ChinaRxiv

AI translation · View original & related papers at
chinarxiv.org/items/chinaxiv-202303.00505

Advances and Challenges in TiAl Intermetallic Compounds: Postprint

Authors: Yang Rui

Date: 2023-03-19T00:00:00+00:00

Abstract

The research and development history of titanium-aluminum intermetallic compounds is reviewed across four stages: the initiation period (1974–1985), the boom period (1986–1995), the rise period (1996–2005), and the stage of specific applications (2006–present). Milestone events that played a dominant role in the development of titanium-aluminum alloys in each stage are discussed, and the main progress in six aspects is briefly summarized: alloying, microstructure categories, primary processing (melting), secondary processing (hot working), properties, and tertiary processing (forming). Five challenges facing the future development of titanium-aluminum alloys are proposed: further advancement of cast alloys and casting technologies, low-cost wrought alloy technology, development of third-generation alloys, new applications based on novel preparation technologies, and development of new forming processes.

Full Text

Preamble

Acta Metallurgica Sinica, Vol. 51, No. 2, February 2015, pp. 129-147

Advances and Challenges of TiAl-Based Alloys

YANG Rui
Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016

Abstract

The history of research and development of γ-TiAl intermetallic alloys is outlined and divided into four stages: starting (1974–1985), revolutionary (1986–1995), emerging (1996–2005), and specialty materials (2006–). Major events and landmarks at the different stages are recounted to provide a framework for understanding scientific and technological progress. Key advances in the following six areas are reviewed: alloying, microstructure type, primary processing (melting), secondary processing (hot working), properties (including creep, fracture and fatigue, and oxidation), and tertiary processing (forming, covering both investment casting and near-net-shape powder metallurgy). Future challenges are identified as follows: improvement of centrifugal casting technology, low-cost wrought process, development of third-generation alloys that meet design specifications, new applications based on new technologies, and viability of new forming routes such as additive manufacturing.

Keywords
γ-TiAl intermetallic alloy, cost-effective processing route, application, future challenge

1.1 Starting Stage (1974–1985)

TiAl has a density only half that of nickel-based superalloys and could potentially replace superalloys in certain aerospace structural components and ground power system rotating or reciprocating parts operating in the 600–900 °C temperature range, enabling substantial improvements in thrust-to-weight ratio and fuel efficiency. Although the excellent high-temperature strength and creep resistance of γ-TiAl were recognized in the mid-1950s, and its oxidation resistance could be improved by adding Ta, Nb, and Ag [1], research on γ-TiAl truly began in the mid-1970s. Shechtman et al. [2] and Lipsitt et al. [3] studied the deformation and fracture mechanisms of γ-TiAl and found that, regardless of annealing treatment, Ti-50Al alloys always exhibited a γ-TiAl + α_2-Ti$_3$Al two-phase lamellar microstructure under transmission electron microscopy, making it difficult to identify deformation dislocations in the γ-TiAl phase. Consequently, they prepared Al-rich Ti-54Al single-phase alloys to determine the slip systems of the γ phase. Regarding the appearance of the α_2 phase in Ti-50Al alloys, Shechtman et al. [2] initially attributed it to the alloy composition lying within the $\gamma + \alpha_2$ two-phase region. The exact position of the γ-phase region boundary has long been a point of controversy in the Ti-Al binary phase diagram. The most authoritative version currently available is that evaluated by Schuster and Palm [4] in 2006 based on over 370 relevant literature sources, shown in [Figure 1: see original paper]. According to this diagram, the Ti-50Al alloy lies within the single-phase γ region, but because the primary solidification phase is α (which undergoes ordering to become α_2), γ appears as a secondary phase at grain boundaries accompanied by Al segregation. Only when the Al content exceeds 55 at% does γ become the primary phase [5]. The volume fraction of the γ phase depends on solidification rate: for Ti-50Al alloys, it is only about 0.3 in arc-melted button ingots and approximately 0.5 in investment cast ingots.

The accuracy of the γ-phase region boundary in the phase diagram thus depends on whether the non-equilibrium microstructure caused by Al segregation can be effectively eliminated. Furthermore, if impurity elements (such as O) have significantly different solubilities in the two phases, the phase boundary position also depends on the impurity content in the alloy. Greater controversies concern the high-temperature region, where two questions related to ordering reactions remain unresolved: First, whether the β phase in the Ti-Al binary system orders to a B2 phase—some studies [6,7] suggest this ordering reaction occurs, while others [8] argue it is impossible, with [Figure 1: see original paper] adopting the latter view. Second, although it is confirmed that the α phase transforms to α_2, it remains uncertain whether this occurs through an $\alpha + \beta$ peritectoid reaction [6] or through a congruent ordering reaction [8,9]. These issues fully demonstrate the complexity of the Ti-Al binary phase diagram, and the version evaluated by Witusiewicz et al. [10] in 2008 is not entirely consistent with [Figure 1: see original paper].

From 1974–1982, Pratt & Whitney Aircraft conducted the first round of TiAl materials research [11], screening out the first practically valuable alloy composition in 1979: Ti-48Al-1V-0.1C, and conducting extensive studies on mechanical properties, forming processes, and typical test components. This alloy is generally considered representative of first-generation TiAl alloys. It exhibited good fracture toughness, machinability, and castability, but low room-temperature ductility and impact properties, with castings prone to surface porosity. Typical structural components cast from this alloy included F100 engine compressor blade blanks [11] and JT9D engine low-pressure turbine blades [12]. Between 1974 and 1985, only about 15 papers on γ-TiAl were published worldwide [12]; these early pioneering works laid the foundation for the explosive growth of research in the next stage and pointed the general direction forward.

Advanced materials, particularly structural materials for demanding environments, generally experience four stages from concept to application ([Figure 2: see original paper]) [13]. During the revolutionary stage, materials are described as transformative. When the enthusiasm cools, the material enters a challenging valley of death where research activity is low; the material is then described as emerging. This stage is typically long, and in fact, most advanced materials never escape this "valley of death" [14]. Once the technical challenges are overcome and the material is first applied under the pull of an important demand, it enters the third stage of achieving specific applications. Only after issues of material stability, cost, and supply chain are properly resolved does the material become a commercial or off-the-shelf material. In these two stages, the material gradually matures. To date, the development history of γ-TiAl alloys basically follows the pattern shown in [Figure 2: see original paper]. Based on the development history of the 4822 alloy (Ti-48Al-2Cr-2Nb), which was first industrially applied in GE engines, the approximate time nodes for each development stage of γ-TiAl alloys can be identified.

1.2 Revolutionary Stage (1986-1995)

Aoki and Izumi [15] discovered in 1979 that B could improve the room-temperature ductility of Ni_3Al, and further research showed that the effect of B in improving Ni_3Al ductility was quite significant [16], sparking a surge of interest in intermetallic compound research. In the Ti-Al system, early expectations for Ti_3Al were much higher than for TiAl, but as research progressed, the importance of TiAl surpassed that of Ti_3Al [17].

The revolutionary stage began with the emergence of two typical second-generation γ-TiAl alloys, namely the 4822 alloy and 45XD (Ti-45Al-2Mn-2Nb-0.8 vol% TiB_2), and ended with the convening of the first International Conference on γ-TiAl organized by TMS [18]. During this decade, both 4822 and 45XD completed a full cycle from alloy melting to testing of typical structural components, with research progress documented in references [5,19-23].

The 4822 alloy, developed by GE, remains the γ-TiAl alloy with the highest room-temperature ductility to date. In 1988, GE recognized the engineering development value of this alloy and, after comprehensive comparison, identified casting as the preferred process route, beginning casting process research in 1989. The weight reduction requirement for the GE90 engine drove recognition of the importance of γ-TiAl alloys, leading to the decision to conduct experimental research on manufacturing stage 5 low-pressure turbine blades using the 4822 alloy in the CF6-80C engine program [24]. Howmet cast the blade blanks, which were then electrochemically machined to final dimensions, and engine testing was conducted for 1,529 cycles during 1993-1994. In 1995-1996, a seal support ring for the F414 engine was manufactured and tested.

The 45XD alloy was developed under the National Aerospace Plane (NASP) program as a joint research project undertaken by Lockheed Martin and 14 other organizations. From the mid-1980s to mid-1990s, Howmet and Rolls-Royce conducted application development for typical components using this alloy. Howmet developed precision casting technology for the alloy [25] and accumulated extensive data on material properties, processes, and structural component design and manufacturing.

During the same period, ABB developed the 47WSi alloy (Ti-47Al-2W-0.5Si) and conducted application research and component testing for industrial gas turbine blades and automotive engine components [18].

These three alloys all belong to the second generation of γ-TiAl alloys, each with distinct performance characteristics [18]: 4822 has the highest room-temperature ductility; 45XD has good castability, optimal as-cast microstructure, and excellent high-temperature strength and fatigue properties; and 47WSi alloy exhibits superior high-temperature (760 °C) creep performance.

1.3 Emerging Stage (1996-2005)

In this stage, research became more focused on process and processing methods for specific applications. For example, the U.S. PRET project [26] primarily investigated pathways for transitioning basic γ-TiAl research results to technology, covering: defects and impurities in casting and forming, microstructure evolution and characterization, property scatter and its causes, notch strengthening and size effects under uniaxial loading, surface damage and foreign object damage, and fatigue behavior of different microstructure types. NASA-supported durability research on γ-TiAl alloys included impact fatigue, impact process simulation, and wear [27]. Surface integrity was also an important research theme [28]. These were all critical issues that had to be resolved for γ-TiAl alloys to be used as rotating component materials in aeroengines.

Progress was achieved in applying γ-TiAl alloy components to high-temperature reciprocating or rotating parts such as automotive turbocharger impellers and exhaust valves. Japan pioneered the use of cast γ-TiAl turbocharger impellers in racing and other high-end automobiles [29], while several countries, particularly Germany, investigated cast and wrought γ-TiAl exhaust valves. Under the EU Sixth Framework Program, Germany’ s TRW Company, the University of Birmingham in the UK, and the Institute of Metal Research of the Chinese Academy of Sciences jointly studied ceramic crucible melting and casting processes for exhaust valve components [30,31]. Using ceramic crucibles instead of water-cooled metal crucibles increased O content and reduced ductility, but improved melt superheat and yield while reducing energy consumption and manufacturing costs during melting [32]. Cost is the primary factor limiting the application of γ-TiAl automotive engine components. From this perspective, casting is the preferred process. However, to date, large-scale application of γ-TiAl alloys in the automotive industry has not been realized.

The stable service temperature for second-generation γ-TiAl alloys in aeroengine blades is 650 °C. To further increase the service temperature, third-generation alloys need to be developed. During this stage, researchers worldwide proposed many compositions, but few underwent comprehensive property evaluation, and even fewer met application requirements. These alloys can be broadly divided into three categories [33]: high-niobium alloys, β-solidifying alloys, and massive transformation alloys.

High-niobium alloys were first proposed by Chen et al. at the University of Science and Technology Beijing [34], and extensive work on these alloys was conducted by the GKSS Research Center in Germany [35]. High-niobium alloys are characterized by good high-temperature creep and oxidation resistance, but suffer from low room-temperature ductility and casting difficulties. Wrought processes can improve room-temperature ductility to some extent, but Al segregation issues remain to be resolved [36].

Massive transformation alloys are those in which the high-temperature α phase transforms directly to the γ phase without diffusion at moderate cooling rates (approximately 10^2 K/s). The relationship between microstructure and cooling rate for the Ti-46Al-8Nb alloy is shown in [Figure 3: see original paper] [37]. As the cooling rate increases, the alloy sequentially develops lamellar microstructures (including Widmanstätten and feathery lamellar), massively transformed γ phase, and supercooled retained α_2 phase. When heat-treated in the $\alpha_2 + \gamma$ two-phase region, lamellar α precipitates from four $\{111\}$ planes of the γ phase following the Blackburn orientation relationship [38], producing a near-isotropic fine-grained microstructure. Massive transformation can effectively refine the as-cast grain structure and improve texture, but typically requires higher cooling rates, which may cause alloy cracking due to thermal stresses. The University of Birmingham systematically studied the conditions and influencing factors of massive transformation in γ-TiAl alloys, finding that fine-grained alloys formed by B addition [40] and alloys with high O content [41] are both difficult to undergo massive transformation.

Since massive transformation is a diffusionless displacive transformation, adding refractory metals that are difficult to diffuse can generally promote massive transformation. However, refractory metals all have high densities, and as alloying elements they increase the density of γ-TiAl alloys. β-solidifying alloys were first explicitly proposed by Naka et al. [42], where the initial solidification phase is β and β is the only phase coexisting with the liquid. In fact, many high-niobium alloys also belong to this category. It should be noted that the previously mentioned second-generation alloy 45XD was already a β-solidifying alloy, although this was not emphasized at the time. If the initial solidification phase is β, then due to the Burgers orientation relationship [43], the basal plane of the α phase precipitates parallel to the six $\{110\}$ planes of the β phase, resulting in a near-isotropic fine-grained microstructure, similar to the grain refinement principle in massive transformation alloys. Subsequent $\alpha + \gamma$ transformation can produce a weakly textured fine lamellar microstructure. Kim et al. [44] referred to such alloys as β-γ alloys. A joint research group composed of German and Austrian universities, research institutions, material companies, and engine companies conducted in-depth studies on β-solidifying alloys [45,46], developing the Ti-43Al-4Nb-1Mo-0.1B alloy (TNM). The guiding principle was to obtain a high volume fraction of β phase at high temperatures through alloying, enabling the alloy to be forged using conventional equipment by exploiting the relatively easy deformability of the β phase. At the application temperature near 700 °C, the equilibrium volume fraction of β phase is very low, which helps eliminate this phase as much as possible to avoid reducing creep resistance. In practice, depending on the alloy composition, the β phase in some alloys is difficult to completely eliminate, leading to reduced room-temperature ductility and formation of ω phase in the β phase during long-term service at application temperatures, causing further embrittlement [47].

In June 2006, GE announced that it would adopt the 4822 alloy for manufacturing stage 6 and 7 low-pressure turbine blades in the GEnx engine [48]. This marked the first application of a key structural component made from γ-TiAl alloy, signifying that after approximately 30 years of research and development, this material finally broke through barriers and entered the specialty materials stage.

With the industrial application of second-generation γ-TiAl alloys, scientific and technological issues related to product manufacturing processes, supply chains, and quality stability became research priorities. From the perspective of application cost, casting is currently the only acceptable manufacturing process. However, because net-shape precision casting is extremely difficult, the process adopted by PCC Precision Castparts for producing 4822 alloy blades for GE involves first gravity casting an oversized blank, then machining it to final dimensions [49]. Due to the curved airfoil shape and the difficulty of machining TiAl, manufacturing costs remain high. By 2014, PCC' s annual production of TiAl blades had reached nearly 40,000 pieces [50].

Accumulating relevant data and application experience under industrial production conditions requires strong support from fundamental research. Targeting aeroengine γ-TiAl alloy turbine blade applications, the EU Sixth Framework Program launched the IMPRESS project [51,52], conducting five years (2005–2009) of vertically and horizontally integrated research on critical applications of intermetallic compounds. Through the IMPRESS project, Europe integrated fragmented γ-TiAl fundamental research and moved to the international forefront [53]. In 2011, China' s 973 Program launched a project on lightweight high-temperature TiAl intermetallic compounds.

2 Main Research Progress

After nearly 40 years of research, γ-TiAl alloys have achieved tremendous progress in both fundamental science and application technology. In addition to numerous journal papers, the proceedings of five international conferences have comprehensively documented these stage-by-stage research advances [18,54–57]. In 2011, Appel et al. [33] published the monograph *Gamma Titanium Aluminide Alloys: Science and Technology*, providing a systematic summary of research in this field. These proceedings and monographs comprehensively introduce the current research status of γ-TiAl alloys. This article only briefly reviews the main research progress from six aspects: alloying, microstructure categories, primary processing (solidification), secondary processing (hot working), properties, and tertiary processing (forming).

2.1 Alloying

For γ-TiAl alloy composition design, the first step is selecting the Al content, one of the two main elements, which can be varied between 42–48 at% as needed. As Al content increases, oxidation resistance improves, strength decreases, and room-temperature ductility generally shows an increasing trend. However, for different alloy systems and processing routes, the situation is more complex, and ductility data show no clear pattern. This is primarily because microstructure type and texture also significantly affect room-temperature ductility. Overall, the most obvious effect of Al content is on the solidification category; only low-Al alloys can achieve β-solidification, with the specific Al content boundary depending on other added elements and their amounts.

Alloying elements in γ-TiAl can generally be divided into three categories [17,33], occupying definite positions in the periodic table. The first category lies to the right of Ti (V, Cr, Mn), which can improve alloy ductility, though the mechanisms differ and remain unresolved. For example, V is believed to improve intermediate-temperature ductility but has little effect on room-temperature ductility [11]. Mn is thought to favor twin deformation [58], while Cr reduces the c/a ratio of the γ-phase unit cell, weakens covalent bond directionality, decreases α_2-phase volume fraction, and refines grains [59,60].

The second category comprises refractory metals located to the lower right of Ti (Nb, Mo, Ta, W). These are all slow-diffusing elements; small additions can improve high-temperature properties such as strength, oxidation resistance, and creep resistance. These refractory metals all have a bcc structure and stabilize the β phase; large additions tend to form β/β_0 phases (β_0 has a B2 structure), which have complex effects on high-temperature properties [61,62] due to precipitation of ω phase or ω-like phases [63,64]. These elements can be further divided: Mo, Ta, and W mainly dissolve in the α_2 phase, while Nb partitions nearly equally between γ and α_2 phases [42]; the effects of Mo, Ta, and W on high-temperature creep performance are related to their selective partitioning in the α_2 phase. Due to the $\alpha \rightarrow \gamma + \alpha_2$ peritectoid reaction in γ-TiAl alloys, for compositions away from the peritectoid point, the volume fraction of γ suddenly increases when cooled below the peritectoid reaction temperature [33]. However, in practice, cooling rates are too fast to achieve phase equilibrium, resulting in actual α/α_2 volume fractions higher than equilibrium values, which gradually decompose during long-term thermal exposure at service temperatures [63]. Studies [65] show that during creep, W segregates at α_2/γ interfaces due to α_2-phase dissolution, thereby slowing α_2 dissolution. Particularly when α_2-phase dissolution proceeds mainly by interface sweeping of steps, W segregation near steps is especially pronounced, even inducing B2-phase precipitation. These factors all hinder α_2-phase dissolution and improve lamellar microstructure stability.

The situation with Nb is different and more complex. The strengthening mechanism of Nb, especially in high-niobium alloys, has long been controversial. Proposed mechanisms include low-Al-content strengthening [66], solid solution strengthening by Nb [67], and anti-structural bridge (ASB) strengthening [68]. However, calculations by Woodward et al. [69] show that Al anti-site atoms provide significant strengthening, while Ti anti-site atoms are weak. Solid solution strengthening by Nb is also weak. Thus, low-Al-content strengthening and Nb solid solution strengthening cannot explain the high strength of high-niobium alloys. ASB strengthening is similar to Snoek atmospheres, consisting of an anti-site atom bound to a vacancy that attracts and impedes dislocation motion. However, calculations [70] show that both types of ASBs on the Ti-rich side increase system energy, while ASBs form more readily on the Al-rich side, making the ASB mechanism also unable to explain the high strength of high-niobium alloys. At low Nb contents, experimental and computational results both indicate that Nb occupies Ti sublattice sites in TiAl [71]. At high Nb contents, calculations [70] show that Nb switches to occupying Al sublattice sites and forms short-range order on this sublattice. This short-range order provides significant strengthening that persists to high temperatures, offering a plausible explanation for the high strength of high-niobium alloys [70,72].

The third category includes elements in the upper right of the periodic table: B, C, Si, and in some sense O and N can also be considered alloying elements. B is an important element; Bryant et al. [73] first reported that adding TiB_2 to cast γ-TiAl alloys had a grain-refining effect, and adding elemental B to form TiB_2 has the same effect. However, the grain refinement mechanism is complex [74], with effectiveness depending not only on Al content [75] but also on other alloying elements [76]. Depending on alloy system and reaction kinetics, borides have complex and variable structures and morphologies [77]. Hecht et al. [76] studied the grain-refining effect of low B content in high-niobium alloys, finding that in β-solidifying alloys, as long as the B content exceeds its solubility in the β phase, the formed borides can provide heterogeneous nucleation sites for the α phase, thereby significantly refining α grains. However, once peritectic α appears, the refining effect is greatly reduced.

C can substantially improve the creep resistance of γ-TiAl alloys; for example, adding 0.2 at% C can increase the creep resistance of Ti-48Al-1V by six times [11], and similar effects are observed in TNM alloy with 0.2 at% C addition [78]. However, C significantly reduces room-temperature ductility, particularly in cast alloys. The strengthening effect of C mainly originates from MAX phase precipitates [79,80]. After thermomechanical processing, MAX phase carbides can be refined to tens of nanometers and can even become heterogeneous nucleation sites for nano-twins, thereby relieving stress concentration and improving plastic deformation [81]. The embrittling effect of C on as-cast alloys likely stems mainly from the coarse size and distribution morphology of carbides.

Small amounts of Si (below 1 at%) in γ-TiAl alloys mainly form Ti_5Si_3 phase, thereby improving creep strength and enhancing microstructural stability by hindering dynamic recrystallization [82,83]. Although the crystal structures of Ti_5Si_3 and γ-TiAl differ considerably, geometric analysis and electron microscopy show that the two have an almost fully coherent interface [84]. The low interfacial energy gives Ti_5Si_3 high stability, making it resistant to Ostwald ripening; even when coarsening occurs, it does not easily lose coherency with γ-TiAl.

O and N affect γ-TiAl alloy properties similarly to C; for example, O is used to enhance creep resistance [23]. The solubility of O in the γ phase is only about 0.03 at% [85,86]; therefore, different O contents provide both solid solution strengthening and precipitation strengthening (Al_2O_3) in γ-TiAl alloys, but degrade room-temperature ductility. For instance, adding 0.3 at% O increases the room- and high-temperature yield strength of Ti-50Al alloy by 1.5 times, while increasing O content from 0.03 to 0.08 at% reduces elongation by about 2–3 times [87,88].

Other elements (such as Zr, Re, Fe) are uncommon in γ-TiAl alloys but have been studied. Zr is in the same group as Ti in the periodic table; adding it to γ-TiAl reduces the γ-phase c/a ratio, thereby promoting isotropic deformation [89]. Meanwhile, Zr has a smaller atomic volume than Ti, providing solid solution strengthening, and Zr slightly increases bond directionality in the γ phase, increasing the lattice resistance to dislocation slip and providing strengthening. From an electronic structure perspective, Fe has a strong effect because Fe-Ti and Fe-Al bonds have similar bond strengths [71]; therefore, adding Fe may reduce the sensitivity of γ-TiAl alloy properties to Al content. The Ti-45Al-1.3Fe-1.1V-0.25B alloy developed by Japan' s IHI Corporation includes Fe addition. Re is an extremely critical and expensive element in single-crystal superalloys; due to cost and density considerations, it is extremely rare as an alloying element in γ-TiAl, with only the G4 alloy (Ti-47Al-1Re-1W-0.2Si) developed by the French National Aerospace Research Center using it [90]. Notably, Re and W are both refractory elements but have different crystal structures (Re has an hcp structure) and strengthening mechanisms in γ-TiAl alloys. The creep resistance of the G4 alloy, which has the lowest creep rate, does not depend on the lamellar microstructure but on the deformation substructure; the Re-rich interdendritic γ phase determines the alloy' s high creep resistance [91].

2.2 Microstructure Categories

Like other intermetallic compounds, the properties of γ-TiAl alloys depend not only on microstructure but are also sensitively dependent on defects introduced by solidification and hot working. For certain microstructure morphologies, texture causes strongly anisotropic properties. This discussion of microstructure will be combined with solidification reactions and hot working, without a dedicated section. However, for narrative convenience, the microstructure categories of γ-TiAl alloys are briefly introduced here.

For $\gamma + \alpha_2$ two-phase alloys, four general microstructure types can be obtained: near-γ, duplex, near-lamellar, and fully lamellar. These four microstructures can be obtained through heat treatment at different temperatures in the $\gamma + \alpha$ two-phase region shown in [Figure 1: see original paper] [19]. For any given composition, the intersection temperature of its vertical line with the $\alpha/\gamma + \alpha$ phase boundary is Tα, and the eutectoid temperature is Te (1120 °C in [Figure 1: see original paper]). The segment between Tα and Te can be divided into upper, middle, and lower sections.

Heat treatment in the lower temperature range typically yields a near-γ microstructure consisting of relatively coarse γ phase and finer γ phase pinned by α_2 particles. Heat treatment in the middle temperature range produces a duplex microstructure with approximately equal volume fractions of γ and α phases, whose competitive growth leads to relatively fine grain sizes. Heat treatment in the upper temperature range yields a near-lamellar microstructure composed of coarse α lamellar grains and a small amount of γ grains. Short-term heat treatment above Tα followed by cooling produces a fully lamellar $\gamma + \alpha_2$ two-phase microstructure. The lamellar planes are parallel to the basal plane of the α_2 phase and the $\{111\}$ planes of the γ phase, with γ precipitation from α following the Blackburn orientation relationship [38]. This reaction is exactly opposite to massive transformation (where α precipitates from rapidly cooled metastable γ).

2.3 Melting and Solidification Reactions

Melting raw materials and master alloys to produce ingots is the foundation for all subsequent processing and forming. It directly affects the as-cast microstructure, texture, and distribution of alloying elements, and also significantly influences hot working processes such as isothermal forging and hot extrusion, as well as powder metallurgy processes.

As seen in [Figure 1: see original paper], the high-temperature region of γ-TiAl alloys contains two peritectic reactions within a relatively narrow Al content range, making the microstructure very sensitive to Al content variations and consequently making properties highly sensitive to composition, particularly Al content. Macroscopic segregation is mainly related to melting method and parameter control, while microsegregation and texture are primarily related to solidification reactions. Melting methods, especially industrial-scale melting methods, are a critical link in establishing material supply chains and are of great significance for γ-TiAl alloy research and application. A famous example is the difficulty GE encountered in the early 1990s when trial-producing CF6-80C low-pressure turbine blades using the 4822 alloy. To ensure performance consistency of 4822 alloy, Al content had to be controlled within $\pm$0.75 wt%, but the vacuum arc remelting (VAR) technology of Howmet and Timet at that time could only achieve $\pm$3 wt% Al uniformity. Due to insufficient composition uniformity, GE had to develop a special heat treatment process to make cast blade properties meet requirements [24]. Later, Allvac developed improved VAR processes to meet GE' s Al content variation requirements, thereby establishing industrial-scale melting technology for 4822 alloy and removing a major obstacle to γ-TiAl alloy application.

Currently, three main melting methods are suitable for γ-TiAl alloys: VAR, plasma arc melting (PAM), and induction skull melting (ISM). Each method has advantages and disadvantages: VAR can melt large ingots but cannot easily eliminate high- and low-density inclusions; PAM can eliminate high- and low-density inclusions but may entrap gas bubbles and is not suitable as the final melting method; ISM provides uniform composition but small ingot size and low superheat, generally only about 20 °C. Therefore, for wrought alloys requiring large ingots, VAR should be used for the final melting; for component casting, only ISM can be used. Possible melting combinations for wrought alloys are:

VAR + VAR (+VAR), or PAM + VAR, or ISM + VAR. For precision casting, possible combinations are: VAR (+VAR) + ISM, or PAM + ISM. The melting steps in parentheses are optional depending on specific quality requirements for the alloy ingot.

In terms of alloy quality and economics, using PAM for the first melting is the best choice for both wrought alloys (with final melting by VAR) and master alloy preparation for casting (with final melting by ISM). The composition variation from center to edge in PAM ingots is not a major issue because it can be further homogenized during final melting, but macroscopic segregation from head to tail cannot be eliminated (VAR has a small molten pool and only partial melting; ISM requires cutting a master alloy ingot into several sections for casting different parts). The volatile element Al is the most difficult to control, and as a light element, its accurate quantitative analysis is also very difficult. Howmet' s study of PAM ingots [92] showed that Al content analysis errors accounted for 32% and 47% of the technical specification tolerance range for 45XD and 47WSi alloys, respectively, clearly making it difficult to meet control targets (especially for 47WSi). Melting quality issues such as composition deviation are also related to melting parameters including molten pool depth, melt residence time, master alloy quality, and feeding method and speed [33]. For example, for 47WSi alloy [92], when fine-grained W-Al master alloy was used, the Al content variation along a 2.5 m ingot length was 3.1 at%, whereas with coarse-grained master alloy, the variation was only 0.6 at%.

The initial phase formed during solidification of γ-TiAl alloys and its texture are related to both composition and cooling rate. Experimental results from Witusiewicz et al. [10] show that for Ti-Al binary alloys at conventional cooling rates, β-solidification occurs below 45 at% Al, α is the initial solidification phase above 49 at% Al, and β dendrites first form in the 45–49 at% Al range, followed by α formation through peritectic reaction. Based on results from De Graef et al. [93], it can be inferred that secondary α does not follow the Burgers orientation relationship [43] with primary β. For the 4822 alloy, at high cooling rates the [0001] direction of α phase aligns with the heat flow direction, causing the subsequently formed $\gamma\{111\}$ lamellar planes to be perpendicular to the heat flow direction; at slow cooling rates, the direction parallel to heat flow becomes <10-10>, causing $\gamma\{202\}$ planes to be perpendicular to heat flow. Johnson et al. [94] therefore proposed that peritectic α does not nucleate on primary β but solidifies directly from the melt.

The Ti-48Al alloy involves two peritectic reactions during solidification, resulting in Al microsegregation as high as 9 at% over very short interdendritic distances [95], due to slow diffusion in the peritectic α phase. In contrast, β-solidifying alloys such as Ti-45Al have much less microsegregation because the diffusion coefficient in β phase is two orders of magnitude higher than in α phase, making the alloy solidify closer to equilibrium [96]. However, the situation is quite different for the also β-solidifying Ti-45Al-8Nb alloy, where microsegregation exists during β-phase solidification due to the difficulty of Nb diffusion.

In addition to controlling composition segregation, the significance of studying solidification reactions lies in seeking approaches to refine as-cast grain structures. Solidification paths and subsequent solid-state transformations determine the microstructure, while the size and shape of grains and lamellar colonies depend on competitive growth of primary and peritectic phases, solidification conditions, and nucleation modes and kinetics of solid-state transformations. For binary Ti-Al alloys, Al content affects dendrite size but not significantly. Experimental results [97] show that dendrite size has a minimum at 47 at% Al, while nucleation and constitutional undercooling models assuming a 2 K undercooling predict a composition range of 46.1–48.6 at% Al for coexistence of primary β and peritectic α [33], consistent with experiments. Phase-field simulation results from Eiken et al. [98] indicate that for peritectic alloys, reducing nucleation undercooling can refine grains. For casting processes, the only controllable solidification condition is cooling rate, typically adjusted by controlling mold preheat temperature.

2.4 Hot Working

Hot working utilizes principles of deformation, recrystallization, and phase transformation to break up solidification structures, heal solidification defects, control texture, optimize properties, and even prepare component blanks from ingots or powder metallurgy preforms. Applicable breakdown processes for γ-TiAl alloys are mainly isothermal or near-isothermal forging and hot extrusion, with billets requiring hot isostatic pressing and most alloys needing canning. Secondary hot working or forming processes mainly include die forging and rolling. Appel et al. [33] summarized reported hot deformation experiments, finding that deformation of cast and coarse-grained alloys is controlled by dislocation climb and dynamic recrystallization, while fine-grained billets obtained through deformation and recrystallization or powder metallurgy can also undergo grain boundary sliding during deformation [99].

The hot working process that breaks down coarse solidification structures is called breakdown. The vast majority of γ-TiAl alloys have coarse $\gamma + \alpha_2$ lamellar structures after solidification. The two-phase deformation temperature range for most alloys is 1100–1300 °C, significantly higher than for titanium alloys (800–1000 °C), and lamellar structures are much more difficult to deform than equiaxed structures. These characteristics make γ-TiAl alloy breakdown difficult to perform on conventional industrial equipment. Breakdown failures generally occur in three ways: fracture, damage from grain boundary voids, and failure from flow localization. Deformation in the low-temperature, high-strain-rate region causes intergranular brittle fracture; in the low-temperature, low-strain-rate region, wedge-shaped cracks easily appear at lamellar interfaces; and in the high-temperature, low-strain-rate region, materials fail by ductile void formation [100]. The main factor determining the transition from brittle to ductile failure is dynamic recrystallization. Due to composition inhomogeneity and non-uniform recrystallization in lamellar structures, γ-TiAl alloys are prone to flow localization and deformation failures such as shear bands.

Hot working in the α single-phase region (generally above 1300 °C) can refine grains, forming a fine fully lamellar microstructure upon cooling, but has two disadvantages: First, the time spent in the α single-phase region after hot working should be as short as possible to avoid grain growth, requiring high cooling rates that are difficult to achieve for large components. Second, this microstructure is only suitable as a final microstructure; for intermediate billets requiring further deformation or forming, it is unsuitable because fully lamellar structures are far more difficult to deform than equiaxed or duplex structures.

Based on these considerations, most reported hot working of alloys has been conducted in the $\gamma + \alpha_2$ two-phase region. Dynamic recrystallization of γ is accompanied by spheroidization of α_2, inevitably involving interphase transformation. The grain boundary migration rate of ordered phases can be two orders of magnitude lower than in disordered alloys [101,102], making recrystallization much slower than in disordered alloys. Semiatin et al. [103] showed that for a given deformation strain, the volume fraction undergoing recrystallization and spheroidization increases with decreasing strain rate, and the recrystallized volume fraction increases with temperature [104,105]. In other words, in addition to avoiding forging cracking, high temperatures and low strain rates are also required to fully break down and transform coarse as-cast structures through recrystallization. Imayev et al. [106,107] and Fröbel et al. [108] observed that dynamic recrystallization first occurs at lamellar colony boundaries, forming a pearl necklace morphology. For coarse as-cast lamellar structures, deformation is extremely inhomogeneous, producing highly localized deformation bands that can even penetrate the entire workpiece, with fine equiaxed γ grains or fine two-phase mixed grains forming within the bands. Outside the bands, deformation stored energy is very small and recrystallization proceeds slowly. For hard-oriented grains with lamellar planes parallel to the loading direction, the lamellae become unstable through bending and kinking. These inhomogeneous local deformations and dynamic recrystallization are responsible for the dynamic softening observed in stress-strain curves. Sun Wei [109] used hot compression experiments to simulate the isothermal forging process of two alloys, systematically studying the breakdown process of the original coarse lamellar structure by varying temperature, strain rate, pass reduction, and inter-pass holding time. [Figure 4: see original paper] shows the microstructure of Ti-47Al alloy after single-pass compression to 70% at 1200 °C, with the compression direction vertical. Lamellae perpendicular to the compression direction at the bottom have fragmented; inclined lamellae at the top remain largely intact but show microcracks at lamellar interfaces (arrows); the intermediate region at two colony boundaries has undergone recrystallization. The results show that spheroidization of α_2 lags behind recrystallization of γ, and both depend on strain and lamellar orientation. Grains with lamellae perpendicular to the loading direction are most prone to recrystallization; inclined lamellae are more stable, possibly because dislocation slip parallel to lamellar interfaces accommodates strain, but these grains eventually rotate to approximately perpendicular to the loading direction through grain boundary sliding; lamellae parallel to the loading direction undergo bending, kinking, and fracture to achieve fragmentation and spheroidization. [Figure 5: see original paper] schematically illustrates the observed recrystallization and spheroidization process [109].

Hot extrusion is another common breakdown method. Since dies are not heated, canning and insulation layers must be used to ensure temperature consistency in the billet. Main considerations for hot extrusion include: matching of can and billet strength at extrusion temperature; temperature rise in the billet center due to deformation heating; banded structures along the extrusion direction caused by composition inhomogeneity; and deformation texture. Overall, hot extrusion offers better controllability than isothermal forging, resulting in better property consistency. Like unidirectional isothermal forging, mechanical properties are anisotropic, possibly arising from microstructural anisotropy such as deformation band direction and elongated grain shape, or from deformation texture [110,111]. For axisymmetric billets (e.g., cylindrical billets forged into drum shapes or extruded into round bars), texture is not obvious, but the microstructure is anisotropic, mainly with lamellar planes perpendicular to the forging direction and parallel to the extrusion direction, leading to anisotropic mechanical properties [110,111]. This anisotropy can be utilized to manufacture certain rod-shaped components, such as high-performance automotive engine exhaust valves that can be directly machined from extruded round bars. [Figure 6: see original paper] shows γ-TiAl alloy exhaust valves and extruded preforms manufactured by the Institute of Metal Research, Chinese Academy of Sciences for Ilmore Automotive Engine Company in the UK.

For cross forging or non-circular section extrusion, texture inevitably changes. Only by tracking deformation steps and texture evolution in detail can the variation of microstructure and mechanical properties with orientation be fully understood, but few studies have been reported. Liu et al. [112] performed rectangular-section two-phase region hot extrusion of 4722-0.15B alloy and systematically studied the evolution of microstructure, texture, and mechanical properties in the as-extruded and heat-treated conditions. [Figure 7: see original paper] schematically summarizes texture evolution during extrusion and heat treatment [112]. The texture of γ phase at the extrudate surface (mid-width position) differs greatly from that at the center: the center is dominated by β-fiber texture composed of Copper, S, and Brass components, while the surface is dominated by α-fiber texture composed of Brass and B/G auxiliary components. Both surface and center undergo recrystallization during extrusion, but the surface has a higher recrystallized volume fraction. The rich texture formed in the γ phase reflects the non-uniform deformation, phase transformation, and recrystallization processes it experiences. The presence of C-twin, Y, and Z texture components in the surface region indicates that mechanical twinning and shear bands occurred at the extrudate surface. The B/G auxiliary component is a transition component from deformation to cube recrystallization texture. An unresolved question in fcc metal recrystallization is whether cube texture components originate from oriented nucleation or oriented growth

[113,114]; the existence of B/G auxiliary components provides direct evidence for the oriented nucleation theory. The Brass texture component in the center results from α-phase transformation caused by deformation overheating. The texture of α_2 phase at both surface and center is similar, dominated by {10-10} <11-20>, which forms {0001} <10-10> components through oriented-growth recrystallization after α-phase solution treatment. This oriented-growth recrystallization texture provides a new method for grain refinement: since most α-phase grains have low-angle boundaries after recrystallization and grow slowly during primary recrystallization, only accelerating during secondary recrystallization, controlling heat treatment time between the two recrystallization stages can achieve α solution treatment while avoiding rapid grain growth, obtaining a desirable fine-grained fully lamellar microstructure after cooling. These results show that for non-circular section extrusion, in addition to microstructural anisotropy, texture-induced anisotropy is also an important cause of mechanical property anisotropy.

2.5 Properties

The main properties determining the high-temperature application temperature potential of γ-TiAl alloys are creep and oxidation resistance, while fatigue characteristics and fracture toughness determine stress levels and service life. Although it is difficult to improve the room-temperature ductility of these materials, ensuring a minimum value is necessary for machining, assembly, and preventing component fracture from local stress concentration. This article does not specifically discuss high-temperature strength, room-temperature ductility, and deformation mechanisms, but focuses on three property categories closely related to applications: creep, oxidation, and fatigue/fracture.

2.5.1 Creep

Many reviews on γ-TiAl alloy creep have been published [33,115,116]. Among various microstructures, fully lamellar microstructures exhibit the best creep performance [117,118]. Creep in γ-TiAl alloys differs from that in conventional metals in several ways: the primary stage strain is large; there is almost no secondary (steady-state) creep stage; and the tertiary stage can be very long. Thus, despite long creep life, creep deformation can be excessive, which is unfavorable for manufacturing components with high dimensional accuracy. Only a minimum creep rate can typically be measured between the primary and tertiary stages. Steady-state creep in metals results from a sustained balance between work hardening and dynamic recovery, with dislocation substructures fully developing during this stage. However, in γ-TiAl, no dislocation substructures form; only uniformly distributed ordinary dislocations and deformation twins are observed [119,120]. Multiple mechanisms act simultaneously in the complex microstructure of γ-TiAl alloys, making creep rate control mechanisms difficult to identify. The stress exponent factor increases continuously with stress, rendering model analysis non-predictive and non-guiding.

Numerous studies show that microstructure is the dominant factor determining creep characteristics of lamellar γ-TiAl alloys. First, creep rate does not change significantly with grain size (especially when grain size is large) [121], but grain boundary morphology has an obvious effect, with interlocking serrated grain boundaries significantly reducing creep rate. Second, creep rate is insensitive to α_2-phase volume fraction but very sensitive to lamellar thickness, particularly under high-stress conditions, where fine lamellae significantly reduce creep rate. However, overly thin lamellae are unstable and prone to phase transformation. Under low stress, the effect of lamellar thickness is not obvious due to dynamic recrystallization and lamellar interface sliding. Third, creep rate is sensitive to lamellar orientation, with hard orientations showing significantly higher creep resistance than soft orientations [122].

Tertiary creep strains in γ-TiAl alloys are typically as high as 15–25%, with mechanisms not limited to voids and necking (which only operate before fracture in γ-TiAl alloys) but also including dynamic recrystallization [123], deformation bands [124], grain boundary sliding [125], and $\alpha_2 \rightarrow \gamma$ transformation [126]. Among these processes, dynamic recrystallization and phase transformation appear to dominate [33].

Since γ-TiAl alloys have low primary creep resistance, with creep strains potentially exceeding design allowable values under some application conditions, reducing primary creep rate has been an important research focus for the past 20 years. Studies [127] show that lamellar interface dislocation sources and pre-existing dislocations are the main reasons for high primary creep rates in fully lamellar microstructures. As interface sources gradually become exhausted, the primary creep rate decreases. An interesting phenomenon is that primary creep strain is stress-dependent [128]; only above a certain critical stress does primary creep increase rapidly. Adding elements such as C, O, and N to form precipitates at lamellar interfaces that hinder dislocation source operation, and alloying with refractory metals to increase the critical stress, are effective means to improve primary creep resistance of γ-TiAl alloys.

2.5.2 Oxidation

High-temperature oxidation of γ-TiAl alloys appears relatively simple but is actually a very complex physical and chemical process. Oxidation resistance fundamentally depends on the formation and competitive growth of α-Al_2O_3 and various Ti oxides such as TiO_2, as well as the influence of chemical composition, phase constitution, microstructure, atmosphere, temperature, surface mechanical and chemical state, and diffusion elements and pathways on the competitive reactions. Multiple mechanisms operate simultaneously or sequentially in this complex system, causing oxidation reactions to change with time and sample depth, possibly accompanied by the generation and disappearance of various transition states and metastable phases.

Due to different experimental details, different researchers often obtain seemingly contradictory results for the same problem. For example, Taniguchi et al. [129] found that water vapor significantly accelerates oxidation of Ti-50Al, while Brady et al. [130] found that water vapor has little effect on oxidation of alloys forming Al_2O_3 layers, and Zeller et al. [131] concluded that water vapor effects depend on the relative contents of TiO_2 and Al_2O_3 in the oxide layer. For the same element, its effect on oxidation performance is also stage-dependent: Cr promotes Al_2O_3 formation in the first stage, beneficial for oxidation resistance, but accelerates Al_2O_3 decomposition in the second stage, accelerating oxidation [132]. N has the opposite effect, interfering with Al_2O_3 formation by forming TiN in the first stage, detrimental to oxidation resistance, but if a relatively continuous nitride layer can form later, it can slow internal oxidation in the subsurface layer and reduce Al_2O_3 layer dissolution [132,133]. To date, the only undisputed alloying element is Nb, with all reported results agreeing that Nb improves oxidation resistance of γ-TiAl alloys.

Given the complexity of oxidation in γ-TiAl alloys and the difficulty of experimentally studying each mechanism, theoretical investigation is necessary to understand these mechanisms and oxidation reaction details. First-principles calculations help understand thermodynamic and kinetic processes of oxidation reactions. For the simplest case of pure Ti, its excellent corrosion resistance originates from the TiO_2/Ti system, while calculations show this system has higher energy than several lower oxides TiO_2 , making the oxide film a diffusion-controlled non-equilibrium structure [134]. In fact, these lower oxides have all been observed in early oxidation stages of γ-TiAl [135]. Fundamental issues in γ-TiAl oxidation include: O atom adsorption behavior, effects of alloy atoms on Ti-O and Al-O bonds, and effects of alloying on oxide film growth. Song et al. [136] showed that except for Al atom-covered (001) surfaces, O atom adsorption at other positions makes O-Ti bonds stronger than Al-O bonds, but when TiO_2 already exists, Al-O bonds become stronger than O-Ti bonds [137], favoring Al_2O_3 layer formation. This is consistent with experimental observations that γ-TiAl surface oxide films consist of TiO_2, while subsurface layers consist of $Al_2O_3 + TiO_2$ [138]. Calculations [137] show that Nb atoms on γ-TiAl surfaces cause O to leave TiO_2 and bond with Al, which should be the fundamental reason for Nb improving oxidation resistance of γ-TiAl alloys. Calculation results for oxidation energies [139] show that most elements except Sc reduce the stability of both Al_2O_3 and TiO_2. Co, Ni, Cu, and Zn increase the stability of Al_2O_3 relative to TiO_2, while Nb, Mo, W, and Re have the opposite effect. Excessive stability of Al_2O_3 may lead to columnar growth, making it difficult to form a continuous oxide film, while lower stability Al_2O_3 grows more laterally, hindering internal oxidation and thereby improving oxidation resistance.

The vast majority of oxidation studies use air or O_2 or oxidizing atmospheres, with only one study using a simulated combustion atmosphere [140]. Results show that as long as a continuous Al_2O_3 film forms on the surface, oxidation resistance in simulated gas is better than in air. Kumagai et al. [141] found that halogen elements on γ-TiAl alloy surfaces can promote formation of continuous Al_2O_3 films, with F being more effective than Cl [142].

An important issue related to oxidation is thermal stability after exposure at service temperatures (e.g., 650-700 °C), namely the room-temperature embrittlement problem, for which various explanations have been proposed. The French National Aerospace Research Center conducted more systematic research on this [90], showing that embrittlement after long-term thermal exposure is caused by a brittle surface layer (including oxide layer, Al-depleted layer, and Nb-rich precipitates), while embrittlement after short-term thermal exposure is related to the combined effects of: oxygen-enriched surface, hindered mechanical twin extension at the surface, and residual stress gradients from cooling. Although halogen elements can improve oxidation resistance, they seem ineffective for solving surface embrittlement [33].

2.5.3 Fatigue and Fracture

For intrinsically brittle intermetallic compounds, fracture and crack propagation behavior fundamentally depend on: atomic-scale bond strength determined by alloying; interaction between cracks and defects such as dislocations, twins, grain boundaries, and phase boundaries; and environmental parameters including temperature, loading rate, and atmosphere.

Numerous studies [143-145] show that single-phase γ alloys are extremely brittle, with fracture toughness much lower than two-phase alloys. This is mainly because d-electron hybridization with anisotropically distributed p-electrons in the γ phase leads to extremely strong directional bonding [146-148]. Among two-phase alloys, fully lamellar microstructures have significantly higher fracture toughness (25-30 $\mathrm{MPa}\cdot\mathrm{m}^1/^2$) than duplex microstructures (9-17 $\mathrm{MPa}\cdot\mathrm{m}^1/^2$). For fully lamellar microstructures, coarse-grained alloys have better toughness than fine-grained ones, but lamellar thickness has no obvious effect [145]. The effects of these microstructural parameters and lamellar orientation on fracture toughness stem from crack-lamellar interface interactions.

Theoretical studies by Yoo et al. [149,150] show that the lowest cleavage strengths are for $(100)\gamma$, $(111)\gamma$, and $(0001)\alpha$, while $(111)\gamma \mid\mid (0001)\alpha$ is exactly the lamellar interface. Therefore, when the crack plane is parallel to lamellar interfaces, fracture toughness is very low, only about 3.3-4.3 $\mathrm{MPa}\cdot\mathrm{m}^1/^2$ [151,152]. This indicates that if fully lamellar microstructures develop texture due to hot working or casting, fracture toughness will be significantly affected.

Generally, crystal defects generated by deformation such as twins and dislocations more or less hinder cracks, but this depends largely on local crystallographic orientation and is difficult to verify experimentally at the macroscopic level. Indirect evidence for dislocations hindering crack propagation is provided by observations of increased fracture toughness after pre-deformation introduces large numbers of dislocations [153].

With increasing temperature, plastic blunting at crack tips becomes more significant, and fracture toughness increases. For most materials, increasing loading rate causes crack tip dislocation motion to gradually fall behind crack propagation speed, leading to decreased toughness. However, the opposite trend was observed in room-temperature testing of γ-TiAl alloys [154], explained as an environmental effect: hydrogen embrittlement reduces toughness at low loading rates, while at high loading rates the crack surfaces are fresh and thus have higher toughness.

In early studies, Sastry and Lipsitt [155] found that fatigue strength of γ-TiAl was insensitive to temperature from room temperature to 700 °C. The shape of fatigue limit vs. cycles curves depends on microstructure type [156], but all are above 75% of ultimate tensile strength. This conclusion is independent of material strength and therefore holds for high-strength alloys. In most cases, fatigue cracks originate from the surface, so surface machining condition, stress distribution, and defect nature have obvious effects on fatigue resistance [157,158]. Overall, non-sharp cracks are not a major problem for γ-TiAl alloys. For long cracks, damage tolerance methods based on threshold values are also applicable [159,160], but for short cracks smaller than microstructural units, threshold methods fail [161].

Low-cycle fatigue performance is mainly related to alloy composition. Umakoshi et al. [162] studied PST (polysynthetically twinned) crystals and found that as Al content decreases, lamellar thickness decreases, and material strength and low-cycle fatigue resistance increase. For the three second-generation alloys with near-fully lamellar microstructures, 45XD has the best low-cycle fatigue performance, 4822 is intermediate, and 48WSi is the lowest. Since duplex microstructures have better room-temperature ductility than fully lamellar microstructures, their low-cycle fatigue performance is also superior [163].

Due to the low room-temperature ductility of γ-TiAl alloys, few low-cycle fatigue studies have been reported. Gloanec et al. [164] studied as-cast 4822 alloy and found that at low strain amplitudes, the deformation structure consists mainly of ordinary dislocations with minimal initial hardening; at medium strain amplitudes, vein-like substructures form; and at high strain amplitudes, the deformation structure is twin-dominated with significant cyclic strain hardening. At 750 °C, the deformation structure consists of curved long dislocations, indicating that cross-slip and climb mechanisms are activated. High temperature also causes recovery of the deformation structure, with competition between dislocation tangle and loop annihilation and loop expansion, leading to disappearance of strain hardening and even strain softening [164]. Under high-temperature cyclic conditions, stress-induced phase transformation and recrystallization occur more readily [165,166], with α_2-phase dissolution and precipitation of γ or other metastable phases.

Since defects in γ-TiAl alloys are inevitable and blades and other components suffer foreign object damage during service, understanding crack propagation laws to predict remaining life is very important. Microstructure has a significant effect on crack propagation; lamellar microstructures provide the greatest resistance to long crack propagation, and coarse-grained alloys are better than fine-grained ones (due to more significant crack closure effects in coarse grains).

Overall, at low growth rates, microstructure effects are relatively small, but differences become obvious when fatigue crack growth rate da/dN $> 10^{-8}$ m/cyc [167].

Vacuum environment test results [168] show that the effective crack propagation threshold value corrected by elastic modulus remains unchanged with temperature. Environmental effects mainly change the shape of the da/dN curve, reducing the threshold value and increasing the slope. The most important environmental factor is water vapor, which adsorbs at crack tips, decomposes, and causes hydrogen embrittlement [167].

Although coarse lamellar microstructures have the highest crack propagation threshold values, this concept applies to long crack propagation and is difficult to apply to short cracks. Short cracks can propagate below the threshold value and at higher speeds. For duplex microstructures, an effective crack propagation threshold value lower than the long crack threshold can be obtained, which is useful for design [169]. For lamellar microstructures, such an effective threshold cannot be established [170] because crack propagation resistance along lamellar interfaces is very low [151,152]. Therefore, although coarse lamellar microstructures have the highest crack propagation threshold values, considering short crack initiation and propagation comprehensively, fine lamellar microstructures provide better fatigue life.

2.6 Forming

Forming is the process of making components or their blanks from some form of preform. For wrought alloys, forming can be considered tertiary processing, including processes such as die forging and rolling + superplastic forming. For cast alloys, forming is secondary processing beyond master alloy melting. Powder metallurgy processes are more complex; near-net-shape hot isostatic pressing and 3D printing can be considered secondary processing, but this secondary processing method can also first be used to prepare powder metallurgy billets, followed by tertiary processing such as isothermal forging, extrusion, or rolling. Obviously, structural component manufacturing costs increase proportionally with processing chain length and complexity, which is the main obstacle preventing widespread application of wrought γ-TiAl alloys. The deformation processes used in forming are not fundamentally different from hot working in principle and will not be discussed further here. Only two relatively low-cost near-net-shape processes that do not require further deformation are briefly discussed: precision casting and powder metallurgy + hot isostatic pressing.

2.6.1 Precision Casting

Applicable precision casting methods for γ-TiAl alloys [33,171] depend on combinations of melting method, pouring method, and mold material, with many variations. Melting methods include induction melting (ceramic or water-cooled metal crucibles; ceramic crucibles can achieve high superheat but are unsuitable for critical applications such as aerospace components due to contamination and inclusions; metal crucibles can achieve melt suspension at high power, also called levitation melting) and skull melting. Pouring methods include static gravity, counter-gravity, suction casting, and centrifugal (horizontal and vertical, each subdivided into pour and spin-off types). Mold materials include reusable metal molds and single-use ceramic molds. The use of ceramic molds is also called investment casting, the most widely used type in precision casting. Only casting methods reported in the literature for aeroengine turbine blades are briefly discussed here.

Currently, PCC Precision Castparts uses gravity casting for 4822 alloy low-pressure turbine blades for GEnx engines, with blades designed oversize requiring machining [49,50]. Meanwhile, GE is also developing net-shape blade forming processes, with simulation results for a horizontal spin-off centrifugal precision casting process reported in [49]. The European IMPRESS project supported development of a vertical spin-off centrifugal casting process [172]. These new processes have distinctive technical features, but reports on yield, defect statistical characterization, and batch production cost analysis and control are not yet available.

The Institute of Metal Research, Chinese Academy of Sciences and Germany' s ACCESS Company have successively developed a pour-type horizontal rotational centrifugal casting process for γ-TiAl alloy turbine blades, which is the precision casting process most widely used for conventional materials and has the greatest potential for cost reduction. It should be noted that although these casting technologies differ in process details, they are all investment casting processes. For γ-TiAl alloy turbine blade manufacturing, the process is extremely complex, all including four parts: master alloy preparation, mold preparation, casting, and quality inspection and control. [Figure 8: see original paper] shows the main steps of these process links [173].

Due to the high chemical activity of Ti, casting of γ-TiAl alloys must use oxides more stable than Ti oxides for mold face coats to minimize interstitial element contamination and inclusions. Near the melting point of γ-TiAl alloys, only three element oxides meet this requirement: Ca, Th, and Y. CaO is hygroscopic, ThO_2 is radioactive, and in practice only Y_2O_3 can be used. Preparing Y_2O_3 face coats with high chemical, mechanical, and thermal stability is one of the key technologies for precision casting of γ-TiAl alloys.

Due to the long length, wide chord, thin trailing edge, large camber, and high requirements for metallurgical quality, mechanical properties, and dimensional accuracy of low-pressure turbine blades in large-thrust, high-bypass-ratio engines, they are among the most difficult precision castings. For net-shape casting, the most common defects include: incomplete filling of the trailing edge, inclusions, gas pores, and surface porosity. Casting processes involve trade-offs and optimization of more than a dozen parameters. Only by using highly stable mold face coats can the above four types of defects be eliminated [72]. [Figure 9: see original paper] shows a γ-TiAl alloy low-pressure turbine blade manufactured by centrifugal precision casting at the Institute of Metal Research, Chinese Academy of Sciences, which has completed 1,750 simulated flight cycle tests covering one major overhaul cycle on Rolls-Royce' s Trent XWB engine. [Figure 10: see original paper] shows a piston for a new concept automotive engine from General Motors manufactured by centrifugal precision casting.

As previously mentioned, alloy design and master alloy preparation are prerequisites for obtaining high-quality precision castings. γ-TiAl alloys suitable for precision casting should have the following characteristics: fine grains not overly sensitive to cooling rate, no texture, microstructure insensitive to small composition fluctuations, and no need for complex heat treatment. From these requirements, β-solidifying alloys are more suitable for casting applications than peritectic reaction alloys, provided mechanical properties meet requirements.

Appel et al. [33] provided an example where microstructure is sensitively dependent on composition. When casting automotive turbocharger impellers with Ti-45Al-5Nb-0.2B-0.2C alloy, two completely different microstructures were obtained from the same batch. Analysis showed this difference originated from a small composition fluctuation (only 0.3 at%), causing the two impellers to follow β-solidification and peritectic reaction solidification paths, respectively. This demonstrates that this alloy is not particularly suitable for casting applications.

B is a grain-refining element widely used in γ-TiAl alloys. Depending on alloy system and phase equilibrium, various boride structures can form. The grain refinement mechanism of B is complex and was briefly discussed earlier. First, for alloys with TiB_2 addition [73], unmelted TiB_2 particles can serve as nucleation sites for primary phases to refine grains. Second, in β-solidifying alloys, low B content can form borides that provide α nucleation sites from β transformation to refine grains [76]. Notably, this grain refinement mechanism becomes more significant as cooling rate decreases [174], making it possible to maintain fine grain structures in castings under the moderate cooling rates of investment casting. However, this refinement method reduces ductility when adjacent fine lamellar grains have similar orientations [175]. Third, borides distributed at grain boundaries can limit grain growth [176].

As McQuay and Sikka [171] pointed out, casting of new materials such as γ-TiAl alloys is a systems engineering problem requiring comprehensive consideration from component design and technology development to quality control and supply chain establishment. The narrow sense of “castability” usually refers to the ability of melt to fill mold cavities, while the broad sense of “castability” should be the optimal process obtained through joint efforts of aeroengine designers, materials scientists, and casting engineers based on comprehensive balancing of weight reduction effects, performance improvement, and cost [171], with paths and plans for improving technology readiness and production maturity designed from the initial stages of research and development.

2.6.2 Powder Metallurgy + Hot Isostatic Pressing

As a near-net-shape method, powder metallurgy offers advantages of uniform composition, fine and uniform grains, no texture, and low property scatter [177]. For extremely difficult-to-deform materials like γ-TiAl alloys, using powder metallurgy preforms has two additional advantages: avoiding breakdown deformation and significantly improving material utilization. Aerospace applications require high-quality pre-alloyed powders, which have two main disadvantages or risks: first, some electrode-based powder production methods have high requirements for electrode composition uniformity; second, gas atomization-based powder production methods can entrap gas in some powder particles, particularly large ones, and evidence shows these gas bubbles adversely affect superplastic deformation of sheet materials [178]. Due to the chemical activity of Ti, preparation of γ-TiAl alloy powders must avoid ceramic inclusions and interstitial element contamination; powder preparation, storage, transfer, and handling must all be conducted in protective atmospheres.

During pre-alloyed powder preparation, rapid solidification of droplets is a non-equilibrium process with insufficient or even suppressed diffusion, and incomplete $\alpha \rightarrow \gamma + \alpha_2$ transformation, resulting in excessively high α_2 volume fractions in powders, more pronounced in fine powders and in He atmospheres due to higher cooling rates [179]. Vacuum powder production methods such as rotating electrode, due to slower cooling rates, also cause high α_2 volume fractions from Al loss. It should be noted that the former does not change composition but is a non-equilibrium state that can be essentially eliminated by annealing at 600 °C for 1 hour; the latter changes composition [180]. During hot isostatic pressing of γ-TiAl alloys in the $\alpha_2 + \gamma$ two-phase region, the opposite change occurs: the volume fraction of γ phase abnormally increases. Huang et al. [181] explained this by the smaller "atomic volume" of γ phase compared to α_2 phase, so hydrostatic pressure conditions promote excess γ formation. B addition can effectively prevent grain growth during hot isostatic pressing.

Although powders are handled in protective atmospheres, powder surfaces inevitably adsorb O_2 and water vapor due to atmosphere purity issues. Oxides formed on powder surfaces hinder metallurgical bonding between particles during hot isostatic pressing, requiring appropriate HIP parameters to break surface oxides and eliminate prior particle boundaries [182]. H_2 from water vapor decomposition can be effectively removed by vacuum degassing; degassed powders after hot isostatic pressing show rotating bending fatigue life three times higher at room temperature and two times higher at 650 °C compared to non-degassed powders [183]. [Figure 11: see original paper] shows a γ-TiAl alloy automotive engine connecting rod manufactured by near-net-shape powder metallurgy at the Institute of Metal Research, Chinese Academy of Sciences for General Motors.

3.1 Core Issues

After more than 30 years of research, γ-TiAl alloys have finally emerged among many structural intermetallic compounds and achieved application in key aero-engine components, representing an important step forward. Application of new materials, especially in high-risk components such as turbine blades, requires extensive knowledge and data support. In a sense, successful "insertion" of a new material and its acceptance by industry marks a new starting point for research. In the summary discussion of the Fifth International Conference on γ-TiAl organized by TMS in early 2014, the following issues were raised: (1) How to further improve the maturity of casting alloys and technologies that have already been applied, increasing yield and reducing costs? (2) Wrought alloys have been most thoroughly studied over the past decades, so why have they not achieved large-scale application? Can further research remove obstacles and find a way forward? (3) Can third-generation alloys with good comprehensive properties be found? Can high-performance β-solidifying alloys achieve conventional forging and casting? (4) How to evaluate various new processes? How to ensure composition and microstructure uniformity and consistency? What are the real advantages and feasibility of new processes? (5) What new applications can be expanded in the future, and what problems need to be solved?

3.2.1 Further Development of Casting Alloys and Technologies

The complexity of phase diagrams ([Figure 1: see original paper]) and the high sensitivity of solidification microstructure to solidification conditions and alloy composition, even more so for ternary and quaternary alloys, mean that phase equilibrium data are still lacking even for alloys already in application. The integrated computational approach advocated by the Materials Genome Initiative [184] should be adopted to combine multi-scale computational simulations to provide a framework for composition-phase-microstructure relationships, supplemented by necessary experimental verification, to better understand solidification segregation and improve microstructure uniformity. For example, why is the accurate position of the $\gamma/\gamma + \alpha_2$ phase boundary in [Figure 1: see original paper] difficult to determine? As mentioned earlier, O solubility in the γ phase is about 0.03 at%, but O can dissolve 0.8-2.2 at% in the α_2 phase [86]. Such a large difference makes phase boundary position significantly affected by O content, possibly causing different researchers to measure different phase boundary positions. To clarify this issue, more accurate calculation and experimental study of the Ti-Al-O phase diagram are needed. Another example: although B refines grains, when adjacent fine lamellar grains have similar orientations, room-temperature elongation is only 0.45% [175]. It is necessary to clarify whether texture occurs in B-containing alloys and under what conditions (alloy system, Al content, B content, boride type) texture appears.

3.2.2 Challenges for Wrought Alloys

For difficult-to-deform alloys such as γ-TiAl, using wrought processes means very low material utilization and high cost, which is one of the main reasons why wrought alloys have not achieved large-scale application. Although a large amount of work has been reported over 40 years, systematic studies on some basic issues are still lacking, such as the recrystallization process and mechanism of the α phase, details of microstructure evolution with two-phase region deformation, and more importantly, the anisotropy of deformation microstructure and properties. It is necessary to systematically characterize microstructure and texture evolution with deformation steps, and on this basis obtain optimal microstructures with minimum processing steps to reduce costs.

3.2.3 Design of Third-Generation Alloys

Second-generation alloys such as 4822 and 45XD are currently mainly used in service environments at 650 °C (occasionally 700 °C). New-generation aeroengines require increased turbine speeds (e.g., geared turbofan engines) and thus higher stress-bearing capacity, or require increased application temperatures for better fuel efficiency, both necessitating the development of third-generation γ-TiAl alloys with higher fatigue strength and creep resistance. In terms of tensile strength, third-generation alloys are much higher than second-generation ones ([Figure 12: see original paper]) [185], but other more critical properties such as oxidation and creep have not been systematically characterized and evaluated, and comprehensive properties are still far from application requirements.

As mentioned earlier, alloys such as TNM mainly use refractory elements like Nb and Mo for strengthening while exploiting the β phase for high-temperature deformation processing, then trying to eliminate the β phase at the target application temperature. Many fundamental issues remain unclear, such as the effect of β phase (and precipitated ω or ω-like phases) on creep performance; details of the interaction between creep and phase transformation; recrystallization kinetics of ordered phases during creep and their effect on creep rate; and evaluation of oxidation and environmental effects on creep life.

3.2.4 New Applications Based on New Technologies

The low ductility of γ-TiAl alloys makes welding and joining very challenging. Solving problems in diffusion bonding, brazing, electron beam welding, and laser welding will expand the application range of γ-TiAl alloys. Another technology requiring in-depth study is directional growth of PST crystals of γ-TiAl alloys [186,187]; room-temperature elongation up to 10% can be obtained along the growth direction, but there are three issues: first, strength is relatively low; second, alloy compositions that can be grown as crystals are very limited; third, methods for growing large crystals needed for components remain to be breakthrough. Further optimization of growth processes can broaden the alloy compositions for PST crystals, such as 4722 alloy, where adjusting O content can achieve excellent comprehensive properties of room-temperature yield strength >500 MPa, tensile strength >600 MPa, and elongation >5% [188]. Obtaining large crystals with engineering application value remains challenging.

3.2.5 Suitability of New Forming Processes

Many new metal forming processes can help solve forming difficulties of γ-TiAl alloys, such as spark plasma sintering of pre-alloyed powders [189], which can achieve one-step forming of components or billets with fine-grained fully lamellar microstructures, but process parameters for thick-section components need optimization, and comprehensive properties and property consistency require further study. Laser-based rapid prototyping and other additive manufacturing technologies were attempted for preparing γ-TiAl alloys in the 1990s [190,191]. In recent years, with the rise of 3D printing technology, Europe and America have conducted research with significant investment. The University of Texas and University of California have successively studied electron beam printing of γ-TiAl alloys [192,193]; Turin Polytechnic University and Italian Aviation Industry Group, together with Sweden' s Arcam Company, have used electron beam powder bed technology to conduct in-depth research on preparing various γ-TiAl alloys and blade/impeller mockups [194–196]; Germany is currently implementing a research program on laser additive manufacturing of γ-TiAl alloys [197]. These 3D printing technologies for γ-TiAl alloy preparation will undoubtedly promote progress in new-generation manufacturing methods. Although progress has been rapid, many technical issues remain unresolved, such as property consistency between different parts of the same workpiece and between different batches, the contradiction between deposition quality and manufacturing efficiency, and interlayer segregation caused by high electron beam scanning speeds, all requiring further in-depth study [198].

The European Science Foundation' s Materials Science and Engineering Outlook report published at the end of 2013 [199] listed nine key research topics, with γ-TiAl alloys and additive manufacturing technology ranking first and second, respectively. Applying additive manufacturing technology to prepare low-ductility γ-TiAl alloy components is obviously more challenging. Various 3D printing technologies are still developing and need to mature [200,201]. The closest to mature application are prototype mold manufacturing and non-critical aerospace component manufacturing, while the most highly expected aerospace critical component manufacturing remains technically challenging from a technical perspective, and cost reduction in batch production also needs to be addressed.

Acknowledgments
Part of this work was supported by the National Key Basic Research Development Program Project (2011CB606404), Rolls-Royce plc, and General Motors. Team members including Researcher Cui Yuyou, Associate Researchers

Jia Qing, Liu Ronghua, Liu Dong, Assistant Researcher Liu Renci, and Senior Experimentalist Li Wei contributed to the work described in this article, and their contributions are gratefully acknowledged.

References

[1] McAndrew J B, Kessler H D. JOM, 1956; 10: 1348
[2] Shechtman D, Blackburn M J, Lipsitt H A. Metall Trans, 1974; 5: 1373
[3] Lipsitt H A, Shechtman D, Schafrik R E. Metall Trans, 1975; 6A: 1991
[4] Schuster J C, Palm M. J Phase Equilib Diffus, 2006; 27: 255
[5] Huang S C, Chesnutt J C. In: Westbrook J H, Fleischer R L eds., Structural Applications of Intermetallic Compounds. Chapter 4, New York: Wiley, 2000: 1
[6] Kainuma R, Palm M, Inden G. Intermetallics, 1994; 2: 321
[7] Ohnuma I, Fujita Y, Mitsui H, Ishikawa K, Kainuma R, Ishida K. Acta Mater, 2000; 48: 3113
[8] Suzuki A, Takeyama M, Matsuo T. Intermetallics, 2002; 10: 915
[9] Veeraraghavan D, Pilchowski U, Natarajan, B, Vasudevan V K. Acta Mater, 1998; 46: 405
[10] Witusiewicz V T, Bondar A A, Hecht U, Rex S, Velikanova T Ya. J Alloys Compd, 2008; 465: 64
[11] Blackburn M J, Smith M P. R&D on Composition and Processing of Titanium Aluminide Alloys for Turbine Engines, AFWAL-TR-82-4086, June, 1982
[12] Lipsitt H A. In: Koch C C, Liu C T, Stoloff N S eds., High-Temperature Ordered Intermetallic Alloys. Materials Research Society Symposia Procedings. Vol.39, Warrendale, PA: MRS, 1985: 193
[13] Dimiduk D M, Dutton R. Technical Report OMB No. 0704-0188, Materials and Manufacturing Directorate Air Force Research Laboratory, January, 2004
[14] National Research Council (NRC). Accelerating Technology Transition: Bridging the Valley of Death for Materials and Processes in Defense Systems. Washington: The National Academies Press, 2004: 1
[15] Aoki K, Izumi O. Nippon Kinzoku Gakkaishi, 1979; 43: 1190
[16] Liu C T, White C L, Horton J A. Acta Metall, 1985; 33: 213
[17] Djanarthany S, Viala J C, Bouix J. Mater Chem Phys, 2001; 72: 301
[18] Kim Y W, Wagner R, Yamaguchi M eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1995: 1
[19] Kim Y W. JOM, 1989; 41(7): 24
[20] Kim Y W, Dimiduk D M. JOM, 1991; 43(8): 40
[21] Kim Y W. JOM, 1994; 46(7): 30
[22] Kim Y W. JOM, 1995; 47(7): 39
[23] Larsen D E Jr. Mater Sci Eng, 1996; A213: 128
[24] National Materials and Manufacturing Board. Materials Needs and Research and Development Strategy for Future Military Aerospace Propulsion Systems. Washington: National Academies Press, 2011: 188
[25] Sadler P, Kumar K S, Green J A S. Martin Marietta Laboratories Technical Report MML-TR-93-09, 1993

[26] Pollock T M, Steif P S. A University-Industry Partnership for Research and Transition of Gamma Titanium Aluminides: Final Report, AFRL-SR-BL-TR-01-0633, 1999

[27] Draper S L, Lerch B A, Pereira M, Miyoshi K, Arya V K, Zhuang W. Durability Assessment of Gamma TiAl-Final Report, NASA/TM-2004-212303, 2004

[28] Murtagian G R. PhD Dissertation, Georgia Institute of Technology, 2004

[29] Tetsui T. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 15

[30] Wu X. Intermetallics, 2006; 14: 1114

[31] Gebauer K. Intermetallics, 2006; 14: 355

[32] European Commission DG Research and Innovation. Lightweight Valves for High-Efficiency Engines, 2000-2004. http://ec.europa.eu/research/transport/projects/items/*{{{livalves}}*}{{eur
Accessed February, 2012

[33] Appel F, Paul D H, Oehring M. Gamma Titanium Aluminide Alloys: Science and Technology. Weinheim, Germany: Wiley, 2011: 1

[34] Chen G L, Sun Z Q, Zhou X. Mater Sci Eng, 1992; A153: 597

[35] Paul J D H, Appel F, Wagner R. Acta Mater, 1998; 46: 1075

[36] Xu X J, Lin J P, Zhang L Q, Liang Y F. In: Kim Y W, Smarsly W, Lin J P, Dimiduk D eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2014: 71

[37] Hu D, Huang A J, Gregoire A, Li X, Wu X, Loretto M. Mater Sci Forum, 2005; 29: 172

[38] Blackburn M J. In: Jaffee R, Promisel N eds., The Science, Technology and Applications of Titanium. London: Pergamon, 1970: 633

[39] Kumagai T, Abe E, Takeyama M, Nakamura M. Scr Mater, 1997; 36: 523

[40] Hu D, Huang A J, Novovic D, Wu X. Intermetallics, 2006; 14: 818

[41] Huang A J, Loretto M H, Hu D, Liu K, Wu X. Intermetallics, 2006; 14: 838

[42] Naka S. In: Nathal M V, Darolia R, Liu C T, Martin P L, Miracle D B, Wagner R, Yamaguchi M eds., Structural Intermetallics, Warrendale, PA: TMS, 1997: 313

[43] Burgers W G. Physica, 1934; 1: 561

[44] Kim Y W, Kim S L, Dimiduk D, Woodward C. In: Kim Y W, Morris D, Yang R, Leyens C eds., Structural Applications for High Temperatures, Warrendale, PA: TMS, 2008: 215

[45] Clemens H, Chladil H F, Wallgram W, Zickler G A, Gerling R, Liss K D, Kremmer S, Güther V, Smarsly W. Intermetallics, 2008; 16: 827

[46] Wallgram W, Schmölzer T, Cha L M, Das G, Güther V, Clemens H. Int J Mater Res, 2009; 100: 1021

[47] Huang Z W, Cong T. Intermetallics, 2010; 18: 161

[48] Norris G. Flight International 13th, Power House, June, 2006

[49] Bewlay B P, Weimer M, Kelly T, Suzuki A, Subramanian P R. In: Baker I, Heilmaier M, Kuma S, Yoshimi K eds., Intermetallic-Based Alloys—Science, Technology and Applications, Materials Research Society Symposia Procedings, Vol.1516, Warrendale, PA: MRS, 2013: 49

[50] McQuay P. In: Kim Y W, Smarsly W, Lin J P, Dimiduk D eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2014: in press
[51] Javis D J, Voss D. Mater Sci Eng, 2005; A413-414: 583
[52] Heppener M, Minster O, Jarvis D J. Acta Astronaut, 2008; 63: 20
[53] European Space Agency. Final Report of IMPRESS Project: Publishable Executive Summary, 2009: 1
[54] Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 1
[55] Kim Y W, Clemens H, Rosenberger A H eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2003: 1
[56] Kim Y W, Morris D, Yang R, Leyens C eds., Structural Aluminides for Elevated Temperatures, Warrendale, PA: TMS, 2008: 1
[57] Kim Y W, Smarsly W, Lin J P, Dimikuk D eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2014: 1
[58] Hanamura T, Uemori R, Tanino M. J Mater Res, 1988; 3: 656
[59] Huang S C, Hall E L. Metall Trans, 1991; 22A: 2619
[60] Kawabata T, Tamura T, Izumi O. Metall Trans, 1993; 24A: 141
[61] Sun F S, Cao C X, Kim S E, Lee Y T, Yan M G. Metall Mater Trans, 2001; 32A: 1573
[62] Beddoes J, Seo D Y, Chen W R, Zhao L. Intermetallics, 2001; 9: 223
[63] Huang Z W, Voice W, Bowen P. In: Hemker K J, Dimiduk D M, Clemens H, Darolia R, Inui H, Larsen J M, Sikka V K, Thomas M, Whittenberger J D eds., Structural Intermetallics, Warrendale, PA: TMS, 2001: 551
[64] Stark A, Oehring M, Pyczak F, Schrreyer A. Adv Eng Mater, 2011; 13: 700
[65] Yu R, He L L, Cheng Z Y, Zhu J, Ye H Q. Intermetallics, 2002; 10: 661
[66] Paul J D H, Appel F, Wagner R. Acta Mater, 1998; 46: 1075
[67] Zhang W J, Deevi S C, Chen G L. Intermetallics, 2002; 10: 403
[68] Fröbel U, Appel F. Acta Mater, 2002; 50: 3693
[69] Woodward C, Kajihara S A, Rao S I, Dimiduk D M. In: George E P, Mills M J, Yamaguchi M eds., High-Temperature Ordered Intermetallic Alloys VIII. Warrendale, PA: MRS, 1999: KK281
[70] Li Y J, Hu Q M, Xu D S, Yang R. Intermetallics, 2011; 19: 793
[71] Hao Y L, Xu D S, Cui Y Y, Yang R, Li D. Acta Mater, 1999; 47: 1129
[72] Yang R. In: Kim Y W, Smarsly W, Lin J P, Dimiduk D eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2014: 123
[73] Bryant J D, Christodoulou L, Maisano J R. Scr Metall Mater, 1990; 24: 33
[74] Cheng T T. Intermetallics, 2000; 8: 29
[75] Hu D. Intermetallics, 2001; 9: 1037
[76] Hecht U, Witusiewicz V, Drevermann A, Zollinger J. Intermetallics, 2008; 16: 969
[77] Kitkamthorn U, Zhang L C, Aindow M. Intermetallics, 2006; 14: 161
[78] Lindemann J, Glavatskikh M, Leyens C, Ross-Fagaraseanu D. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 209
[79] Chen S, Beaven P A, Wagner R. Scr Metall Mater, 1992; 26: 1205

[80] Tian W H, Sano T, Nemoto M. Philos Mag, 1993; 68A: 965
[81] Appel F, Fischer F D, Clemens H. Acta Mater, 2007; 55: 4915
[82] Tsuyama S, Mitao S, Minakawa K N. Mater Sci Eng, 1992; A153: 469
[83] Noda T, Okabe M, Isobe S, Sayashi M. Mater Sci Eng, 1995; A192-193: 774
[84] Yu R, He L L, Guo J T, Ye H Q, Lupinc V. Acta Mater, 2000; 48: 3701
[85] Huguet A, Menand A. Appl Surf Sci, 1994; 76-77: 191
[86] Neroc-Partaix A, Menand A. Scr Mater, 1996; 35: 199
[87] Kawabata T, Tadano M, Izumi O. Scr Metall, 1988; 22: 1725
[88] Kawabata T, Abumiya T, Izumi O. Acta Metall Mater, 1992; 40: 1719
[89] Ponchel A. PhD Dissertation, Universite Pierre et Marie Curie Paris VI, 2001
[90] Thomas M, Bacos M P. Aerosp Lab, 2011; 3: 1
[91] Grange M, Raiart J L, Thomas M. Metall Mater Trans, 2004; 35A: 2087
[92] Clemens D R. In: Hemker K J, Dimiduk D M, Clemens H, Darolia R, Inui H, Larsen J M, Sikka V K, Thomas M, Whittenberger J D eds., Structural Intermetallics 2001, Warrendale, PA: TMS, 2001: 217
[93] De Graef M, Biery N, Rishel L, Pollock T M, Cramb A. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 247
[94] Johnson D R, Inui H, Yamaguchi M. Intermetallics, 1998; 6: 647
[95] Küstner V, Oehring M, Chatterjee A, Güther V, Brokmeier H G, Clemens H, Appel F. In: Kim Y W, Clemens H, Rosenberger A H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 2003: 219
[96] Hecht U, Daloz D, Lapin J, Drevermann A, Witusiewicz V T, Zollinger J. In: Palm M, Bewlay P B, He Y H, Takeyama M, Wiezorek J M K eds., Mater Research Society Symposium Proceedings, Warrendale, PA: MRS, 2009: paper No.1128-U03-01
[97] Jung J Y, Park J K, Chun C H. Intermetallics, 1999; 7: 1033
[98] Eiken J, Appel M, Witsuiewicz V T, Zollinger J, Hecht U. J Phys Condens Matter, 2009; 21: 464104
[99] Kim J H, Shin D H, Semiatin S L, Lee C S. Mater Sci Eng, 2003; A344: 146
[100] Seetharaman V, Semiatin S L. Metall Mater Trans, 2002; 33A: 381
[101] Cahn R W, Takeyama M, Horton J A, Liu C T. J Mater Res, 1991; 6: 57
[102] Yang R, Botton G A, Cahn R W. Acta Mater, 1996; 44: 3869
[103] Semiatin S L, Chesnutt J C, Austin C, Seetharaman V. In: Nathal M V, Darolia R, Liu C T, Martin P L, Miracle D B, Wagner R, Yamaguchi M eds., Structural Intermetallics, Warrendale, PA: TMS, 1997: 263
[104] Fukutomi H, Nomoto A, Osuga Y, Ikeda S, Mecking H. Intermetallics, 1996; 4: S49
[105] Salishchev G A, Imayev R M, Senkov O N, Imayev V M, Gabdullin N K, Shagiev M R, Kuznetsov A V, Froes F H. Mater Sci Eng, 2000; A286: 236
[106] Imayev R M, Salishchev G A, Imayev V M, Shagiev M R, Kuznetsov M R, Appel F, Oehring M, Senkov O N, Froes F H. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999:

565
[107] Imayev R M, Imayev V M, Oehring M, Appel F. Metall Mater Trans, 2005; 36A: 859
[108] Fröbel U, Appel F. Metall Mater Trans, 2007; 38A: 1817
[109] Sun W. PhD Dissertation, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 2009
[110] Oehring M, Lorenz U, Niefanger R, Christoph U, Appe F, Wagner R, Clemens H, Eberhardt N. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 439
[111] Oehring M, Lorenz U, Appel F, Roth-Fagaraseanu D. In: Hemker K J, Dimiduk D M, Clemens H, Darolia R, Inui H, Larsen J M, Sikka V K, Thomas M, Whittenberger J D eds., Structural Intermetallics, Warrendale, PA: TMS, 2001: 157
[112] Liu R C, Liu D, Tan J, Cui Y Y, Yang R, Liu F Y, Withey P A. Intermetallics, 2014; 52: 110
[113] Doherty R D, Hughes D A, Humphreys F J, Jonas J J, Jensen D J, Kassner M E, King W E, McNelley T R, McQueen H J, Rollett A D. Mater Sci Eng, 1997; A238: 219
[114] Brokmeier H G, Oehring M, Lorenz U, Clemens H, Appel F. Metall Mater Trans, 2004; 35A: 3563
[115] Zhang W J, Deevi S C. In: Hemker K J, Dimiduk D M, Clemens H, Darolia R, Inui H, Larsen J M, Sikka V K, Thomas M, Whittenberger J D eds., Structural Intermetallics, Warrendale, PA: TMS, 2001: 699
[116] Veyssière P. Mater Sci Eng, 2001; A309-310: 44
[117] Es-Souni M, Bartels A, Wagner R. Mater Sci Eng, 1995; A192-193: 698
[118] Worth D B, Jones J W, Allison J E. Metall Trans, 1995; 26A: 2947
[119] Morris M A, Leboeuf T. Intermetallics, 1997; 5: 339
[120] Wang J G, Hsiung L M, Nieh T G. Scr Mater, 1998; 39: 957
[121] Maruyama K, Yamamoto R, Nakakuki H, Fujitsuna N. Mater Sci Eng, 1997; A239-240: 419
[122] Parthasarathy T A, Subramanian P R, Mendiratta M G, Dimiduk D M. Acta Mater, 2000; 48: 541
[123] Hayes R W, Martin P L. Acta Metall Mater, 1995; 43: 2761
[124] Zhang W J, Spigarelli S, Cerri E, Evangelista E, Francesconi L. Mater Sci Eng, 1996; A211: 15
[125] Du X W, Zhu J, Kim Y W. Intermetallics, 2001; 9: 137
[126] Appel F. Intermetallics, 2001; 9: 907
[127] Es-Souni M, Bartels A, Wagner R. Acta Metall Mater, 1995; 43: 1539
[128] Zhang W J, Deevi S C. Intermetallics, 2003; 11: 177
[129] Taniguchi S, Hongawara N, Shibata T. Mater Sci Eng, 2001; A307: 107
[130] Brady M P, Smialek J L, Humphrey D L, Smith J. Acta Mater, 1997; 45: 2371
[131] Zeller A, Dettenwanger F, Schütze M. Intermetallics, 2002; 10: 511
[132] Rahmel A, Quadakkers W J, Schütze M. Mater Corros, 1995; 46: 271
[133] Quadakkers W J, Schaaf P, Zheng N, Gil A, Wallura E. Mater Corros, 1997; 48: 28

[134] Zhu L G, Hu Q M, Yang R, Ackland G J. J Phys Chem, 2012; 116C: 24201
[135] Schmiedgen M, Graat P C J, Baretzky B, Mittemeijer E J. Thin Solid Films, 2002; 415: 114
[136] Song Y, Dai J H, Yang R. Surf Sci, 2012; 606: 852
[137] Song Y, Xing F J, Dai J H, Yang R. Intermetallics, 2014; 49: 1
[138] Lang C, Schutze M. Oxid Met, 1996; 46: 284
[139] Ping F P, Hu Q M, Yang R. Acta Metall Sin, 2013; 49: 385
[140] Li X Y, Taniguchi S. Intermetallics, 2004; 12: 11
[141] Kumagai M, Shibue K, Kim M S, Furuyama T. US Pat, 5,451,366., 1995
[142] Masset P J, Neve S, Zschau H E, Schütze M. Mater Corros, 2008; 59: 609
[143] Deve H E, Evans A G. Acta Metall Mater, 1991; 39: 1171
[144] Mitao S, Tsuyama S, Minakawa K. Mater Sci Eng, 1991; A143: 51
[145] Chan K S, Kim Y W. Acta Metall Mater, 1995; 43: 439
[146] Song Y, Xu D S, Yang R, Li D, Hu Z Q. Intermetallics, 1998; 6: 421
[147] Song Y, Yang R, Li D, Hu Z Q, Guo Z X. Intermetallics, 2000; 8: 611
[148] Song Y, Guo Z X, Yang R, Li D. Comput Mater Sci, 2002; 23: 55
[149] Yoo M H, Fu C L. Mater Sci Eng, 1992; A153: 470
[150] Yoo M H, Zou J, Fu C L. Mater Sci Eng, 1995; A192-193: 14
[151] Nakano T, Kawanaka T, Yasuda H Y, Umakoshi Y. Mater Sci Eng, 1995; A194: 43
[152] Yokoshima S, Yamaguchi M. Acta Mater, 1996; 44: 873
[153] Appel F. Philos Mag, 2005; 85: 205
[154] Lorenz U, Appel F, Wagner R. Mater Sci Eng, 1997; A234-236: 221
[155] Sastry S M L, Lipsitt H A. Metall Trans, 1977; 8A: 299
[156] Larsen J M. In: Kim Y W, Dimiduck D M, Loretto M eds., Gamma Titanium Aluminides, Warrendal, PA: TMS, 1999: 463
[157] Vaidya W V, Schwalbe K H, Wagner R. In: Kim Y W, Wagner R, Yamaguchi M eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1995: 867
[158] Trail S J, Bowen P. Mater Sci Eng, 1995; A193: 427
[159] Harding T S, Jones J W. Scr Mater, 2000; 43: 623
[160] Draper S L, Lerch B A, Pereira J M, Nathal M V, Nazmy M Y, Staubli M. In: Hemker K J, Dimiduk D M, Clemens H, Darolia R, Inui H, Larsen J M, Sikka V K, Thomas M, Whittenberger J D eds., Structural Intermetallics, Warrendale, PA: TMS, 2001: 571
[161] Harding T S, Jones J W. Metall Mater Trans, 2001; 32A: 2975
[162] Umakoshi Y, Yasuda H Y, Nakano T. Intermetallics, 1996; 4: S65
[163] Recina V. Mater Sci Technol, 2000; 16: 333
[164] Gloanec A L, Bertheau D, Jouiad M, Henaff G, Grange M, Belaygue P. In: Kim Y W, Rosenberger A H, Clemens H eds., Gamma Titanium Aluminides, San Diego, CA: TMS, 2003: 485
[165] Park Y S, Nam S W, Hwang S K. Mater Lett, 2002; 53: 392
[166] Appel F, Heckel T K, Christ H J. Int J Fatigue, 2010; 32: 792
[167] Hénaff G, Gloanec A L. Intermetallics, 2005; 13: 543
[168] Hénaff G, Tonneau A, Mabru C. In: Hemker K J, Dimiduk D M, Clemens

H, Darolia R, Inui H, Larsen J M, Sikka V K, Thomas M, Whittenberger J D eds., Structural Intermetallics 2001, Warrendale, PA: TMS, 2001: 699
[169] Kruzic J J, Campbell J P, McKelvey A L, Choe H, Ritchi R O. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 495
[170] Campbell J P, Kruzic J J, Lillibridge S, Venkateswara Rao K T, Ritchie R O. Scr Mater, 1997; 37: 707
[171] McQuay P A, Sikka V K. In: Westbrook J H, Fleischer R L eds., Intermetallic Compounds—Principles and Practice. Vol.3, London: Wiley, 2002: 591
[172] Harding R A, Wickins M, Wang H, Djambazov G, Pericleous K A. Intermetallics, 2011; 19: 805
[173] Aguilar J, Schievenbusch A, Kättlitz O. Intermetallics, 2011; 19: 1
[174] Oehring M, Appel F, Paul J D H, Imayev R M, Imaye V M, Lorenz U. Mater Sci Forum, 2010; 638-642: 1394
[175] Hu D, Jiang H, Wu X. Intermetallics, 2009; 17: 744
[176] Imayev R M, Imayev V M, Oehring M, Appel F. Intermetallics, 2007; 15: 451
[177] Thomas M, Raviart J L, Popoff F. Intermetallics, 2005; 13: 944
[178] Clemens H, Kestler H, Eberhardt N, Knabl W. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 209
[179] Gerling R, Clemens H, Schimansky F P. Adv Eng Mater, 2004; 6: 809
[180] Graves J A, Perepezko J H, Ward C H, Froes F H. Scr Metall, 1987; 21: 567
[181] Huang A, Hu D, Loretto M H, Mei J, Wu X. Scr Mater, 2007; 56: 253
[182] Xu L, Bai C G, Liu D, Sun W, Yu D J, Cui Y Y, Yang R. In: Kim Y W, Morris D, Yang R, Leyens C eds., Structural Aluminides for Elevated Temperatures, Warrendale, PA: TMS, 2008: 179
[183] Xu L, Wu J, Cui Y Y, Yang R. In: Kim Y W, Smarsly W, Lin J P, Dimiduk D eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2014: 195
[184] Integrated Computational Materials Engineering (ICME). Implementing ICME in the Aerospace, Automotive and Maritime Industries. Warrendale, PA: TMS, 2013: 1
[185] Lasalmonie A. Intermetallics, 2006; 14: 1123
[186] Inui H, Oh M H, Nakamura A, Yamaguchi M. Acta Metall Mater, 1992; 40: 3095
[187] Yokoshima S, Yamaguchi M. Acta Mater, 1996; 44: 873
[188] Jin H, Liu R H, Cui Y Y, Xian Q G, Xu D S, Yang R. In: Kim Y W, Smarsly W, Lin J P, Dimiduk D eds., Gamma Titanium Aluminide, Warrendale, PA: TMS, 2014: 143
[189] Couret A, Molenat G, Galy J, Thomas M. Intermetallics, 2008; 16: 1134
[190] Moll J H, Whitney E, Yolton C F, Habel U. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 255

[191] Srivastava D, Chang I T H, Loretto M H. In: Kim Y W, Dimiduk D M, Loretto M H eds., Gamma Titanium Aluminides, Warrendale, PA: TMS, 1999: 265
[192] Murr L E, Gaytan S M, Ceylan A, Martinez E, Martinez J L, Hernandez D H, Bachado B I, Ramirez D A, Medina F, Collins S, Wicker R B. Acta Mater, 2010; 58: 1887
[193] Porter J, Wooten J, Harrysson O, Knowlson K. Materials Science and Technology—Association for Iron & Steel Technology. Vol.2, Warrendal, PA: Association for Iron & Steel Technology, 2011: 1434
[194] Franzén S F, Karlsson J. Diploma Work No.37/2010, Chalmers University of Technology, Sweden, 2010
[195] Terner M, Biamino S, Epicoco P, Penna A, Hedin O, Sabbadini S, Fino P, Pavese M, Ackelid U, Gennaro P, Pelissero F, Badni C. Steel Res Int, 2012; 83: 943
[196] Biamino S, Klöden B, Weissgärber T, Kieback B, Ackelid U. Franuhofer Direct Digital Manufacturing Conference, Berlin, Germany: DDMC, 2014: 1
[197] Leyens C, Frückner F, Nowotny S. Presented at TMS Symposium on Gamma Titanium Aluminide, 16-20 February 2014, San Diego, USA
[198] Jüchter V, Schwerdtfeger J, Körner C. Presented at TMS Symposium on Gamma Titanium Aluminide, 16-20 February 2014, San Diego, USA
[199] European Science Foundation, Materials Science and Engineering Expert Committee (MatSEEC). Materials Science and Engineering in Europe: Challengers and Opportunities. Science Position Paper, November, 2013
[200] Gartner s 2012 Hype Cycle for Emerging Technologies Identifies 'Tipping Point' Technologies That Will Unlock Long-Awaited Technology Scenarios. http://www.gartner.com/newsroom/id/2124315 9 (accessed 2014.06.10)
[201] Harrop J. Application of 3D Printing 2014-2024: Forcasts, Markets, Players. IDTechEx Report, 2014

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.