Advanced Heat-Resistant TiAl (Nb,Cr,Zr)-Based Intermetallics with the Stabilized β (Ti)-Phase

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Abstract The paper represents a brief review of authors' research results and publications in the area of materials science and engineering of innovated light-weight heat-resistant TiAl-based intermetallic alloys. The system TiAl(Nb,Cr,Zr) under development is being considered as the advanced basis for the creation of TiAl-intermetallics of 3rd generation (TNM) TiAl(Nb,Mo)-like alloys, those being the most promising nowadays for an application in aviation jet engines design. This research is implemented within the frame of Federal Targeted Program for R&D in Priority Areas of Development of the Russian Scientific and Technological Complex for 2014–2020 (Russian FTP for R&D 2014–2020).

Keywords Structural intermetallics • Gamma-Titanium aluminides
Multicomponent alloying • Heat resistance • Microstructure • High-Gradient float-zone processing • Aerojet turbine design

Introduction

In the review [1, 2] in 2013, we analyzed the state-of-the-art of materials science and technology of alloyed TiAl-intermetallics intended for extreme performances. In this review, we have predicted the technology transfer of these materials within the nearest future from the research stage to industrial application in aviation jet turbine-building corporations of the most developed countries. Indeed, the prospective at that time TiAl-intermetallics of the second generation have firstly been used in the low-pressure turbine (LPT) of serial engine GENx-1B by General

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Electric for the equipping of long-range passenger aircraft Boeing 787 Dreamliner [3]. This breakthrough event, being almost synchronous with the review publication, has marked the new stage of TiAl-alloys application—their successful worldwide commercialization beginning. The strategy of application of the new class material in GENx-1B turbine is rather cautious: from the lightweight alloy GE48-2-2 (of Ti-48Al-2Nb-2Cr at.% composition) only 2 final LPT stages (turbine blade discs) are manufactured out of 5 in total, with the “softest” temperature service mode up to 650 °C. Even such limited γ -TiAl application allows saving 180 kg per engine when compared to its precursor CF6-80 that best illustrates the cutting edge of γ -TiAl-alloys potential. The GENx offers up to 15% better fuel consumption, which translates to 15% less CO₂ emission [3]. However, the heat-resistant structural potential of the GE48-2-2 alloy is seemingly near to be exhausted and limited by the final LPT stages operating at the “softest” thermal and pressure modes. The following progress of γ -TiAl application in aircraft turbines requires the improvement of heat resistance and heat strength within the temperature range expanded towards 800 °C and higher. That led to the recent development of novel γ -TiAl-based alloys family, so-called TNM, i.e., TiAl(Nb,Mo)-like alloys which define the upper strength limit of titanium aluminides. Present paper represents the brief review of authors’ research and publications in the area of properties engineering of TiAl(Nb,Cr,Zr) system. The intermetallics of this elemental system could offer the improved basis for the γ -TiAl materials creation of 3rd generation.

The Concept of Development and Engineering the Composition of β -Stabilized Alloys

The development of new generation of TiAl-intermetallics is being addressed to solve the problem of insufficient mechanical ductility, strength and stability of items at elevated temperatures, as well as adaptation of thermo-mechanical regimes of alloys processing (forging, rolling, etc.) to the technical specifications of industrial metalworking equipment.

Innovated gamma-titanium aluminides (TNM-like alloys) contain 42–46 at.% of aluminum, and up to 10–12 at.% functional additives of transient metals, those stabilize the primary β -Ti phase (known also as B2 phase being in low-temperature ordered state). Apart from the obligatory Nb, such β -stabilizers as Mo, Ta, Zr, Cr, W, and V could be used. Such alloying leads to the retaining in solidified alloy of a relatively low volumetric fraction of residual B2-phase on the base of *bcc* lattice, which is ductile at high temperatures. The development concept and achieved properties of TNM-alloys are represented rather comprehensively in recent monograph [4] and in the review [5].

Historically for the first time the molybdenum was used as a β -stabilizing additive, which possesses utmost stabilizing activity (and the acronym TNM = TiAl-Nb-Mo is originated from hence). However, it was revealed that Mo

is worsening the corrosion resistance of γ -TiAl [6]. Nevertheless, the effect of β -stabilizers on the phase diagram transformation of an alloyed material was first studied using the Ti-43.5Al-4Nb-1Mo (at.%) alloy as the typical example [7].

Authors in collaboration with the E.O. Paton Electric Welding Institute have elaborated the alternative alloy Ti-44Al-5Nb-3Cr-1.5Zr (at.%) as the basic composition possessing enhanced corrosion stability due to a homogeneous distribution of anti-corrosion additives Cr and Zr through the constituting intermetallic phases. Particularly, this feature results also in high tribological and tribochemical resistance of the material at the high-temperature friction against heavily alloyed chromium steels [8].

Strong β -stabilizing doping results in a specific change of phase diagram and schematic of solid-state temperature-phase transformations of cast alloy with the participation of stabilized β (Ti)/B2 phase in all technologically important domains (see Fig. 1a, b in comparison), that is the general trait of TNM-like alloys [7].

Key features of TiAl(Nb,Cr,Zr) diagram are the following: strong expansion of primary β (Ti) phase area toward Al and lower temperatures; narrowing and shift of high-temperature α , ($\alpha + \gamma$) domains toward Al, that leads to their excluding from the transformation pathway of the Ti-44Al-5Nb-3Cr-1.5Zr composition (this pathway is marked by the arrow in Fig. 1b). The latter feature is defined substantially the specifics of microstructure forming of Ti-44Al-5Nb-3Cr-1.5Zr in comparison with conventional compositions, including the Ti-46Al-8Nb—precursor of our elaborating alloy. The mechanism of solid-state phase transformations of TiAl(Nb,Cr,Zr) could be simplified by the following sequence of stages:

Fig. 1 The quasi-binary isopleths of systems TiAl-8at.%Nb (a) and TiAl-10at.%(Nb + Cr + Zr) (b), where phase transformation pathways are marked by the arrows for Ti-46Al-8Nb and Ti-44Al-5Nb-3Cr-1.5Zr (at.%) alloys, respectively. The reference binary TiAl diagram is drawn with dotted lines

It will be shown in Section 2.2 that stage (b) is characterized by two kinetic mechanisms, proceeding at cooling of the solid alloy generally in a nonequilibrium manner. That leads to the formation of γ -granular and $(\alpha_2\text{-Ti}_3\text{Al} + \gamma\text{-TiAl})$ -lamellar substructures, being in coexistence with a residual B2-interlayer phase that is located along the boundaries of former transformed α -grains:

Since the volumetric fractions of these substructures are being formed as a result of nonequilibrium reactions, one can control them to some extent, applying different cooling rates and targeted thermal treatments [7, 9].

Engineering the Microstructure and Mechanical Properties of TiAl(Nb,Cr,Zr)

Microalloying with LaB₆

It is well known that ductility of a multiphase intermetallic alloy could be improved by the grain refinement of isotropic equiaxed-granular microstructure [10]. For this purpose, one can apply the doping of Nb-alloying titanium gamma-aluminides with boron-containing additives (usually with TiB₂). That leads to the precipitation of micro/nanoscaled particles of monoboride-based solid solution (Ti,Nb)B within high-temperature domains of the phase diagram. These micro-crystals act as the local (point) seeds at the appearance of major intermetallic phases, leading to the numerous nucleation events and competitive statistic growth of fine equiaxed structural grains. This approach was earlier successfully applied, and the structure-forming mechanism was studied in detail by us in the different technological routes of the TiAl(Nb)B system solidification [11–13]. Additionally, the ductility can be enhanced by the lowering of interstitial embrittle impurity content of oxygen. Working with the complicated TNM-like system TiAl(Nb,Cr,Zr), we firstly applied joint doping with boron and rare-earth element (lanthanum) in the form of LaB₆ compound [14]. That results in the ultra-fine microstructure formation of derivative alloys Ti-44Al-5Nb-2Cr-1.5Zr-0.4B-0.07La and Ti-44Al-5Nb-1Cr-1.5Zr-1B-0.17La (at.%) with the smallest achieved mean diameter of a structural grain of 30 μm , and low (300 wt.ppm) content of dissolved oxygen due to the joint effect of boron and lanthanum internal getter. The enhanced efficiency of LaB₆ ligature application when compared to the microalloying with TiB₂ is clearly seen in Fig. 2 from the comparison of microstructures refinement degree of TiAl(Nb)B vs. TiAl(Nb,Cr,Zr)B,L a alloys.

Fig. 2 Isotropic refined microstructures of the alloys (electron microscopy data), and the functions of their structural grains distribution by the diameter: **a, b**—Ti-44Al-7Nb-2B (at.%), micro-alloyed with TiB_2 [11, 12]; **c, d**—Ti-44Al-5Nb-1Cr-1.5Zr-1B-0.17La (at.%), with LaB_6 [15]

The difference in microstructures of Ti-44Al-7Nb-2B and Ti-44Al-5Nb-1Cr-1.5Zr-1B-0.17La alloys, as displayed in Fig. 2, is related to the different phase-forming mechanisms at the microalloying of TiAl(Nb) and TiAl(Nb, Cr,Zr) systems with boron. In the TiAl(Nb) system the borides $(\text{Ti,Nb})\text{B}$ act as the seeds of high-temperature α -phase at the transformation $\beta(\text{Ti}) \rightarrow \alpha$ (Fig. 1a). When avoiding the domains α and $(\alpha + \gamma)$ in the system TiAl(Nb,Cr,Zr) (Fig. 1b), the ribbon-like borides display the activity in the more low-temperature field $(\text{B}_2 + \alpha_2 + \gamma)$. Here they act as the centers of solid-state germination (seeding) of $\alpha_2\text{-Ti}_3\text{Al}$ phase, which is growing afterward through the matrix of basic $\gamma\text{-TiAl}$ phase as lamellae (Fig. 3). This particular boride-induced mechanism of phase- and structure-forming in a TNM-like alloy have been studied and published by us for the first time in papers [15, 16].

Fig. 3 Boride ribbons resolved in Ti-44Al-5Nb-2Cr-1.5Zr-0.4B-0.07La (a) and three consecutive stages of structure refining mechanism development: event of solid-state germination (seeding) of α_2 -Ti₃Al phase on boride facet (b); morphological development of α_2 -laths and their growth through γ -TiAl matrix (c); formation of new grain boundary by elongated curved boride surrounded by fine γ + α_2 phase structure inside the delimited grains (d). The electron microscopy micrographs [15, 16]

High-Gradient Float-Zone Processing

Another fruitful approach in structure and properties engineering is using of controlling thermodynamic impact to the intermetallic system, i.e., solidification and cooling (annealing) of alloys in the strong directional fields—in magnetic or/and thermal ones. The directional solidification within thermal gradient is the most studied and therefore is most applicable.

At the directional solidification of TiAl-alloys by Bridgman method or by power-down technique [11, 12], the maximally achieved value of axial thermal gradient amounts to 50–70 °C/cm. In the Ti-46Al-8Nb (at.%) alloy it results in the partial ordering of microstructure by the formation of elongated columnar primary β -grains aligned to the crystallization direction. Finally, the microstructure gets obtained consisting of elongated lamellar colonies, inside of which the separation of (α_2 -Ti₃Al + γ -TiAl) lamellae in the low-temperature-phase domain (Fig. 1a) proceeds chaotically, in disagreement with the neighboring colony.

The application of float-zone technique (FZ) with a narrow zone allows increasing considerably the axial thermal gradient near the solid/melt interface. Induction FZ in an argon stream with the gradient of 300 °C/cm was applied by authors firstly to the TNM-like alloy Ti-44Al-5Nb-3Cr-1.5Zr (at.%) in papers [17, 18], and led to the promising results. Let us consider them in more details.

Figure 4a displays the irregular microstructure of initial virgin ingot of Ti-44Al-5Nb-3Cr-1.5Zr, which was manufactured by semi-continuous electron-beam synthesis/casting technique from the pure metals [14]. Basic phase γ -TiAl is imaged here by gray, α_2 -Ti₃Al—by black and B2—as bright phase. For comparison in Fig. 4b the oriented duplex (lamellar-granular) microstructure is given of the same alloy after FZ-processing. It consists of the axially aligned lamellar α_2 -Ti₃Al + γ -TiAl matrix (80% volumetric), granular γ -TiAl microstructure (15%), and 5% of bright inter-granular layers of stabilized β -Ti (B2) phase. Thus, the sub-structural volumetric formula of the FZ-processed Ti-44Al-5Nb-3Cr-1.5Zr alloy can be expressed as $(\gamma + \alpha_2)/\gamma/B2 = 85:15:5$.

The lamellar matrix is magnified in Fig. 4d, being consisted of alternating lamellae of γ -TiAl and α_2 -Ti₃Al phases of sub-micron thicknesses, aligned with the direction of the high-temperature gradient. Figure 4c represents the magnified

Fig. 4 **a**—Irregular microstructure of cast Ti-44Al-5Nb-3Cr-1.5Zr; **b**—ordered microstructure of the alloy after FZ-processing; **c**—magnified transition between the lamellar area and $(\gamma + B2)$ interlayer; **d**—magnified axially aligned $(\gamma + \alpha_2)$ lamellae. The electron microscopy micrographs after [17, 18]

transient area between the lamellar and γ -granular fractions, where the details of structural transition and “relaxing” grains of B2-interlayer are seen; the latter are ductile at elevated temperature. Evidently, as a result of FZ-processing, the microstructure of the alloy is cardinally modified, refined and ordered at the conservation of an unchanged set of constituting phases. Therefore, the microstructural engineering is carefully being performed.

The duplex structure, represented in general view in Fig. 4b was formed within the low-temperature domain ($B2 + \alpha_2 + \gamma$) of phase diagram (Fig. 1b) during the nonequilibrium cooling under high thermal gradient impact. The gradient promotes the ordering, “pooling” of growing $\alpha_2 + \gamma$ lamellae along the ingot axis at their formation from α -phase according to the reaction (2). The γ -granular fraction is being formed at the transformation of B2 phase according to reaction (3) and is situated along the former boundaries of columnar textured α -grains, those elongated as well in the thermal gradient direction. The completion degree of this reaction depends on the cooling rate of the alloy within ($B2 + \alpha_2 + \gamma$) area of phase diagram after FZ passing. Therefore it depends on the zone movement rate. Thus, the relative volumetric ratio of sub-structural fractions $(\gamma + \alpha_2)/\gamma/B2$ could be optimized rather easily by the kinetic way, i.e., by the zone movement rate variation.

The ordered microstructure with optimized $(\gamma + \alpha_2)/\gamma/B2$ volumetric quotas (Fig. 4b) possesses more balanced properties when compared to the cast material. Fine lamellar matrix (Fig. 4d) is responsible for the improved strength and creep especially under axial loading. Meanwhile, the heat resistance and plasticity get enhanced thanks to the incorporated interlayers composed of γ -grains and ductile B2-phase (Fig. 4c). At the expense of limited elastic mobility of γ -grains within the medium of B2-phase, such interlayers promote the relaxation of stresses in basic lamellar structure, thus raising the high-temperature threshold of its destruction.

The specimens of virgin and structurally modified alloy Ti-44Al-5Nb-3Cr-1.5Zr were comparatively examined by the uniaxial compression along the ingot's axis at the temperatures from 750 to 1050 °C. The results of high-temperature tests are given in Figs. 5a–d, illustrating the comparative degradation of physical–mechanical properties of the alloys vs. temperature. FZ-processing led to substantial improvement of deformability (Fig. 5a), an increase of yield strength (Fig. 5b) and Young's modulus (Fig. 5c) at the same temperatures. At the same loads, the creep resistance rises. Exemplarily, under the load of 200 MPa the first signs of creep of FZ-alloy appear only at 950 °C (Fig. 5d). In other words, FZ-alloy possesses the identical level of deformability parameters at the temperatures by 100–150 °C higher when compared to cast material. Thus the upper-temperature limit of Ti-44Al-5Nb-3Cr-1.5Zr structural applicability could be expanded from 750 to 800 °C towards 900–950 °C.

Fig. 5 Plots of physical-mechanical properties of cast (in black) and FZ-processed (in red) alloys vs. temperature [18]: **a**—axial deformation curves; **b**—yield strength; **c**—Young's modulus; **d**—creep rate

Conclusions

We have demonstrated in laboratory scale that the system TiAl(Nb,Cr,Zr) under development could represent the advanced basis for the creation of TiAl-intermetallics of third generation, those being the most promising nowadays for an application in aviation jet engines design. Considering the Ti-44Al-5Nb-3Cr-1.5Zr (at.%) composition, the features of phase diagrams and structure formation have been discussed of a new class of γ -TiAl-intermetallics with stabilized β phase, those allow applying the new effective principles of the necessary structural properties creation of the material. The brief review of authors' innovative research and publications is presented in the field of engineering the new types of heat-resistant microstructures in gamma-titanium aluminides by joint microalloying with boron and lanthanum, and by the high-gradient float-zone processing application. The experimental specimens of microstructured alloy possess both increased high-temperature strength, and creep resistance at the uniaxial loading, thus exhibiting the substantial extension of thermal service range when applying γ -TiAl in turbine blades and other crucial components of aircraft jet engines design.

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