

# Phase relationship in the Gd-Ti-Al ternary system at 500°C

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The phase relationship in the Gd-Ti-Al ternary system at 500°C was investigated by powder X-ray diffraction (XRD), differential thermal analysis (DTA), optical microscopy and electron probe microanalysis (EPMA) techniques. The 500°C isothermal section of this ternary system consists of 14 single-phase regions, 27 two-phase regions and 14 three-phase regions. At 500°C, the maximum solid solubilities of Ti in Gd<sub>2</sub>Al, Gd<sub>3</sub>Al<sub>2</sub> and GdAl<sub>2</sub> is 2.0 at.%, 3.5 at.%, 16.3 at.%, respectively and that of Gd in Ti, Ti<sub>3</sub>Al, TiAl is less than 1 at.%.

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## 1. Introduction

Due to their good high-temperature properties and low density, the ordered intermetallic titanium aluminides, especially those based on Ti<sub>x</sub>Al ( $x = 3$  or 1), are currently under active development as attractive candidates for applications in advanced aerospace engine and airframe components [1–5]. However, their application is hindered by low ductility and toughness at ambient temperature. Studies have revealed that certain alloying additions of Cr, Mn, V to the binary Ti-Al system can improve ductility whilst Nb, Mo, W and Ta can improve oxidation resistance and high temperature strength [6–8]. Yang *et al.* [9] investigated the influence of Y in Ti-Al alloys. The result shows that the ductility and strength of TiAl alloys will increase when the Y-addition does not exceeds its solid solubility limit in TiAl alloys, which means that rare earth-addition may improve the ductility of TiAl alloys. Further progress on the development of titanium aluminides alloys, however, is hampered by a lack of RE-Ti-Al phase diagram. In this work, the 500°C isothermal section of the phase diagram of Gd-Ti-Al ternary system is studied.

The Ti-Al binary phase diagram is one of the most controversial phase diagrams [10–14]. Murray [15] calculated this system and indicated that there is only a peritectic reaction  $L + \beta\text{Ti} \rightarrow \alpha\text{Ti}$  in the 0 to 50 at.%Al composition range in high temperature. However, re-

sults of McCulloch [16] show that  $\alpha\text{Ti}$  is formed by two peritectic reactions, which is  $L + \beta\text{Ti} \rightarrow \alpha\text{Ti}$  and  $L + \alpha\text{Ti} \rightarrow \gamma\text{ (AlTi)}$ . Okamoto [17] claimed that McCulloch's result was consistent with well-accepted experimental results. According to Schuster *et al.* [11], TiAl<sub>2</sub> appears in the 55–80 at.% Al composition range, while Raman [18] reported that intermetallic compounds such as Ti<sub>2</sub>Al<sub>5</sub> and Ti<sub>5</sub>Al<sub>11</sub> were formed. According to Okamoto's [17] results, there were four intermetallic phase in this system below 500°C, namely Ti<sub>3</sub>Al, TiAl, TiAl<sub>2</sub> and TiAl<sub>3</sub> respectively.

The Gd-Al system has been studied by Buschow [19–20]. Five intermetallic compounds, namely GdAl<sub>3</sub>, GdAl<sub>2</sub>, GdAl, Gd<sub>3</sub>Al<sub>2</sub>, Gd<sub>2</sub>Al have been reported, all peritectically formed with the exception of GdAl<sub>2</sub>. Some evidence was obtained [21] that indicated the peritectoidal formation of GdAl<sub>4</sub> from the reaction of GdAl<sub>3</sub> with Al at about 400°C. Phase equilibria concerning GdAl<sub>4</sub> are not known. Recently a new hexagonal compound Gd<sub>2</sub>Al<sub>17</sub> was found by Pop *et al.* [22].

The Gd-Ti binary system has been investigated and determined by Murray *et al.* [23], no intermetallic phase was found in this system.

No Gd-Ti-Al ternary phase diagram has been reported in the literature yet. However, two ternary compounds Al<sub>20</sub>Ti<sub>2</sub>Gd [24] and Al<sub>43</sub>Ti<sub>4</sub>Gd<sub>6</sub> [25] have been identified by Niemann *et al.* Of RE-Ti-Al (RE = rare earth metal) ternary system, Yang *et al.* studied Y-Al-Ti

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[26] and Dy-Al-Ti [27] ternary systems by means of the diffusion triple method and electron microprobe analysis. They reported that Ti has a large solid solubility range in  $\text{Al}_2\text{Y}$  or  $\text{Al}_2\text{Dy}$ .

## 2. Experimental details

The starting materials used for the alloys were of high purity (Al 99.9%, Ti 99.9%, Gd 99.9%). 206 samples, each weighing 2 g, were prepared in an arc furnace in an atmosphere of purified argon. All samples were sealed in evacuated quartz tubes for homogenization annealing. The heat treatment temperature was determined by differential thermal analysis (DTA) or based on the previous work of binary systems. The Al-rich alloys were kept at 700°C for 60 days. The other samples were homogenized at 900°C for 30 days. Then the samples were cooled at a rate of 10 K/h to 500°C and kept at 500°C for 7 days. At last, the samples were quenched into an ice-water mixture. The samples for X-ray diffraction (XRD) analysis were ground into powder, annealed at 500°C for 4 days in vacuum glass tubes and quenched into liquid nitrogen. The X-ray diffraction analysis was performed on a Rigaku (3105) X-ray diffractometer with a molybdenum target and a zirconium filter. The metallographic analyses were performed using optical and scanning electron microscopy (SEM) techniques.

## 3. Results and discussion

### 3.1. Compounds $\text{GdAl}_4$ and $\text{Gd}_2\text{Al}_{17}$

Runnals *et al.* [21] reported an aluminum-rich compound  $\text{GdAl}_4$ , isotypic with  $\text{UAl}_4$ , precipitate in aluminum-gadolinium alloys cast from the liquid and decompose by a peritectoid reaction at about 400°C to form  $\alpha$ -Al and  $\text{GdAl}_3$ . Pop *et al.* [22] found a hexagonal binary compound  $\text{Gd}_2\text{Al}_{17}$  with  $\text{Th}_2\text{Zn}_{17}$  structure type ( $a = 8.869 \text{ \AA}$ ,  $c = 9.711 \text{ \AA}$ ) in the Al-Gd system. We prepared a series of samples in the Al-rich ranges of the Al-Gd system and sealed them in a vacuum tube. After annealing at 700°C for 60 days, the samples were cooled to 500°C and kept for 7 days. XRD analysis showed that when aluminum composition was more than 75 at.%Al, all the samples were composed of Al and  $\text{GdAl}_3$ , no other binary compound was found under our experimental conditions. These samples were also examined by SEM and electron probe microanalysis (EPMA) techniques. Results of SEM and EPMA were consistent with XRD analysis. So we draw the conclusion that  $\text{GdAl}_3$  is the compound richest in aluminum at 500°C, while  $\text{GdAl}_4$  and  $\text{Gd}_2\text{Al}_{17}$  are not stable phases at this temperature.

### 3.2. Ternary compounds in the Al-rich regions

Niemann *et al.* [24, 25] reported the existence of two ternary compounds, namely  $\text{Al}_{43}\text{Ti}_4\text{Gd}_6$  and  $\text{Al}_{20}\text{Ti}_2\text{Gd}$ . We prepared two alloy samples with composition of 81 at.%Al, 8 at.%Ti, 11 at.%Gd and 87 at.%Al, 9 at.%Ti, 4 at.%Gd respectively. The X-ray diffraction patterns of these samples are in agreement with the respective JCPDS PDF cards, which confirm that compounds  $\text{Al}_{43}\text{Ti}_4\text{Gd}_6$  and  $\text{Al}_{20}\text{Ti}_2\text{Gd}$  are stable phases at

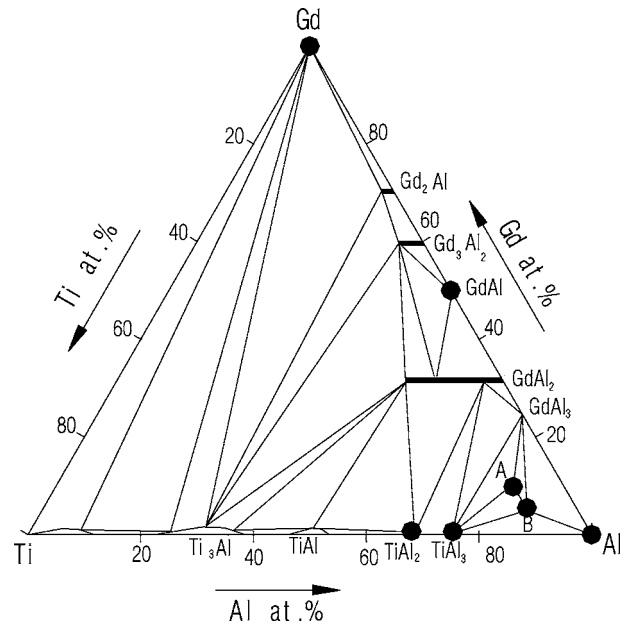


Figure 1 The isothermal section of the Gd-Ti-Al ternary system at 500°C A:  $\text{Al}_{43}\text{Ti}_4\text{Gd}_6$  B:  $\text{Al}_{20}\text{Ti}_2\text{Gd}$ .

500°C. No other ternary compound was found in this system.

### 3.3. Solid solubility

According to Yang *et al.* [26], in the Y-Ti-Al ternary system, there are two pseudobinary intermetallics with considerably extensive homogeneity ranges, namely  $\text{Y}(\text{Al}_x\text{Ti}_{1-x})_2$  and  $\text{Y}_3(\text{Al}_x\text{Ti}_{1-x})_2$  ( $x = 80\% - 100\%$ ) at 1000°C. In the Dy-Ti-Al ternary system [27], they also found two solid solutions, namely  $\text{Dy}(\text{Al}_x\text{Ti}_{1-x})_2$  ( $x = 70\% - 100\%$ ) and  $\text{Dy}_2(\text{Al}_x\text{Ti}_{1-x})$  ( $x = 90\% - 100\%$ ). Therefore, we studied the regions near  $\text{Gd}_2\text{Al}$ ,  $\text{Gd}_3\text{Al}_2$ ,  $\text{GdAl}$ ,  $\text{GdAl}_2$ , and  $\text{GdAl}_3$  carefully by analyzing X-ray diffraction patterns and using electron probe microanalysis (EPMA). No solubility of Ti in  $\text{GdAl}$  and  $\text{GdAl}_3$  are detected in this work, while the maximum solid solubility of Ti in  $\text{Gd}_2\text{Al}$ ,  $\text{Gd}_3\text{Al}_2$  and  $\text{GdAl}_2$  is found to be 2.0 at.%, 3.5 at.% and 16.3 at.% respectively at 500°C. The single phase ranges extend parallel to the Ti-Al line, which means that a certain amount of Al atoms are replaced by Ti in the  $\text{Gd}_2\text{Al}$ ,  $\text{Gd}_3\text{Al}_2$  and  $\text{GdAl}_2$  compounds.

The composition ranges near Ti,  $\text{Ti}_3\text{Al}$ , and  $\text{TiAl}$  were investigated by X-ray powder diffraction, the results indicated that the maximum solid solubility of Gd in Ti,  $\text{Ti}_3\text{Al}$ , and  $\text{TiAl}$  is less than 1 at.% Gd. The single phase ranges of Ti,  $\text{Ti}_3\text{Al}$ , and  $\text{TiAl}$  are from 0 to 12 at.% Al, from 18 to 36 at.% Al and from 50 to 54 at.% Al, respectively.

### 3.4. Isothermal section (500°C)

The isothermal section of the phase diagram of Gd-Ti-Al ternary system at 500°C (Fig. 1) was determined by comparing and analyzing the X-ray diffraction patterns of 206 samples and by identifying the phases in each samples. It consists of 14 single-phase regions, 27 two-phase regions, and 14 three-phase regions.

The 14 single-phase regions are: A( $\text{Al}_{43}\text{Ti}_4\text{Gd}_6$ ), B( $\text{Al}_{20}\text{Ti}_2\text{Gd}$ ), C(Ti), D(Al), E(Gd), F( $\text{Ti}_3\text{Al}$ ), G( $\text{TiAl}$ ),

H(TiAl<sub>2</sub>), I(TiAl<sub>3</sub>), J(GdAl<sub>3</sub>), K(GdAl<sub>2</sub>), L(GdAl), M(Gd<sub>3</sub>Al<sub>2</sub>), N(Gd<sub>2</sub>Al).

The 27 binary-phase regions are: C + F, F + G, G + H, H + I, I + D, D + J, J + K, K + L, L + M, M + N, N + E, E + C, F + E, F + N, F + M, F + K, G + K, H + K, I + K, I + J, I + A, B + A, I + B, B + D, B + J, A + J, K + M.

The 14 ternary-phase regions are: C + F + E, F + N + E, F + M + N, F + K + M, F + G + K, G + H + K, H + I + K, I + J + K, I + A + J, A + J + B, A + I + B, I + D + B, D + B + J and K + L + M.

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