, the temperature in the middle of the sample was higher than on its surface due to the enhanced heat transfer into the pressure die.

Fracture surfaces in Figure 5 illustrate the microstructure scale of the Ti-Al material synthesized *via* thermal explosion under pressure. It can be seen that the grain size of the final product increases with increasing preheating and, correspondingly, combustion temperature. Grain size values for the Ti-Al intermetallics synthesized in this work *via* different processing routes are summarized in Table I.

Thermal Explosion

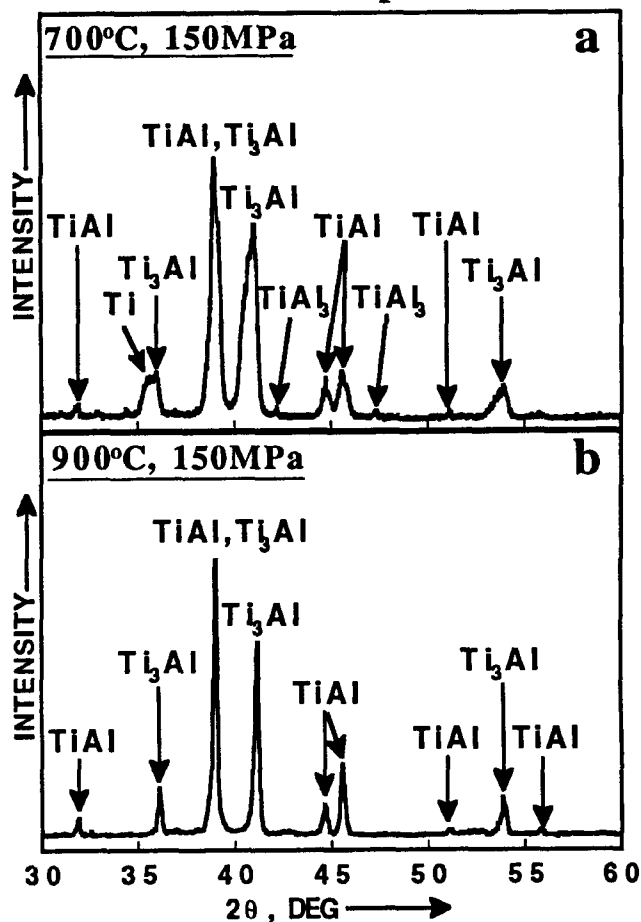


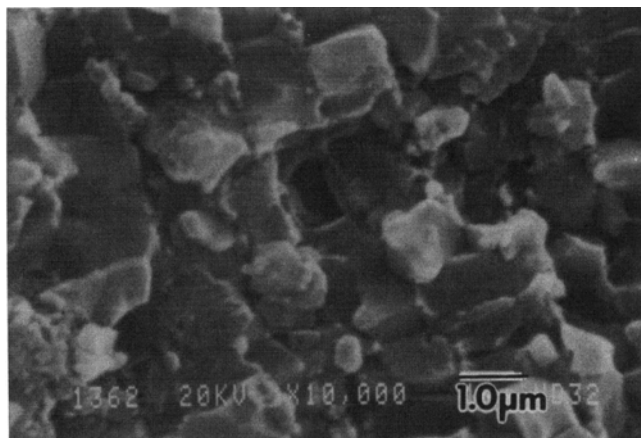
Fig. 4—XRD patterns of cold-sintered (Al, 5 μm-Ti, 10 μm) blends after thermal explosion under pressure: (a) $T_{\text{die}} = 700\text{ °C}$ and (b) $T_{\text{die}} = 900\text{ °C}$.

B. Reactive Hot Pressing

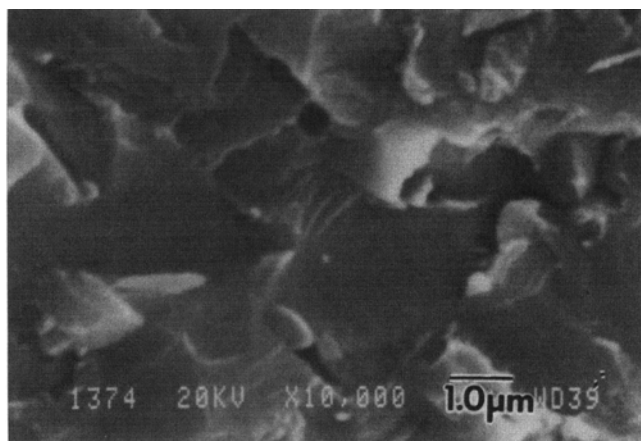
Reactive hot pressing at 700 °C, 250 MPa or 900 °C, 150 MPa of both extruded and unextruded cold-sintered Ti-Al samples yielded a fully dense material. An essentially nil porosity was measured in such samples after processing. Additional hot press runs showed that, for the 900 °C processing temperature, full density could be achieved already at 100 MPa. This is illustrated by a representative SEM backscattered micrograph (Figure 6), showing that the material hot pressed at 900 °C and 100 MPa is pore free. Due to the low processing temperature, the microstructure of the materials synthesized *via* reactive hot pressing is very fine, with the grain size not exceeding 1.5 μm even for the relatively coarse (Al, 5 μm + Ti, 10 μm) initial blend (Figure 7). The grain size of TiAl synthesized from the fine (Al, 1 μm + Ti, 1 μm) blend or from the extruded (Al, 5 μm + Ti, 10 μm) blend was in the submicron range (Table I). Phase composition of the hot-pressed material varied from sample to sample depending on the initial interparticle distance and processing temperature.

1. Samples prepared from coarse (Al, 5 μm + Ti, 10 μm) blend

Figure 8 shows variations in the temperature of a sample prepared from the (Al, 5 μm + Ti, 10 μm) blend during heating in the die. In contrast to the free standing fully



(a)



(b)

Fig. 5—SEM fracture surfaces of Ti-Al samples after thermal explosion under pressure: (a) $T_{\text{die}} = 700\text{ }^{\circ}\text{C}$ and (b) $T_{\text{die}} = 900\text{ }^{\circ}\text{C}$.

dense Ti-Al blend, there are no signs of thermal explosion at $600\text{ }^{\circ}\text{C}$; the temperature on the sample does not rise above the furnace temperature. This must be a result of the rapid heat transfer from the sample to the massive metal die acting as a sink for any heat released during solid-state reaction between Ti and Al. During further heating, a small temperature increase ($\sim 40\text{ }^{\circ}\text{C}$) is observed around the T_m of aluminum. This is significantly lower than the $\sim 400\text{ }^{\circ}\text{C}$ temperature rise registered in the previously described thermal explosion sample rapidly heated to $700\text{ }^{\circ}\text{C}$, just above the aluminum melting point. In both cases, the temperature rise is associated with the melting of Al followed by its rapid reaction with Ti. At the same time, according to the XRD pattern (Figure 9(2)), the amount of aluminum in the “hot press” sample just before melting (at $650\text{ }^{\circ}\text{C}$) is ~ 60 to 65 pct of its initial amount, and the rest has been already consumed in the solid-state formation of TiAl_3 during heating. The presence of TiAl_3 diffusion/reaction barriers at Al/Ti powder particle interfaces, as well as the low amount of available metallic Al, significantly reduces the rate of exothermic heat release during the reaction between Ti and molten Al. This, together with the rapid heat transfer from the sample to the pressure die, explain why no substantial temperature rise has been observed in the hot press samples. As can be seen from the XRD pattern taken at $700\text{ }^{\circ}\text{C}$ (when the temperature of the sample falls down to the fur-

nance temperature) and shown in Figure 9(3), no elemental Al is left in the sample after the temperature rise, the only two phases detected being Ti and TiAl_3 . This, again, is in contrast to the thermal explosion sample which, after 1 minute of exposure at $700\text{ }^{\circ}\text{C}$, contained Ti-rich aluminides and only small amounts of TiAl_2 and Ti (Figure 4(a)).

Holding the samples in the hot press at $700\text{ }^{\circ}\text{C}$ or $900\text{ }^{\circ}\text{C}$ for 1 hour results in phase compositions illustrated by the X-ray patterns in Figure 10. It can be seen that after 1 hour of hot pressing at $700\text{ }^{\circ}\text{C}$, all the intermediate products of the reaction between Ti and Al are observed, *i.e.*, TiAl_3 , TiAl_2 , TiAl , and Ti_3Al . In addition, a large amount of unreacted Ti is still present in the sample. After hot pressing at $900\text{ }^{\circ}\text{C}$, the only phases present in the X-ray pattern are TiAl_2 , TiAl , and Ti_3Al . The three-phase composition of the sample is confirmed by an X-ray map (Al) (Figure 11), featuring black Ti-rich regions (Ti_3Al), white Al-rich regions (TiAl_2), and gray regions containing comparable amounts of Ti and Al (TiAl). Volume fractions of each phase in the sample hot pressed at $900\text{ }^{\circ}\text{C}$ were estimated from the X-ray map (Figure 11) and from the XRD pattern (Figure 10(b)), giving (in vol pct) ~ 6 pct TiAl_2 , ~ 52 pct TiAl , and ~ 42 pct Ti_3Al . A representative SEM backscattered micrograph of the sample (Figure 6) reveals four regions with different contrast. The composition of each region is illustrated by the line EDS analysis in Figure 12. According to EDS, the black Al-rich regions contain 64 ± 1 at. pct Al and are, therefore, TiAl_2 , and the dark gray regions contain 51 ± 2 at. pct Al and are, therefore, an almost equiatomic TiAl . The compositions of the light gray (36 ± 1.5 at. pct Al) and white (25 ± 2 at. pct Al) regions correspond, respectively, to the Al-rich and Ti-rich boundaries of the Ti_3Al homogeneity range at $900\text{ }^{\circ}\text{C}$. Most probably, the Al-rich Ti_3Al (light gray) is formed by interfacial reaction at the TiAl/Ti interface, while the formation of the stoichiometric Al-rich Ti_3Al (white) is preceded by diffusion and dissolution of Al in Ti followed by transformation of saturated Ti(Al) into Ti_3Al .

It is obvious from the preceding results that hot pressing of a 50 at. pct Al ($5\text{ }\mu\text{m}$)-50 at. pct Ti ($10\text{ }\mu\text{m}$) blend for 1 hour at $900\text{ }^{\circ}\text{C}$ does not allow it to reach thermodynamic equilibrium. According to Ti-Al phase diagrams from different sources,^[28-31] the equilibrium composition of a 50Al-50Ti alloy at $900\text{ }^{\circ}\text{C}$ should be either a single-phase equiatomic TiAl or a mixture of the slightly substoichiometric (Ti-deficient) TiAl and the Al-rich Ti_3Al . In order to reach equilibrium, hot-pressed samples were annealed at $1100\text{ }^{\circ}\text{C}$ for different times and then cooled and annealed at $900\text{ }^{\circ}\text{C}$ for 1 hour. The XRD analysis showed that after a 2-hour anneal ($1100\text{ }^{\circ}\text{C}$, 2 h + $900\text{ }^{\circ}\text{C}$, 1 h), the material contained ~ 95 vol pct TiAl and ~ 5 vol pct Ti_3Al . Longer anneals at $1100\text{ }^{\circ}\text{C}$ (up to 10 hours) did not result in any change in the phase composition compared to the 2-hour anneal. It was suggested, therefore, that the preceding composition is the equilibrium phase composition of the 50Al-50Ti alloy at $900\text{ }^{\circ}\text{C}$. The EDS analysis showed that both Ti_3Al and TiAl phases had a fixed Al content: 36 ± 1.5 at. pct (24 wt pct) Al in the former and 51 ± 2 at. pct (37.4 wt pct) Al in the latter. Based on simple mass balance equations, the calculated fractions of each phase in such an alloy are ~ 7 wt pct (6 vol pct) Ti_3Al and ~ 93 wt pct (94 vol pct) TiAl , which are in good agreement with the ex-

Table I. Phase Composition, Estimated Grain Size, and Mechanical Properties of Materials Synthesized from Cold Sintered 50 At. Pct Al-50 At. Pct Ti Powder Blends

Processing Conditions and Starting Powder Blend		XRD Phases	Grain Size (μm)	Yield Stress in Compression, σ_y (MPa)	Vickers Microhardness (MPa)
Hot press 900 °C, 250 MPa	Al, 5 μm + Ti, 10 μm	TiAl ₂ , TiAl, Ti ₃ Al	≤ 2	850	5200
	Al, 5 μm + Ti, 10 μm , extruded	TiAl, Ti ₃ Al	≤ 1	910	5800
Hot press (900 °C) + 1100 °C, 10 h	Al, 1 μm + Ti, 1 μm	TiAl, Ti ₃ Al	≤ 1	930	6000
	Al, 5 μm + Ti, 10 μm	TiAl, Ti ₃ Al	≤ 5	730	4400
	Thermal explosion, 150 MPa	TiAl ₂ , TiAl, Ti ₃ Al, Ti	≤ 2	800	4900
Al, 5 μm + Ti, 10 μm	$T_{\text{die}} = 700$ °C	TiAl ₂ , TiAl, Ti ₃ Al, Ti	≤ 2	800	4900
	$T_{\text{die}} = 900$ °C	TiAl, Ti ₃ Al	≤ 6	780	4800

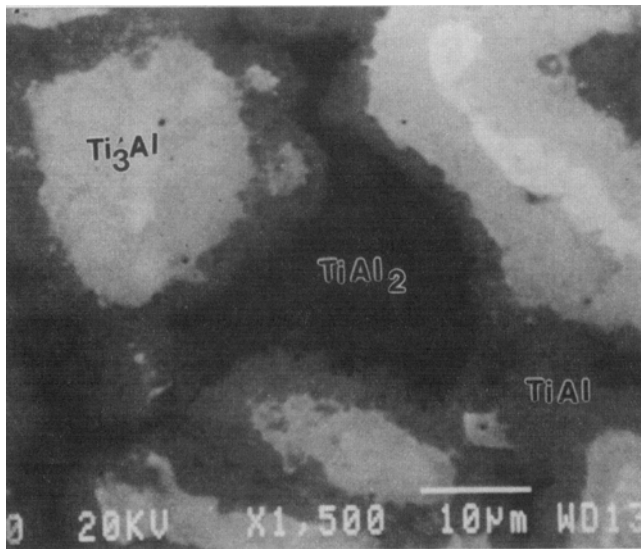


Fig. 6—Backscattered SEM micrograph of a cold-sintered (Al, 5 μm -Ti, 10 μm) sample after hot pressing at 900 °C, 100 MPa for 1 h.

perimental (XRD) data cited earlier. These results indicate that, at least at 900 °C, the equiatomic 50Al-50Ti alloy lies beyond the homogeneity range of γ -TiAl phase in the Ti-Al binary and must, therefore, have a two-phase TiAl-Ti₃Al composition.

2. Samples prepared from fine (Al, 1 μm + Ti, 1 μm) or extruded blends

For the fine (Al, 1 μm + Ti, 1 μm) cold-sintered blend, a near-equilibrium composition containing ~93 vol pct TiAl and ~7 vol pct Ti₃Al was reached after hot pressing at 900 °C for 1 hour (Figure 13(a)). This must be a result of the significantly shorter diffusion distances in the (Al, 1 μm + Ti, 1 μm) blend compared to the coarser (Al, 5 μm + Ti, 10 μm) blend, where solid-state reaction between Ti and Al could only be completed after longer exposures at higher temperatures. Annealing the fine powder hot-pressed sample at 1100 °C did not bring about any measurable changes in the phase composition. The EDS analysis of the phases could not be performed due to the very fine microstructure of the material synthesized with phase dimensions below the resolution of the EDS method. It is assumed, however, that, similarly to the previously dis-

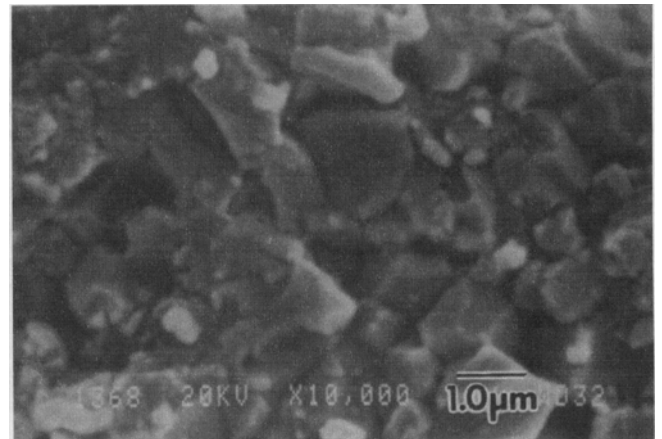


Fig. 7—SEM fracture surface of a cold-sintered (Al, 5 μm -Ti, 10 μm) sample after hot pressing at 900 °C, 150 MPa for 1 h.

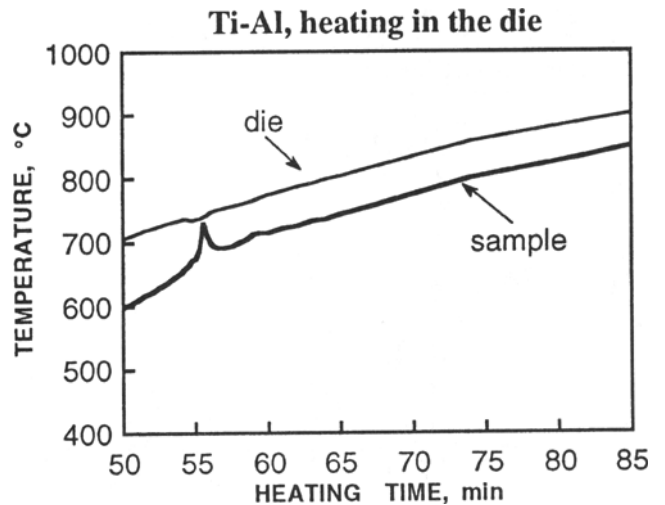


Fig. 8—Temperature of a cold-sintered (Al, 5 μm -Ti, 10 μm) sample during heating in a hot press.

cussed coarser Ti-Al blend, the compositions of the TiAl and Ti₃Al phases correspond, respectively, to the Ti-rich and Al-rich boundaries of their homogeneity range.

It should be noted that, although the synthesis of TiAl from fine powders can be accomplished at lower temperatures and in shorter times, coarser metal powders may be

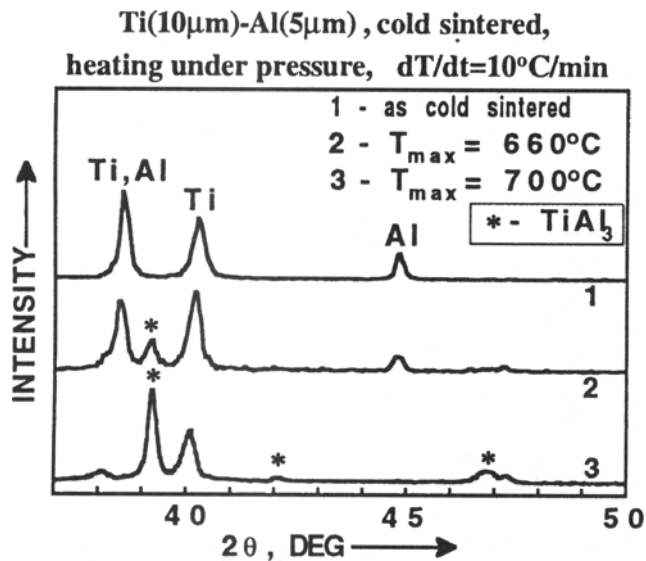


Fig. 9—XRD patterns of a cold-sintered (Al, 5 µm-Ti, 10 µm) sample (2) before and (3) after the temperature rise around 670 °C during heating in a hot press (corresponds to Fig. 8).

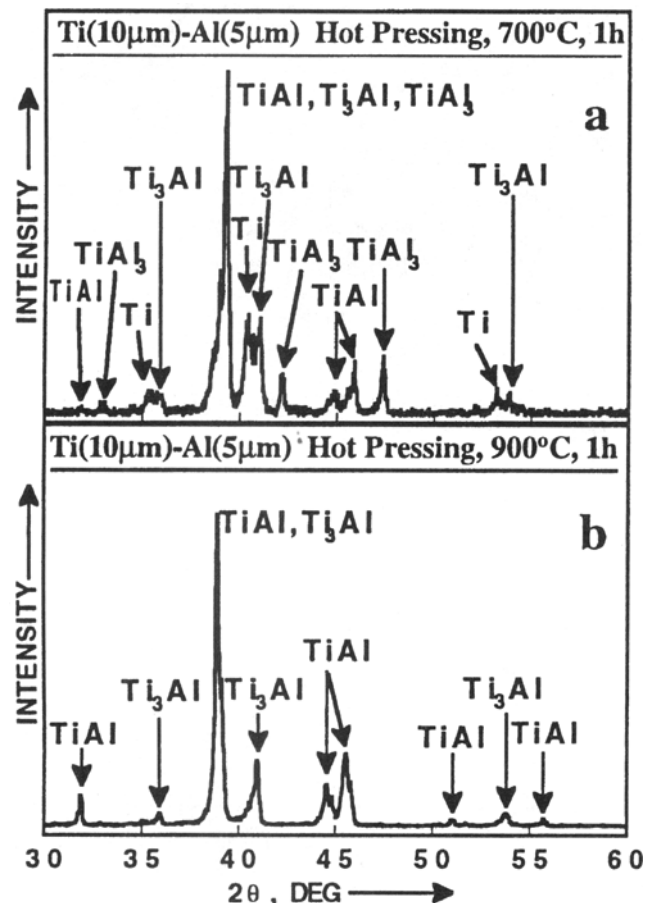


Fig. 10—XRD patterns of a cold-sintered (Al, 5 µm-Ti, 10 µm) blend: (a) after hot pressing at 700 °C, 250 MPa for 1 h and (b) after hot pressing at 900 °C, 150 MPa for 1 h.

potentially more useful in industrial applications since fine powders are more expensive and their handling is difficult. A finer microstructure and correspondingly shorter diffusion distances in coarser powder blends can be achieved,

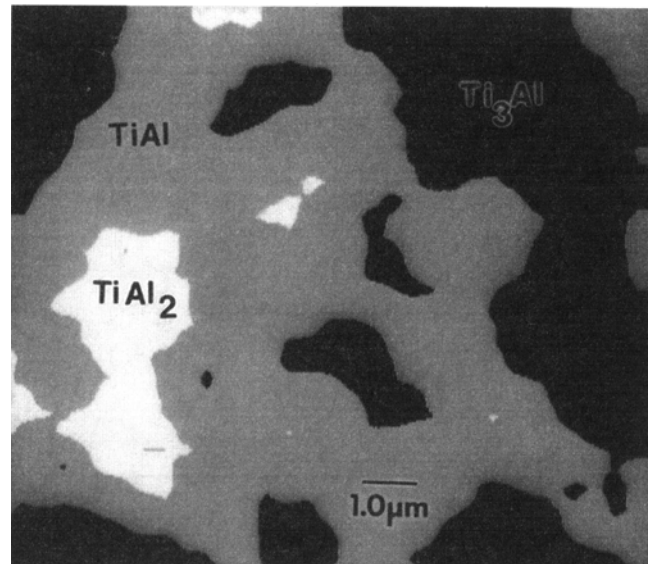


Fig. 11—X-ray map (Al) of a cold-sintered (Al, 5 µm-Ti, 10 µm) sample after hot pressing at 900 °C, 100 MPa for 1 h.

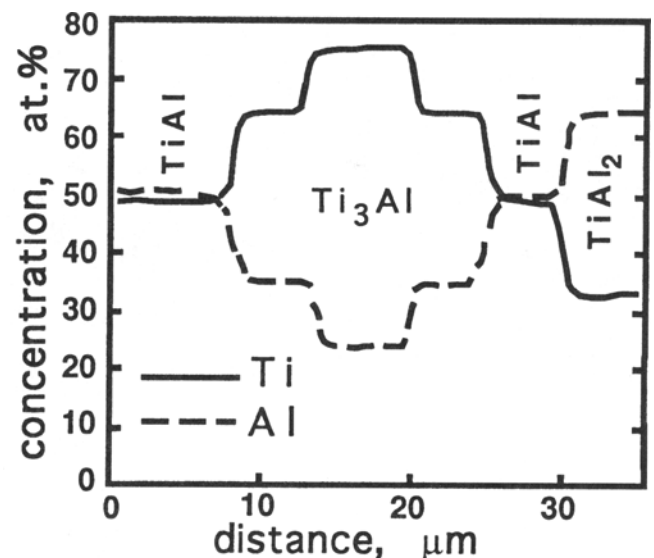


Fig. 12—Line EDS analysis across different phases in a cold-sintered (Al, 5 µm-Ti, 10 µm) sample after hot pressing at 900 °C, 100 MPa for 1 h.

for example, by extrusion. Figure 14 shows the microstructure of an as-extruded (Al, 5 µm + Ti, 10 µm) sample parallel to the extrusion direction. Both Al and Ti powder particles have been elongated to thin fibers, and the mean interparticle distance perpendicular to the extrusion direction has been reduced to 2 to 3 µm. The XRD analysis showed that, within the detection limits of ~3 vol pct, the as-extruded samples contained no phases other than elemental Al and Ti. This indicates that, if their was a local temperature increase above 400 °C during extrusion, it was not enough to initiate reaction between Ti and Al with the formation of Ti-Al intermetallics. After hot pressing at 900 °C for 1 hour the only phases detected by XRD in the extruded sample were TiAl and Ti₃Al (Figure 13(b)). It can be seen that, in contrast to the unextruded (Al, 5 µm + Ti, 10 µm) blend (Figure 10(b)), almost full conversion of Ti + Al into the final products (TiAl and Ti₃Al) was achieved

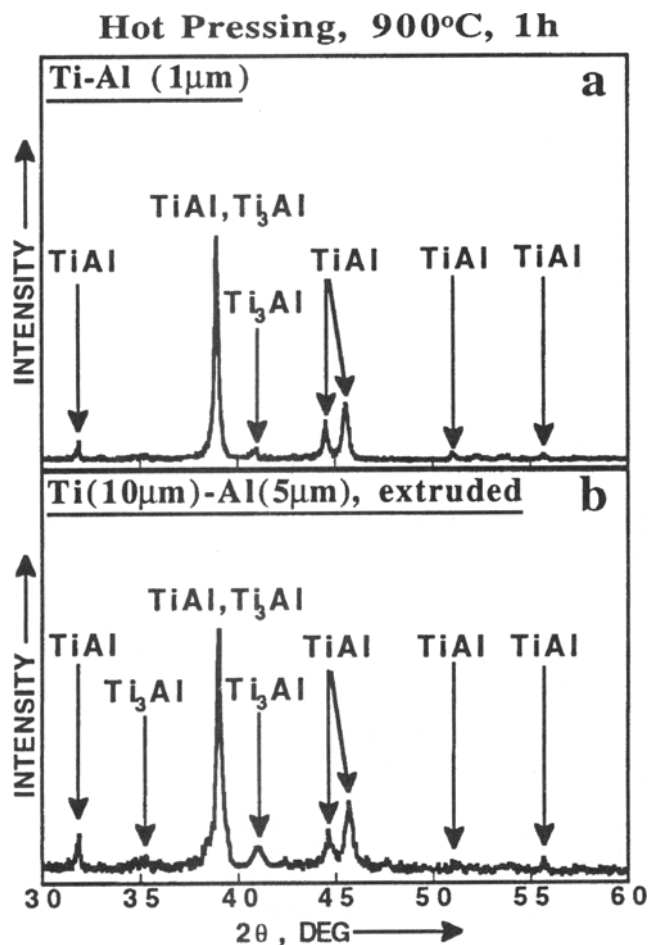


Fig. 13—XRD patterns of cold-sintered Ti-Al blends after hot pressing at 900 °C, 150 MPa for 1 h: (a) fine (Al, 1 μm-Ti, 1 μm) blend and (b) extruded (Al, 5 μm-Ti, 10 μm) blend.

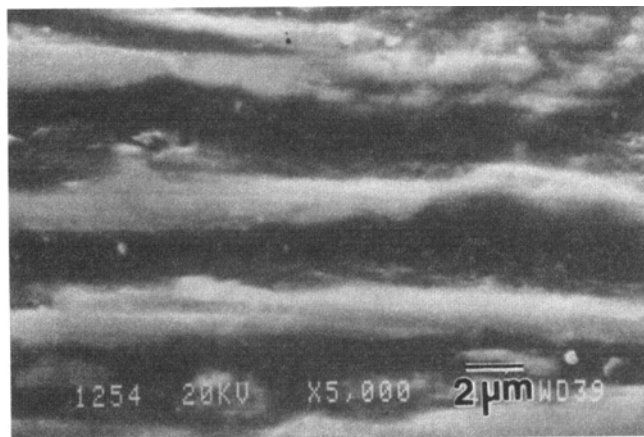


Fig. 14—SEM micrograph of an as-extruded (Al, 5 μm-Ti, 10 μm) blend parallel to the extrusion direction, $R = 25:1$.

in the extruded sample after 1 hour of hot pressing at 900 °C. The phase composition of the extruded (Al, 5 μm + Ti, 10 μm) blend (Figure 13(b)), is very similar to that of the fine 1-μm powder blend after the same treatment (Figure 13(a)). This means that extrusion of relatively coarse Ti-Al powder blends prior to the synthesis treatment allows the reaction of Ti aluminides formation to be completed at lower temperatures and in shorter times. This must

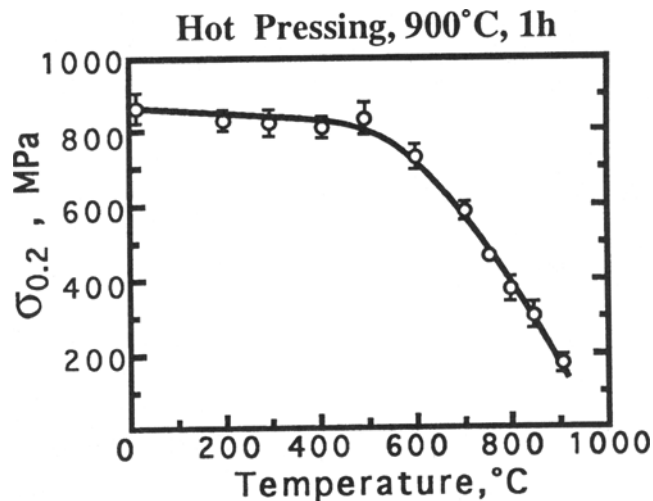


Fig. 15—Temperature dependence of the yield stress of cold-sintered (Al, 5 μm-Ti, 10 μm) samples hot pressed at 900 °C, 150 MPa for 1 h.

be due to the shorter diffusion distances in extruded samples, as well as to the disintegration of surface oxide layers during extrusion, resulting in lower activation barriers during subsequent reaction synthesis.

C. Mechanical Properties

Microhardness and room temperature yield stress (in compression) of the Ti-Al intermetallics synthesized in this work *via* different processing routes are summarized in Table I. It can be seen that the finer the initial powder blend, the smaller the grain size of the final product and the higher its mechanical properties. Similarly, the lower the processing temperature, the finer the grains in the final product and the higher its mechanical properties. The room temperature yield stress values obtained in this work in the reactively hot-pressed TiAl, $\sigma_y = 850$ to 930 MPa, are considerably higher than the data reported for TiAl synthesized from elemental powders^[13] or foils^[17] or consolidated from rapidly solidified prealloyed powders.^[32,33,34] Higher yield strength values were only reported for submicrocrystalline TiAl with 0.4-μm grain size.^[24] The very high σ_y and microhardness obtained here are also attributed to the fine micron size grains of the material synthesized.

In Figure 15, the yield stress in compression, σ_y , of TiAl samples hot pressed from the (Al, 5 μm + Ti, 10 μm) blend at 900 °C is shown as a function of the test temperature. It can be seen that σ_y remains practically unchanged until ~500 °C, after which it drops rather rapidly. Typical examples of compression stress-strain curves in Figure 16 illustrate the ductility of the material at different temperatures. The relatively high plastic strain, $\epsilon_p \approx 20$ pct, obtained in ambient conditions, increases with the temperature reaching, at 850 °C or 900 °C, values in excess of 200 pct. The characteristic feature of the material behavior at high, *e.g.*, 850 °C, temperatures is the absence of strain hardening. Temperature dependence of the strain-rate sensitivity coefficient, m (Figure 17), shows that, starting from ~750 °C, m rapidly increases with temperature and reaches the value of 0.2 at 800 °C. High values of the strain-rate sensitivity coefficient ($m \geq 0.2$) are usually associated with hundreds percent of plastic deformation in tension typical of super-

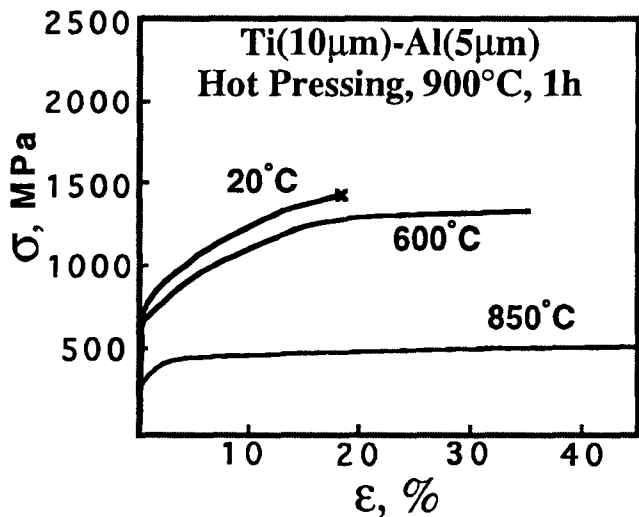


Fig. 16—Representative stress-strain curves in compression of cold-sintered (Al, 5 μm -Ti, 10 μm) samples hot pressed at 900 $^{\circ}\text{C}$, 150 MPa for 1 h: T_{room} , 600 $^{\circ}\text{C}$, and 850 $^{\circ}\text{C}$.

plastic behavior.^[27] For TiAl, superplastic behavior was previously observed in the 1000 $^{\circ}\text{C}$ to 1100 $^{\circ}\text{C}$ temperature range for a material with 5- μm size grains ($m = 0.5$)^[32] and at temperatures as low as 800 $^{\circ}\text{C}$ for a material with the much finer 0.4- μm size grains ($m > 0.3$).^[24] The high m values observed in the present research at relatively low temperatures must also be the result of the fine micron size grains of the TiAl material synthesized (Figure 5). Superplastic behavior is attractive for the forming processes and can be utilized for the processing of complex shape TiAl. In high temperature applications, however, superplasticity will result in enhanced creep rates and should, therefore, be avoided.

IV. SUMMARY AND CONCLUSIONS

The goal of the present research was to synthesize dense γ -TiAl based intermetallic samples from fully dense cold-sintered 50 at. pct Al-50 at. pct Ti powder blends. This was successfully accomplished *via* two different processing routes: combustion consolidation (thermal explosion under pressure) and reactive hot pressing. In both approaches, relatively low processing or preheating temperatures (≤ 900 $^{\circ}\text{C}$) were used. The entire procedure of thermal explosion under pressure could be performed in open air without noticeable oxidation damage to the final product. The application of a moderate external pressure (≤ 250 MPa) during synthesis was enough to accommodate the negative volume change associated with TiAl formation from the elemental components and, thereby, to ensure near full density of the final product. The Ti-Al materials synthesized in this work had encouraging mechanical properties comparable with previously reported data for TiAl based alloys.

It was found that, at elevated temperatures (e.g., 900 $^{\circ}\text{C}$), the equiatomic 50Al-50Ti alloy lies beyond the homogeneity range of the γ -TiAl phase in the Ti-Al binary and contains, in addition to γ -TiAl, Al-rich Ti_3Al . This equilibrium composition could be reached after 1 hour of reactive hot pressing at 900 $^{\circ}\text{C}$ when a fine (Ti, 1 μm + Al, 1 μm) blend was used as a starting material or when a coarser (Al, 5 μm + Ti, 10 μm) blend was extruded prior to hot press-

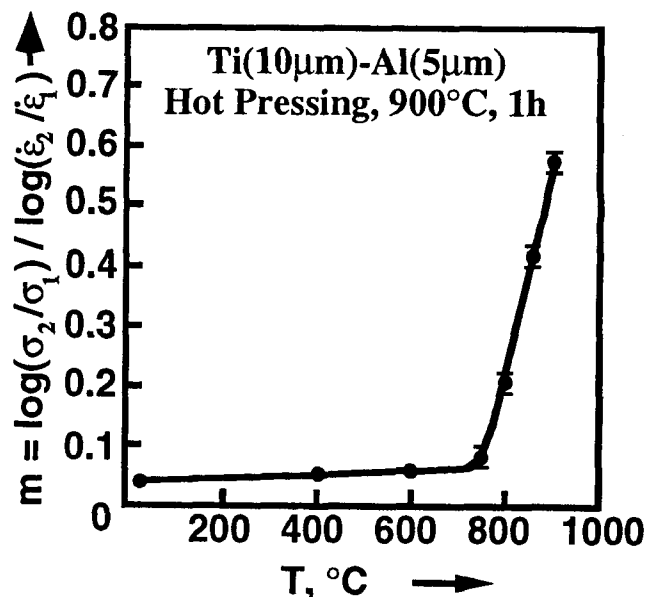


Fig. 17—Temperature dependence of strain-rate sensitivity, m , for cold-sintered (Al, 5 μm -Ti, 10 μm) samples hot pressed at 900 $^{\circ}\text{C}$, 150 MPa for 1 h.

ing. Due to the low processing temperature, the Ti-Al materials obtained *via* reactive hot pressing had a fine microstructure with the grain size not exceeding 1.5 μm . As a result, the reactively hot-pressed TiAl exhibited superplastic behavior at temperatures as low as 800 $^{\circ}\text{C}$. This phenomenon can be further utilized for full density consolidation/processing of complex shape TiAl parts.

The results obtained in the present research indicated that the synthesis of dense TiAl may be accomplished at temperatures considerably lower than those typical of the current TiAl processing/consolidation methods.

ACKNOWLEDGMENTS

This work was supported by the United States-Israel Bi-national Science Foundation (BSF) through Grant No. 92-00208.

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