

Reaction synthesis of titanium aluminides

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The formation of titanium aluminides from the elemental powders has been investigated. A traditional powder metallurgy route of compaction (by cold isostatic pressing, hot pressing or hot extrusion) followed by heat treatment was compared with the novel technique of hot extrusion reaction synthesis (HERS). The products from these different production methods were characterised by x-ray diffraction and microscopy (light and scanning electron). The intermetallic compound formed under most processing conditions was $TiAl_3$. Only when there was a rapid increase in temperature to high temperatures, as found in induction heating of compacts or in HERS, were the compounds Ti_3Al and $TiAl$ formed.

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1. Introduction

The intermetallic compounds Ti_3Al and $TiAl$ have considerable potential in aerospace applications, where they offer significant weight savings over traditional superalloys. However, due to their lack of ductility and the difficulty in their production by conventional methods, powder processing has been employed as a method in which near-net shapes can be obtained with very little post-fabrication machining required. However, powder processing of intermetallic compound powders is expensive, hence interest has developed in producing the compounds by compacting a mixture of aluminium and titanium powders and subsequently initiating the reaction to form the compounds; this process is known as reaction synthesis or reaction sintering [1–7].

A modification of reaction synthesis process, whereby the reaction is initiated during hot extrusion has recently been reported by McShane and co-workers for the $NiAl$ and $TiAl$ systems [8–13]. This process has the potential of being a rapid method of producing near-net shape intermetallic compound products with negligible porosity, although to date the process has not been fully optimised and the porosity content remains high. Work has been, and is continuing to be, carried out on determining the processing conditions (extrusion temperature, speed and ratio) necessary for hot extrusion reaction synthesis (HERS) as a function of composition. In the course of this work it became clear that further knowledge of the effect of factors such as composition, compacting method and reaction initiation procedures, on the compound formed and the rate of formation in reaction sintering was required before a full understanding of HERS was feasible.

This paper reports the results of such a study on the $Ti-Al$ system. Three compacting methods have been

employed, namely isostatic cold pressing, hot pressing and hot extrusion and the reaction has been initiated in the compacts over a range of heat treatment schedules.

2. Experimental procedure

2.1. Powder compositions and compaction methods

Powders of titanium (purity 99.5% and particle size $50\ \mu m$) and aluminium (purity 99.7% and particle size $45\ \mu m$) were blended in a 3D rotating Turbula mixer to give the following compositions (wt%): $Ti-19wt\%Al$, $Ti-20wt\%Al$, $Ti-35wt\%Al$, $Ti-37.5wt\%Al$ and $Ti-70wt\%Al$. In addition a limited amount of work was carried out on mixing using a high energy mill. 80 g batches of powder were loaded into four steel milling vials, lined with titanium, in a Fritsch P5 planetary mill (ball to powder ratio 10 : 1). The mill was run at 275 rpm in an argon atmosphere with 15 min on and 15 min off for total milling times of up to 2 hours.

Room temperature compaction of the blended elemental powders was performed by uniaxially pressing the powders in a 13 mm cylindrical steel die under a maximum pressure of 13 MPa to approximately 85% of the theoretical density. This was followed by cold isostatic pressing at a maximum pressure of 300 MPa for one minute, to produce small pellets of 12 mm diameter and 5 mm thick. This route is designated CPIP for brevity.

For the hot pressing and extrusion routes, larger green billets were first cold compacted in a 60 mm diameter cylindrical steel die, under a uniaxial pressure of 250 MPa to a density of 85%. Subsequent hot pressing or extrusion was carried out in an ENEFCO extrusion press, in the temperature range 350–400°C after first

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preheating the billet in an air furnace. Direct extrusion was employed with an extrusion reduction ratio of 20:1, a ram speed of 3 mm s^{-1} (maximum pressure 1000 MPa). Ytria dag lubricant was used to minimise friction.

2.2. Heat treatment of compacts

Thermal analysis was carried out using differential scanning calorimetry (DSC) and differential thermal analysis (DTA) equipment. The heating rate employed was slow (5°C min^{-1}) and the run was usually terminated in the temperature range 700–800°C.

Isothermal heat treatments were carried out in a tube furnace with an argon atmosphere under normal atmospheric pressure. Slow heating rates of $2.5^\circ\text{C min}^{-1}$ to temperatures in the range 500–600°C with holding times of 1 hr, 10 hrs and 36 hrs were used.

In addition to the slow heating rate treatments, two different high heating rate experiments were undertaken. In the first specimens containing 19 to 37.5 wt% Al were introduced into an air circulating furnace at temperatures of 800, 1100 and 1200°C for 5 mins followed by water quenching. In the second, an alumina tube induction heater was used to heat small CPIP pellets of 19 to 37.5 wt% Al to 1100°C at rates of 20–25°C s⁻¹. As soon as the temperature was reached, the power was switched off. These induction heating tests were conducted in two atmospheres, pure argon and a controlled argon/oxygen mixture (10:1) (flow rate 11 litres min⁻¹).

2.3. Structure of products

Characterisation of the materials produced was achieved using density measurements (Archimedes' principle), x-ray diffraction (XRD) and scanning electron microscopy (SEM). A Philips PW1710 diffractometer with Cu K α radiation, a step scan rate of 1 s per step of size 0.04° (2θ) over the 2θ angle range 5–100°, was used for XRD from polished samples. The microstructure was observed using JEOL JSM-T200 and T220 scanning electron microscopes in both secondary and back-scattered electron image modes. A JEOL JSM-35 equipped with an energy dispersive x-ray analysis system was employed for compositional analysis.

3. Results and discussion

3.1. Structure of compacts

All compaction methods yielded products with an intimate mixture of the two elemental constituents (note that the hot extrusion conditions were chosen so that HERS did not occur). Typical densities (as a percentage of theoretical) of the green compacts are: CPIP 89%, hot pressing 95%, hot extrusion 99%. Fig. 1 shows the well densified, unreacted microstructure of a hot extruded Ti-55wt%Al sample.

The milled material, even with the addition of salt as a process control agent, adhered to the interior of the milling containers and hence very little material was

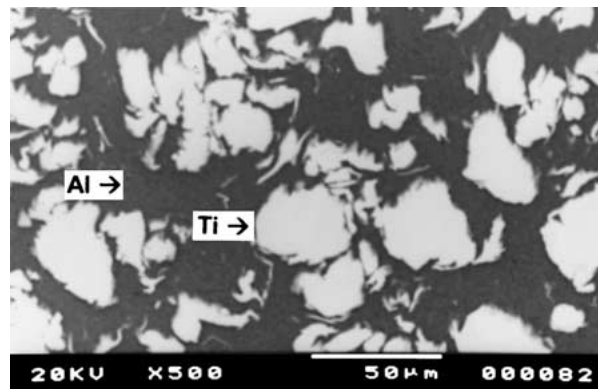


Figure 1 Scanning electron micrograph (BEI) of hot extruded Ti-55wt%Al (the light coloured phase is Ti).

retrieved. XRD demonstrated that only Ti and Al was present even after 2 hours milling, i.e., no mechanical alloying had taken place. Samples milled for 15 minutes showed no significant difference in morphology from powder produced by the Turbula mixer. For longer milling times of up to 2 hours the most noticeable difference was the flattening and elongation of the Al particles. The limited amount of milled material restricted further work to thermal analysis.

3.2. Thermal analysis

XRD demonstrated that, irrespective of compaction method, under the thermal analysis conditions employed in this study the product at the end of a run consisted of TiAl₃ plus Ti and/or Al depending on the composition (Fig. 2). This is consistent with thermodynamic calculations which show that TiAl₃ has the lowest free energy of formation among the compounds TiAl₃, TiAl, TiAl and type-I aluminides [14]. Alternatively, it has been claimed that the first compound to form from constituent elements is that with the most negative heat of formation at the composition of the lowest temperature liquidus in the binary system [15].

Fig. 3 compares the DSC data for Ti-70wt%Al compacted by the different methods. The general features of these curves are (i) evidence of an exothermic reaction (a small rise in the curve) just prior to the aluminium melting endotherm (ii) aluminium melting endotherm, and (iii) a large exothermic peak at a temperature in the range 670–730°C; similar features have been reported by Dahms and coworkers [4, 7]. The two exothermic peaks were due to the formation of TiAl₃; the low temperature peak was associated with a slow solid state

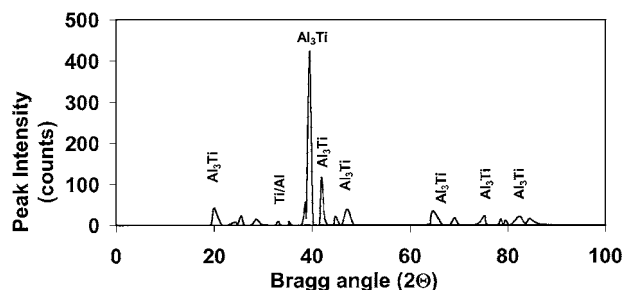


Figure 2 XRD trace for hot extruded Ti-70wt%Al after a DSC run.

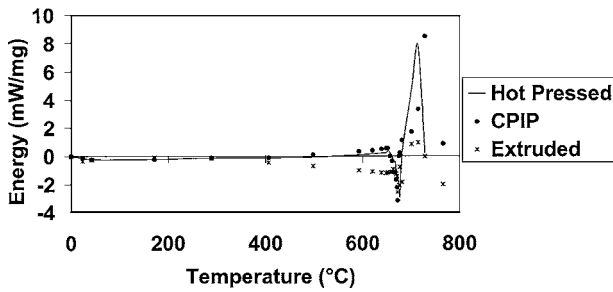


Figure 3 Effect of compaction method on the DSC curves for Ti-70wt%Al.

reaction and the higher peak to a more rapid reaction between liquid Al and solid Ti. The compaction method affected the extent of these features. The lower density CPIP and hot pressed samples showed limited solid state formation of the intermetallic compound but extensive formation by the liquid-solid reaction. In contrast the dense extruded material exhibited extensive compound formation prior to the melting of the aluminium and consequently both subsequent endothermic and exothermic peaks were reduced in magnitude. The liquid-solid exothermic peak temperature also occurred at a lower temperature the more dense the compact. The behaviour of the extruded material is attributed to the good contact between constituents, the increased area of contact associated with change in particle shape and the deformation structure increasing the reactivity.

The effect of composition on the formation of $TiAl_3$ is exemplified by the DSC curves for CPIP material (Fig. 4). As the Ti content increased, the melting endotherm became less pronounced and was absent, or more likely dominated by the exothermic reactions, for Ti-35wt%Al. The peak temperature decreased with increasing Ti content, presumably due to the accompanying increase in Al/Ti interfacial area. (Note that Ti-35wt%Al has nearly equi-proportions by volume (53 vol%Ti) whereas Ti-70wt%Al has only 20 vol%Ti).

The energy associated with the major exothermic reaction as a function of composition is presented in Fig. 5. Assuming that the energy is directly proportional to the amount of $TiAl_3$ formed then the weight ratio of the compound in samples with Al contents of 20%, 35% and 70% is 1 : 1.9 : 2.6. Assuming equilibrium for the Ti-70wt%Al, the proportion of $TiAl_3$ calculated from the phase diagram is about 80 wt%. Therefore the amount of intermetallic in the 20% and 35%Al containing samples would be 25 wt% and 40 wt% respectively. If all

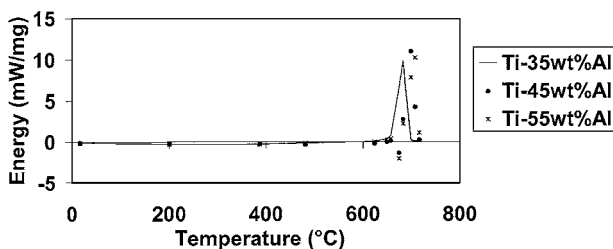


Figure 4 Effect of composition on the DSC curves of CPIP material (Ti-35wt%Al).

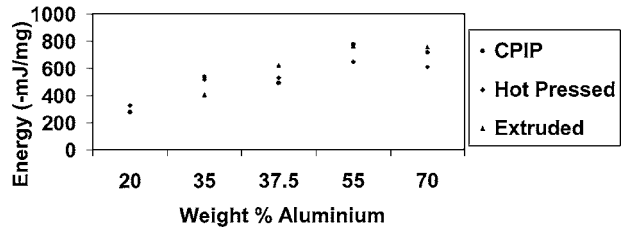


Figure 5 Energy associated with the exothermic reactions as a function of aluminium content.

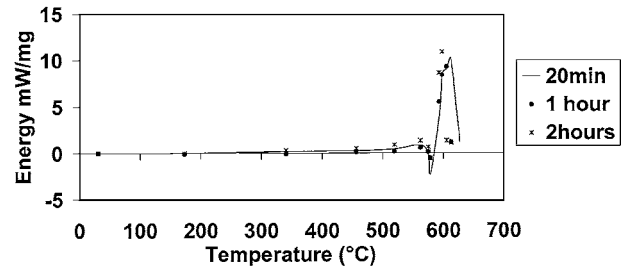


Figure 6 Effect of milling time on the DSC curves of Ti-55wt%Al.

the Al had reacted to form $TiAl_3$ the proportions would be approximately 32 wt% and 56 wt% for 20% and 35%Al containing samples respectively.

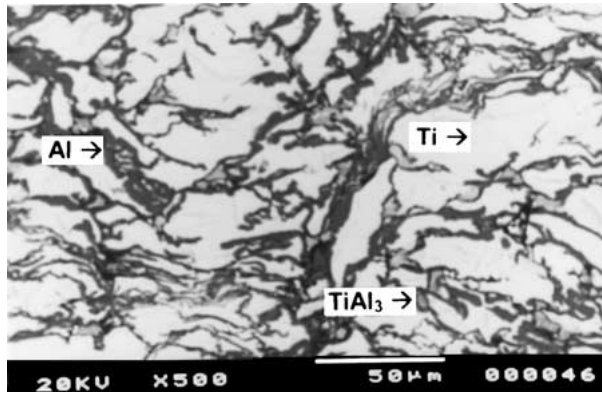
Although the milling was not sufficient to mechanically alloy the powder, it did cause heavy deformation, particularly of the Al, and brought the Al and Ti into intimate contact. Consequently, as demonstrated in Fig. 6, the reactivity increased leading to an increase in the low temperature solid-solid exotherm and a subsequent decrease in the temperature of the liquid-solid exothermic peak.

3.3. Isothermal heat treatments

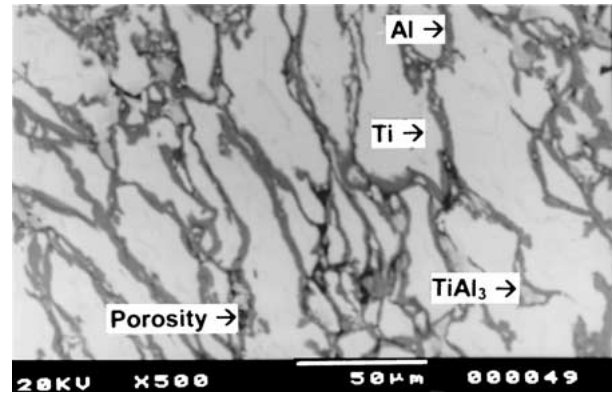
3.3.1. Slow heating

The only intermetallic compound formed from isothermal heat treatments at temperatures in the range 500–600°C was the aluminium-rich $TiAl_3$. The amount of intermetallic compound, and associated porosity due to the Kirkendall effect and differences in molar volume between reactants and product, increased with time at a given temperature (Fig. 7) and with temperature for a given heat treatment time. The total porosity content as determined by image analysis was of the order of 20 vol% after 36 hours heat treatment at 600°C of hot pressed and extruded materials containing 19 to 35 wt%Al (Fig. 8). The porosity content of the hot pressed and extruded Ti-70wt %Al samples heat treated under the same conditions had a much higher porosity of about 40 vol% as a consequence of the greater amount of intermetallic formed. The total porosity content of CPIP material was slightly higher than hot pressed/extruded materials of the same composition and heat treatment due to the lower green density.

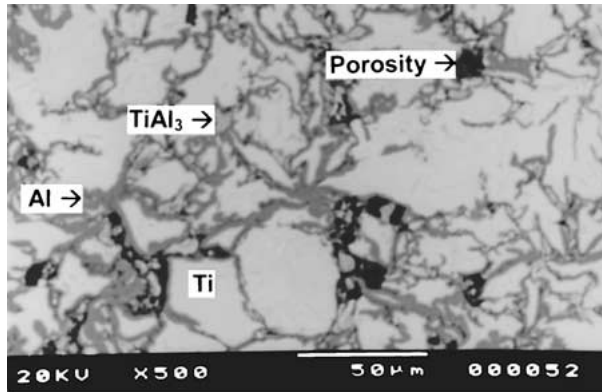
The thickness x of the $TiAl_3$ layer was measured as a function of time and temperature T . The activation energy for formation of the intermetallic was then calculated from the slopes of plots of $\ln x^2$ against $1/T$ for constant heat treatment times. There was considerable



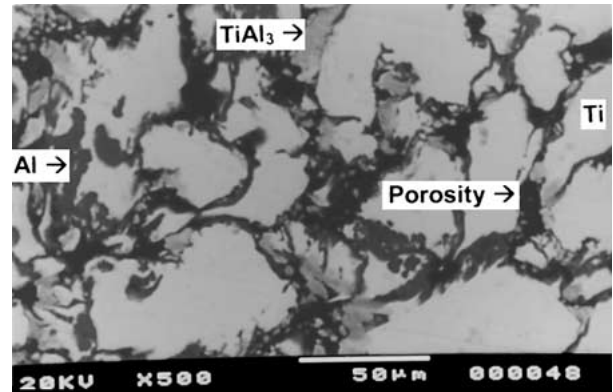
(a)



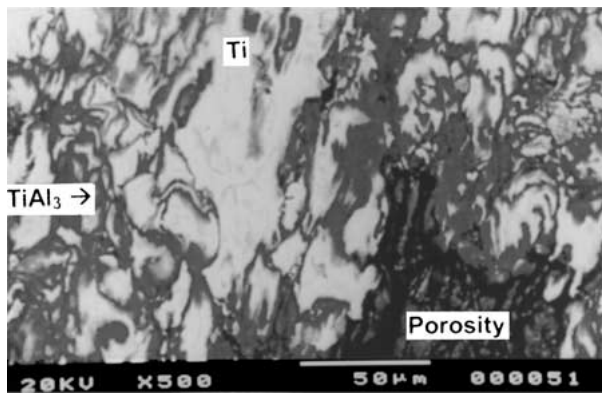
(b)



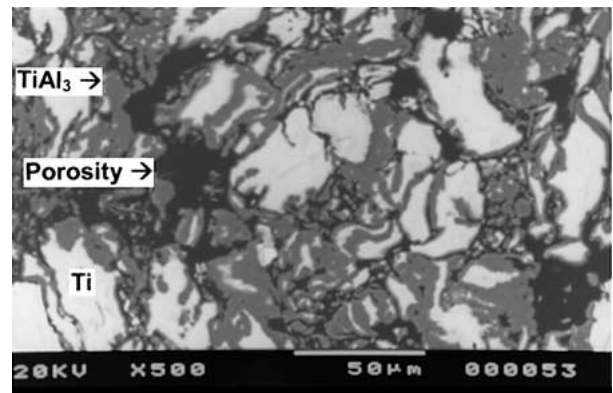
(c)



(d)



(e)



(f)

Figure 7 Scanning electron micrographs (BEI) showing the effect of time at heat treatment temperature of 525°C on the microstructure of extruded material (a) Ti-19wt%Al, 1 hr, transverse section (b) Ti-19wt%Al, 5 hr, longitudinal section (c) Ti-19wt%Al, 36 hr, transverse section (d) Ti-35wt%Al, 1 hr, transverse section (e) Ti-35wt%Al, 5 hr, longitudinal section (f) Ti-35wt%Al, 36 hr, transverse section.

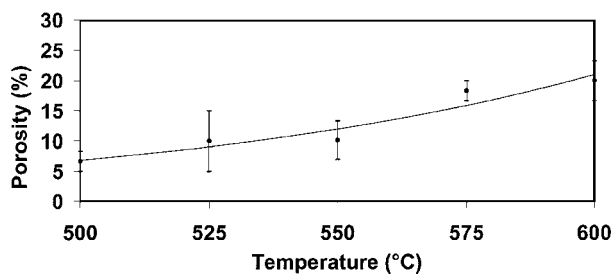


Figure 8 Porosity after 36 hours heat treatment as a function of temperature for alloys containing 19 to 35wt%Al.

scatter in the data and no difference in activation energy, within experimental error, was found for the three compacting routes, namely CPIP, hot pressing and hot extrusion. The average activation energy obtained from

all the data was 207 ± 82 kJ/mol, which is in acceptable agreement with that quoted by van Loo and Rieck from intermetallic layer growth measurements in Ti-Al diffusion couples (180 ± 6 kJ/mol [15]), and that obtained from Kissinger analysis of DSC curves at different heating rates (200 ± 20 kJ/mol [4]).

3.3.2. Rapid heating

The product of these heat treatments, whether carried out in the furnace or by induction heating, was a mixture of the titanium aluminides TiAl and Ti₃Al, with the amount of the former being greater in the higher aluminium content (35 and 37.5 wt%Al) materials (Figs 9 and 10). This contrast with the heat treatments in the temperature range 500–600°C inclusive

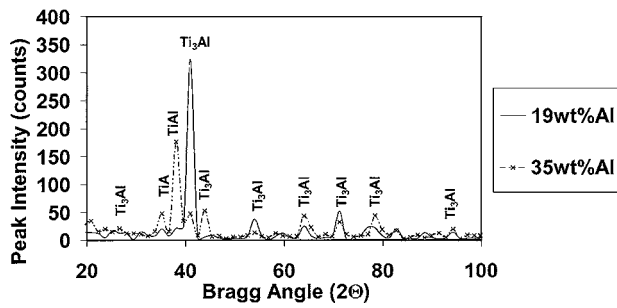


Figure 9 X-ray diffraction patterns from hot pressed Ti-19wt%Al and Ti-35wt%Al rapidly heated to a heat treatment temperature of 1200°C.

that always resulted in the formation of $TiAl_3$. These data are consistent with the findings of Lee and Lee [5] who reported increasing amounts of $TiAl$ and Ti_3Al as the heating rate was increased from 5°C/min to 300°C/min.

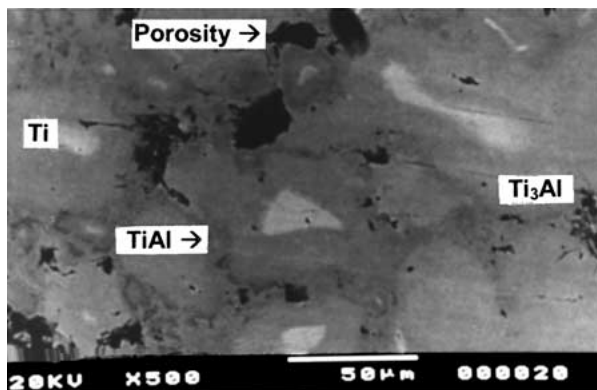
Extrapolation of the thermodynamic data of Sujata *et al.* [14] indicates that $TiAl$ and Ti_3Al will never form directly from Ti and Al in preference to $TiAl_3$. On the other hand, as no residual aluminium was detected in any of the samples subjected to high heating rates, the proposal of these workers that $TiAl$ and Ti_3Al are formed by a reaction between Ti and $TiAl_3$ in the absence of Al is confirmed.

The pores in these samples were larger than in the slowly heated samples (Fig. 10). This is a consequence of the negligible extent of the solid-solid reaction and hence an absence of the smaller Kirkendall porosity

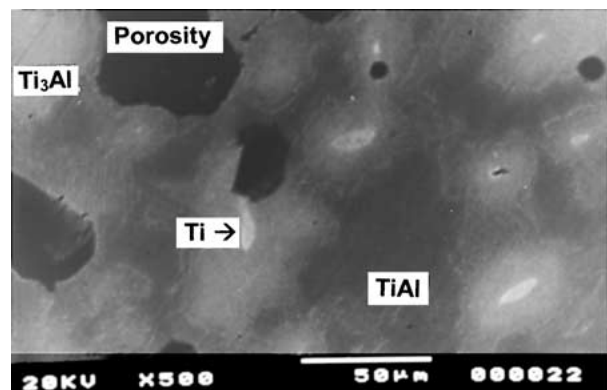
and the presence of a large amount of mobile liquid aluminium giving a rapid reaction.

A typical temperature versus time plot from an induction heating run is presented in Fig. 11. The exothermic reaction was initiated at approximately 900°C (the ignition temperature, T_{ig}) and a maximum temperature (combustion temperature, T_c) of nearly 1200°C was reached. For the solid Ti -liquid Al reaction Yi, Petric and Moore [17] found T_{ig} and T_c to be heating rate independent for rates up to 50°C/min with T_{ig} approximately equal to the melting point of Al and $T_c = 1300°C \pm 100°C$. In contrast, Lee and Lee's data show higher temperatures the faster the heating rate, reaching values of 850°C and 1225°C for T_{ig} and T_c respectively at their fastest heating rate of 300°C/min. The heating rate imposed by induction heating in the current work, was much higher, namely 20–25°C/s (1200–1500°C/min) than in previous investigations. T_{ig} and T_c values are affected by powder size and morphology, and compact density, nevertheless the current results, taken in conjunction with those of [5], indicate that although T_{ig} and T_c may be heating rate dependent at rates less than 300°C/min, they are not a strong function of heating rate at very fast heating rates.

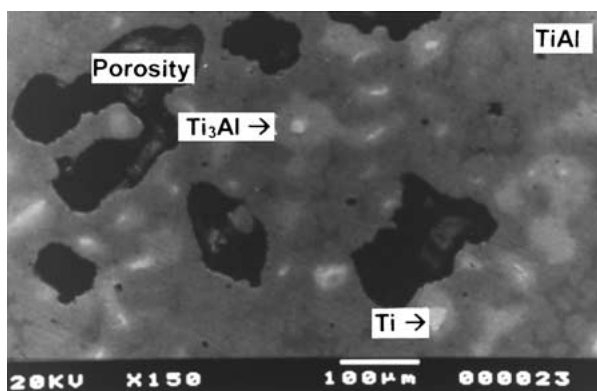
In HERS processing of $Ti-Al$ elemental mixtures containing 19–37.5 wt% Al , an extrusion temperature in excess of 425°C at an extrusion ratio of 1:20 is required for the reaction to take place. However the reaction is not initiated at 425°C but at a much higher temperature which is reached as a result of the work of extrusion and perhaps also the heat associated with



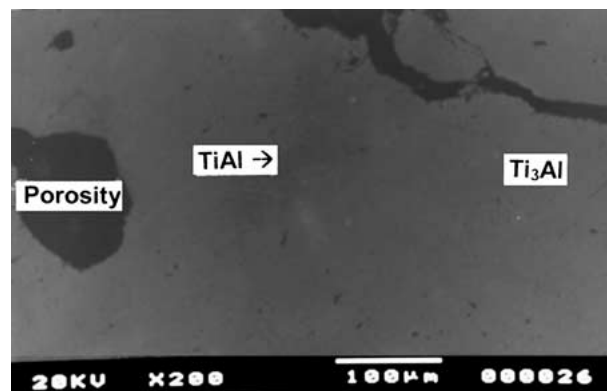
(a)



(b)



(c)



(d)

Figure 10 Scanning electron micrograph (BEI) showing most of the Ti has been converted to aluminides and large pores: (a) $Ti-20wt\%Al$, 1100°C (b) $Ti-35wt\%Al$, 1100°C (c) $Ti-37.5\%Al$, 1100°C (d) $Ti-35wt\%$, 1200°C.

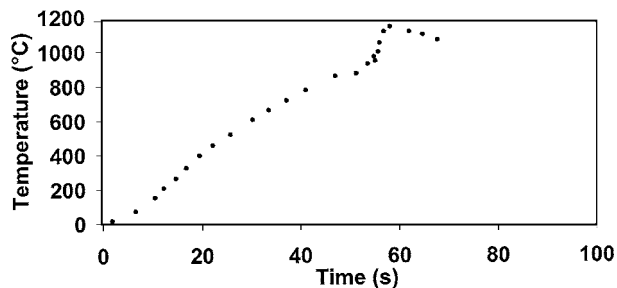


Figure 11 Plot of temperature as a function of time for induction heating of CPIP Ti-37.5wt%Al with $T_{ig} = 900^{\circ}\text{C}$ and $T_c = 1200^{\circ}\text{C}$.

a small amount of oxidation [12]. The temperature is rapidly increased to above the melting point of Al and the reaction is initiated at the exit of the die and cascades down the length of the extrudate. Thus the rapid heating experiments simulate the conditions in HERS. It is therefore understandable that the structure of extrudate produced by HERS consists of a mixture of the intermetallic compounds, TiAl and Ti_3Al , and large pores.

4. Conclusions

The research undertaken showed that irrespective of the compaction method (cold isostatic pressing, hot pressing or hot extrusion) the intermetallic compound TiAl_3 was formed on heat treatment under normal conditions. The rate of formation of TiAl_3 was strongly dependant on heat treatment temperature and less so on time; the relationship between rate and temperature followed the Arrhenius relationship with an activation energy of 207 ± 82 kJ/mol. Only when compacts were heated rapidly to the heat treatment temperatures, e.g., by induction heating, were the intermetallic compounds TiAl and Ti_3Al formed. The other method of obtaining titanium aluminides that was investigated in this study was hot extrusion reaction synthesis (HERS). The rapid increase in temperature associated HERS resulted in the formation of TiAl and Ti_3Al .

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