ADVANCES IN GAMMA TITANIUM ALUMINIDES ALLOYS

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ABSTRACT

Gamma Titanium Aluminides (γ-TiAl) alloys have been recognized for decades to be suitable for aerospace applications due to their low density and high strength at elevated temperatures. The ultimate applications of this technology include hypersonic airplanes and reusable launch vehicles (RLVs). However, TiAl is limited in application due to difficulties during machining which arise from the inherent brittle nature associated with intermetallic phases. But, advances in manufacturing technologies, the concept of micro-alloying, and deeper understanding of Titanium Aluminides microstructure, has led to the production of Gamma Titanium Aluminides and their widespread applications.

The paper includes an in-depth review of key advances in Gamma Titanium Aluminides, including near net-shape processing development, microstructure, and phase transformation in different temperature ranges, alloy development, and their protection from surface layer degradation.

KEYWORDS: Titanium Aluminides, Intermetallics, Microstructure Evolution, Alloy Development

INTRODUCTION

Titanium Aluminides have attracted significant attention in the last 20 years for their attractive properties that have the potential to enable high temperature automobile and aerospace applications. A foremost application under consideration for titanium aluminides is high performance gas turbine engines. They have become front-runners in replacing nickel – based superalloys in gas turbine engines [IV - VII]. Table 1 compares the properties of cast γ – TiAl and Ni – based superalloys. Ni – based superalloys are found to possess superior properties than γ – TiAl. However, low density of γ – TiAl enhances its specific properties considerably in comparison to Ni – based superalloys. Replacement of Ni – based superalloys parts with TiAl alloys is expected to reduce the structural weight of high performance gas turbine engines by 20 – 30%.

Table 1: Comparison between Cast Γ – Tial and Cast Ni – Based Super alloys

<table>
<thead>
<tr>
<th>Property</th>
<th>Cast Γ-Tial</th>
<th>Cast Ni-Based Superalloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.9</td>
<td>8.3</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>275-380</td>
<td>850</td>
</tr>
<tr>
<td>UTS (MPa)</td>
<td>360-500</td>
<td>1000</td>
</tr>
<tr>
<td>Ductility (%)</td>
<td>1-3</td>
<td>3-5</td>
</tr>
<tr>
<td>Modulus of elasticity (GPa)</td>
<td>160-175</td>
<td>206</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.27</td>
<td>0.29</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (10^-6/C)</td>
<td>10.8</td>
<td>14.8</td>
</tr>
<tr>
<td>Thermal conductivity (W/m-K)</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>Maximum use temperature (°C)</td>
<td>800</td>
<td>1000</td>
</tr>
</tbody>
</table>
TITANIUM ALUMINIDES

TiAl has good thermo physical properties; the primary reasons for these properties are the ordered nature, strong bonding of the compounds and the high critical ordering temperature \( T_c \) of the material [5]. For \( \gamma – TiAl \) alloys, the material does not become disordered until the melting temperature of around \( 1440^\circ C \) is reached. Expected service temperature lies in the range between \( 600^\circ C \) to \( 760^\circ C \). High Al content in TiAl improves the corrosion resistance of the material. Contrary, the ordered nature of TiAl also leads to some negative properties like brittleness and low fracture toughness at room temperature, which in turn puts a challenge in structural applications of the alloys. Another challenge is due to hardness of the material as it becomes hard to process with conventional manufacturing methods.

Different intermetallic forms of titanium aluminides have been observed to exist: \( Ti_3Al, TiAl_2, TiAl \) and \( TiAl_3 \). However, the research for structural materials has been concentrated to materials with two different bases: \( \gamma – TiAl \) and \( \alpha_2 – Ti_3Al \), as they have shown potential to meet the design requirements needed for intended applications.

In \( \gamma – TiAl \) with an Al concentration of between 46-52 at.% the microstructure generally consists of either a single phase microstructure of pure \( \gamma \) phase or a two-phase system containing a mixture of \( \gamma \) and \( \alpha_2 \) phase. These single and two phase systems combine to build up different characteristic microstructures available in the material. The two phase system of TiAl alloys is considered to offer the best combination of mechanical strength and ductility making it suitable for structural applications [I].

DESIGN OF MICROSTRUCTURES

The microstructure obtained in the as – produced materials is dependent on the manufacturing methods. As the material cools down from liquid to room temperature, it passes through a series of phases in the phase diagram for a particular composition. Depending on the manufacturing methods the material cools in a different manner and thereby follows different paths through the phase fields. Therefore, resulting microstructures are different for different manufacturing methods and cooling rates [II]. Often the quality or the type of microstructure achieved in as – produced materials are not desirable. To alter the microstructure of the material, it is subjected to different kinds of treatments which include hot isostatic pressing, heat treatments, etc.

Hot Isostatic Pressing

HIP is a processing or post processing technique where both heat and high pressure is applied. Both loose powder and already manufactured parts are acceptable to HIP [III, VIII]. Main objective of utilizing HIP on loose powder is to produce near net shape material of full density. While, the process reduces the amount of porosity within the component if done on already produced component. The technique produces a homogeneous microstructure and removes anisotropy within the material. Physical processes acting during HIP are plastic yielding, creep and diffusion [IX].

While HIPing the already produced TiAl components the temperature needs to be raised into the two phase fields to allow the diffusion of voids. As the voids are pressed and diffused out, strain and plastic energy are supposed to develop around the former pores. However if stresses are high enough they will cause recrystallization to relieve stresses making the microstructure inhomogeneous. Other microstructural changes witnessed during HIP are grain growth and phase transformations.
Advances in Gamma Titanium Aluminides Alloys

Heat Treatment and Microstructural Evolution

Figure 1 shows preliminary temperature ranges and expected microstructures within the range. Depending on the cooling rates, holding times and alloy composition, these temperatures may vary.

![Temperature Dependency to Receive Different Microstructures during Heat Treatment.](image)

The alloy TiAl with a particular composition, say 48 at.% Al, cools down from liquid adopting a general sequence as follows:

\[ L \rightarrow \beta + L \rightarrow \beta + L + \alpha \rightarrow L + \alpha \rightarrow \alpha + \gamma \rightarrow a_2 + \gamma \]  \hspace{1cm} (1)

The development of microstructures in dual phase titanium aluminides can be broadly classified into four categories – near gamma, nearly lamellar, duplex and fully lamellar (see Figure 2).

**Duplex**

This microstructure is produced by heat treatment in \( \alpha + \gamma \) phase field. The temperature in \( \alpha + \gamma \) phase field is such that the \( a/\gamma \) volume ratio is close to 1. In this case the heat treatment results in the dissociation of the existing \( a_2 \) particles. Additional \( \alpha \) precipitates are nucleated to grow into \( \alpha \) plates in the (111) habit planes at the expense of gamma phase. The initially predominant gamma phase is gradually reduced in volume until the equilibrium volume fraction is reached and grain growth occurs. The growth of gamma grains is limited by the dispersed alpha phase, which also experiences growth. These competitive processes result in the formation of fine grained structure.

**Near Gamma**

The near gamma microstructure is formed when the material is heat treated in the \( a_2 + \gamma \) phase field. Heat treatment in this phase field results in the coarsening of the existing \( \gamma \) grains. Microstructure is characterized by coarse gamma grain regions with fine gamma grain stringer regions with dispersed alpha-2 particles.
Nearly Lamellar

At temperatures greater or lower than where the duplex microstructure forms, coarsening of the predominant phase occurs. Hence, heat treatment at temperatures below the duplex microstructure leads to the coarsening of gamma grains and formation of near gamma microstructures, while heat treatment above the duplex microstructure temperature results in the coarsening of alpha grains and formation of nearly lamellar microstructure. The nearly lamellar microstructure is characterized by coarse lamellar structure with fine gamma grains.

Fully Lamella

Heat treatment in the alpha phase field above the alpha-transus line ($T_\alpha$) results in the formation of large grained fully lamellar microstructure. The lamellar structure forms in three different ways and hence is classified into three different types:

- **Type I:** This lamellar structure is formed by heat treatment above the $T_\alpha$ line followed by air cooling. It is formed via the following reaction:

  \[
  \alpha \rightarrow \alpha + \gamma_p \rightarrow L(\alpha/\gamma) \rightarrow L(\alpha_2/\gamma)
  \]  

  In this reaction, plate like gamma precipitates $\gamma_p$ begin to precipitate out of alpha matrix at $\alpha/(\alpha + \gamma)$ line and grow radially to result in the high temperature lamellar structure $L(\alpha/\gamma)$. This structure transforms at low temperatures to $L(\alpha_2/\gamma)$ structure simply by $\alpha \rightarrow \alpha_2$ ordering reaction. This occurs below the $\alpha/(\alpha+\alpha_2)$ line.

- **Type II:** This lamellar structure is observed in the duplex microstructure. In this structure the alpha-2 plates contain anti-phase boundaries (APB) which are continuous across the thin gamma plates. For this type of lamellar structure, the nucleation of gamma precipitates ($\gamma_p$) and their growth into plates ($\gamma_p$) is preceded by $\alpha \rightarrow \alpha_2$ ordering reaction. The whole process can be expressed as:

  \[
  \alpha \rightarrow \alpha_2 \rightarrow \alpha_2 + \gamma_p \rightarrow \alpha_2 + \gamma_p \rightarrow L(\alpha_2/\gamma)
  \]  

- **Type III:** This lamellar structure is formed when the heat treatment is done well below the duplex microstructure temperature. Here, the predominant phase is gamma with minor alpha-2 particles ($\alpha_2^p$). Upon heating, the $\alpha_2^p$ in the gamma matrix $\gamma_m$ disorders to $\alpha^p$ and grow into alpha plates ($\alpha_p$) to yield a lamellar structure $L(\gamma/\alpha)$, which upon cooling transforms to lamellar structure $L(\gamma/\alpha_2)$ by simple $\alpha \rightarrow \alpha_2$ reaction. The entire reaction can be expressed as:

  \[
  \gamma_m + \alpha_2^p \rightarrow (heating) \gamma_m + \alpha_p \rightarrow L(\gamma/\alpha) \rightarrow (cooling) L(\gamma/\alpha_2)
  \]
CURRENT STATUS ON TEMPERATURE LIMITATION OF Γ – TIAL ALLOYS

The thermal stability of high temperature applications of γ – TiAl based alloys after long time exposure at service temperatures suffers deterioration, accompanied with significant reduction in ductility. At elevated temperatures deformation is not accommodated at the surface, thus leading to build – up of stress concentrations in the sub scale. Eventually, cracks are found to be generated either from sub scale or from the surface.

For high temperature applications, oxidation resistance of γ – TiAl based alloys above 700°C still needs improvement. Indeed at high temperatures in air, layers of mixed oxides grow by competitive oxidation of Ti and Al alloying elements, which prevents the formation of a continuous and dense alumina layers. In contrast, γ – TiAl alloys form a continuous alumina scale in pure oxygen up to 1000°C.

Efforts to improve the oxidation resistance of γ – TiAl alloys have concentrated on different approaches. Addition of different alloying elements contributes towards the enhancement of properties (see Table 2). Microalloying with small amounts of halogens may also improve the oxidation resistance up to 1000°C. Halogens can be applied in many ways: treatment with diluted halogen liquid or gas, ion implantation. This improvement is based on the selective transport of aluminium via gas phase from the substrate metal to the oxide scale through pores and micro – cracks by gaseous halogen gas. This leads to the formation of a continuous scale of growing Al₂O₃.

Other techniques to improve the corrosion and oxidation resistance of γ – TiAl alloys involve coating of the material. A typical pack cementation treatment can be used to improve the corrosion resistance of the γ – TiAl alloys [X - XIII]. Cyclic corrosion resistance of the coated TiAl can be improved by aluminizing. An Au – based specific coating designed to prevent pure NaCl corrosion of γ – TiAl alloys has gained popularity in present days. A two TiAlAu₂ and TiAlAu layers coating, obtained after vacuum treatment, is effective in improving NaCl salt corrosion resistance of the coated specimens at 600°C. It is attributable to the formation of Al₂O₃ scale on the surface of the coated specimen. Other than gold, platinum has also shown its merit in improving the corrosion resistance.
Table 2: Mechanical Properties Enhanced by Alloy Additions.

<table>
<thead>
<tr>
<th>Nb</th>
<th>Increases Creep and Oxidation Resistance in Small Amounts. Increases High Temperature Strength if Added between 5% and 10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>Increases creep and oxidation resistance and tendency for hot cracking</td>
</tr>
<tr>
<td>V</td>
<td>Increases ductility</td>
</tr>
<tr>
<td>W</td>
<td>Oxidation and creep resistance.</td>
</tr>
<tr>
<td>B</td>
<td>Grain refiner.</td>
</tr>
<tr>
<td>C</td>
<td>Increases creep and oxidation resistance.</td>
</tr>
<tr>
<td>Cr</td>
<td>Increases ductility if added in small amount. Improves oxidation resistance if added around 8%.</td>
</tr>
<tr>
<td>Mn</td>
<td>Increases ductility</td>
</tr>
<tr>
<td>Mo</td>
<td>Increases strength and creep and oxidation resistance.</td>
</tr>
</tbody>
</table>

STATE OF THE ART OF TITANIUM ALUMINIDES ALLOYS

The alloy development in TiAl over the last 20 years has resulted in four state of the art alloys with exceptional high temperature mechanical properties. These four alloys are listed in Table 3 with their composition and strength.

CONCLUSIONS

- Development in the field of microstructure, manufacturing and processing, alloying addition, coating etc has lead to its successful utilization in automobile, aerospace, defense sectors.
- $\gamma$ - TiAl based alloys are strong candidates for the replacement of Ni – based superalloys offering better specific properties.
- Different mechanisms which can enhance the mechanical properties include control of microstructural morphology, small alloying additions, near net shape processing etc.
- Incorporation of Halogen Effect and coating of TiAl alloys to protect the material from corrosive environments have lightened the path towards development.

Table 3: Tial State of the Art Alloys

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>Composition (At.%)</th>
<th>Alloy Strengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>General electric, USA: 48-2-2</td>
<td>Ti-48Al-2Cr-2Nb</td>
<td>Ductility, fracture toughness and oxidation resistance</td>
</tr>
<tr>
<td>Plansee, Austria: $\gamma$-MET</td>
<td>Ti-46.5Al-(5-10)Nb</td>
<td>High temperature strength, creep, fatigue and oxidation resistance</td>
</tr>
<tr>
<td>GKSS Research Centre, Germany: TNB Alloy</td>
<td>Ti-(45-47)Al-10Nb</td>
<td>High temperature strength, creep, and oxidation resistance</td>
</tr>
<tr>
<td>Martin Marietta Laboratories, USA: XD™ TiAl</td>
<td>Ti-45Al-2Mn-2Nb-0.8B</td>
<td>High temperature strength, ductility, stiffness, creep, and oxidation resistance</td>
</tr>
</tbody>
</table>

REFERENCES


4. Articles in journals:


