M. Thomas
M.-P. Bacos
(Onera)

E-mail: marc.thomas@onera.fr

Processing and Characterization of TiAl-based Alloys: Towards an Industrial Scale

This paper highlights Onera efforts focused on the design of new TiAl-based alloys, the development of a commercially-viable route for the manufacture of aero engine components and the optimization of mechanical properties. The alloy G4, with a duplex microstructure, has been developed with an excellent balance of properties for gas turbine applications up to 800°C. Additionally, a series of TiAl-3(Fe,Zr,Mo) alloys have been designed for applications with good ductility requirements. Since these alloys were developed for the casting route, results show that the minimization of subsequent heat treatments is required for property scatter reduction. Alternatively, the Powder Metallurgy (PM) route was explored with the aim of establishing well defined microstructure-property relationships. Moreover, microstructural changes and related phase transformations were fully clarified in the now well known 47-2-2 alloy. This thorough understanding then enabled us to optimize the microstructure of the 47-2-2 alloy via process parameters, in order to meet industrial requirements in terms of tensile, creep, and fatigue properties. Furthermore, in the last three years, alternative PM processing routes, by means of Spark Plasma Sintering and Direct Metal Deposition processes, were found to provide enhanced tensile properties. Finally, structural factors such as the surface-related embrittlement and the formation of oxide scales that occurs on the degradation of mechanical properties, and in turn on the temperature limitations of the TiAl-based alloys, were identified. Different approaches aimed at improving the oxidation/corrosion resistance are then described to achieve a better environmental durability for TiAl-based alloys.

Introduction

Due to requirements for higher thrust-to-weight ratios and enhanced fuel efficiency, TiAl-based alloys have attracted considerable interest among industrial companies for aeroengine applications. Due to their lower weight, high temperature strength, excellent burn resistance and quite good oxidation resistance, these intermetallic alloys are regarded as strong substitute candidates for conventional titanium alloys in the compressor part of aerospace gas turbine engines and also for Ni-based superalloys in the low pressure turbine part. As a significant pay-off for a considerable amount of research activities devoted to developing gamma alloy technology in the last two decades, γ-TiAl alloys are currently being used for turbocharger rotors in automotive engines [1] and have now been introduced for turbine blades in General Electric's GENx engine [2]. The cast Ti-47Al-2Cr-2Nb alloy, which passed the FAR33 certification in 2007 for GEnx engines that will power the B787, is regarded as the greatest breakthrough in the TiAl technology up to now.

However, a challenge for successful implementation of a variety of γ-TiAl components, is that, in order to meet the specific requirements for gas turbine applications, the selected alloys must possess a number of properties: ductility, fatigue strength, creep resistance, fracture toughness and crack propagation as well as high oxidation and corrosion resistance. An additional and necessary requirement concerns the attainment of a strict control of mechanical properties. Therefore, the non-constant size, morphology, proportion and distribution of the constituent phases in γ-TiAl alloys have to be controlled, and the microstructure has to be optimized over different length scales. A number of structural factors, in particular crystal orientations, boundary misorientations and structural inhomogeneities, can be influenced by some processing parameters. This can lead to unfavorable slip transfer conditions and to localized deformation processes which result in some variability of mechanical properties [3,4]. Large efforts were then devoted to compare the processing routes for different industrial applications (aerospace structural parts, automotive engine parts, turbocharger rotors, etc.). Therefore, Onera efforts in the last years were aimed at manufacturing robust engineering materials with efficient processing strategies to achieve optimized properties. The present paper will highlight Onera research work on designing new TiAl-based alloys, developing a commercially-viable route for the manufacture of aero engine components and optimizing mechanical properties. Finally, the temperature limitations in terms of thermal stability, oxidation and corrosion will be addressed.

Historical background

In the eighties, the development of γ-TiAl alloys was initiated in Japan and in the US. Promising results were obtained on tensile ductility based on the addition of specific alloying elements such as Mn [5]. In the meantime, the now well-known General Electric (GE) alloy composed of Ti-(46.5-48)Al-2Cr-2Nb (at%) was designed with the addition of Cr and Nb for ductility improvement and for a better oxidation resistance, respectively [6]. In the next decade, systematic studies were carried out at General Electric to adjust the composition range and to optimize the microstructure via heat treatments for the best balance of mechanical properties. The Al content was maintained in the 46.5-48% range for a good balance between Yield Stress (YS) and ductility. Hot Isostatic Pressing (HIP) at 1185°C for 4 hours was followed by annealing at 1205°C for 2 hours under controlled cooling rate to provide a good compromise in ductility, creep resistance as well as fracture toughness. Large databases were then produced in this annealing condition, including physical properties such as thermal coefficient, specific heat, thermal conductivity, Poisson's ratio, elastic and shear modulus for high specific stiffness applications. In addition, a number of mechanical properties, i.e. YS, Ultimate Tensile Strength (UTS), ductility, crack growth threshold, creep life, Low and High Cycle Fatigue (LCF and HCF) were compared to those of Ni-based superalloys.

However, the 47-2-2 alloy is typical of the first generation alloys, with a very strong solidification texture. The GE alloy is solidified by the $L+\beta \rightarrow \alpha$ peritectic reaction. Under further cooling, subsequent phase transformation occurs by the α (hcp) -> $\alpha + \beta$ ($L1_0$) -> α_2 (DO_{19}) + γ reaction where nucleation and growth of γ lamellae with the Blackburn relationship is followed by α -> α_2 ordering below the eutectoid temperature. The availability of different TiAl alloy compositions then appears to be a necessary requirement since various applications for automotive, gas and terrestrial turbine components with different stress and temperature regimes are envisaged. For instance, boron-containing TiAl alloys were developed in the early nineties to reduce the cast columnar texture and some investigations are still in progress to understand the underlying mechanisms that makes boron efficient for grain refinement and texture reduction. In the last decade, extensive efforts were focused on $\gamma+\beta$ alloys with the addition of various ternary elements (Nb, Cr, Mo, W, Fe, Ta) that promote the cubic β phase with a higher deformability [7-14].

Results

Alloy development

So far, a number of research activities have been conducted at Onera on alloy development in order to satisfy property requirements in terms of oxidation resistance, thermal stability and of high temperature properties of TiAl-based alloys. For instance, a Ti-47Al-1Re-1W-0.2Si (at%) alloy, namely G4, with a duplex microstructure has been designed as a casting material for high temperature gas turbine applications [15]. Work at Onera concentrated on systematic heat treatment studies to define the most adequate microstructure of this G4 alloy for the best balance of mechanical properties.

Under static load condition, alloy G4 was quite comparable to other commercial γ-TiAl alloys in terms of tensile strength, irrespective of the heat treatment conditions [16]. With regard to HCF, the endurance limit was found to exceed the yield stress, indicating that alloy G4 may not be very sensitive to such cyclic load conditions. Furthermore, in the low temperature regime up to 800°C, alloy G4 was more creep resistant than nickel-based superalloys on a corrected density basis. However, such creep properties were found to vary quite significantly as a function of heat treatment conditions, with the best condition in the as-HIPed condition, which is not consistent with the observations from the literature concerning the beneficial effect of a fully lamellar structure on creep through sub-transus heat treatment conditions [17]. The Onera study shows that the lamellar structure should not be the key factor controlling the creep rate [16]. Instead, creep in this alloy is controlled by deformation-induced substructures such as percolated interdendritic γ grains enriched in Re. Moreover, an as-HIPed condition like this can satisfy service conditions of most industrial installations. Based upon this attractive set of properties, an increasing temperature capability was then demonstrated with alloy G4 for reliable applications of this material at temperature up to 800°C. However, some difficulties encountered in the very last years, which were related to the supply of fine Re and W powders for the master alloys, do not make it easy to implement alloy G4 for gas turbine applications.

In the last years, alloy development at Onera was also focused on ductility enhancement. Apart from the tendency for ternary elements (V, Cr, Mn, Nb, Ta, Zr, W, Mo, Fe, etc) to be substituted either for Al or for Ti in the γ phase, which contributes to shift the $\alpha_2+\gamma/\gamma$ transformation line and to change the proportion of lamellar colonies and γ grains, some other intrinsic factors can also be responsible for the plastic behaviour. Addition of Zr tends to increase the a parameter more rapidly than the c parameter, thus diminishing the tetragonality of the γ phase to the benefit of a more isotropic deformation. As mentioned in [18], a Zr atom with an atomic volume that is different from the matrix is expected to introduce elastic effects which result in solid solution strengthening. The presence of Zr also appears to strengthen the directional bonding, but to a lesser extent, which results in a slight increase in the Peierls potential. Consequently, a loss of dislocation mobility is induced and an additional strengthening is expected. In contrast, Fe addition offers a significant electronic effect instead, which reveals a similar intensity for both Ti-Fe et Al-Fe bondings [19]. A lower sensitivity of the Al content with Fe addition can then be anticipated. Finally, Mo offers a beneficial effect in terms of increased deformability by decreasing the lattice friction for the motion of ordinary dislocations and is a well known creep strengthening element [20].

Based on previous theoretical considerations, a number of TiAl-3(Fe,Zr,Mo) alloys were characterized for tensile behavior. Experimental data in terms of room-temperature ductility were found to be quite encouraging in the different alloys investigated, with plastic elongations between 1 and 2%. Consistently with the electronic effect of Fe, properties are not affected by a difference in Al content for Fe-containing alloys. Tensile properties at 800°C revealed a high level of ductility which can bring the required deformability for post-processing operations.

Comparison of processing routes

In view of the industrial requirements for compressor and turbine blade applications, special attention was paid to the influence of the processing and heat treatment conditions on the microstructure and properties. Some results of the two cast and Powder Metallurgy (PM) processing routes using the same alloy composition TiAl-2Cr-2Nb are reported in this section.

For gas turbine components with complex shapes, the casting texture may not be so regular and axisymmetric. So, property variations are generally observed for different thicknesses of the cast parts and locations of the test specimens whereas, for a jet engine manufacturer, the major concern is to guarantee a minimum value of mechanical properties for every component. Therefore, to control potential cast-induced defects and for a better understanding of the microstructure/property relationship in cast bars, comparative tests were made with respect to the Al content and to the location of the test specimen within the bars. Results in figure 1 demonstrate the predominant effect of the Al content on YS and of the equiaxed-columnar structure transition through the section of the bars on tensile ductility at room temperature. Similarly, both parameters were found to strongly affect the creep behavior (figure 1b).

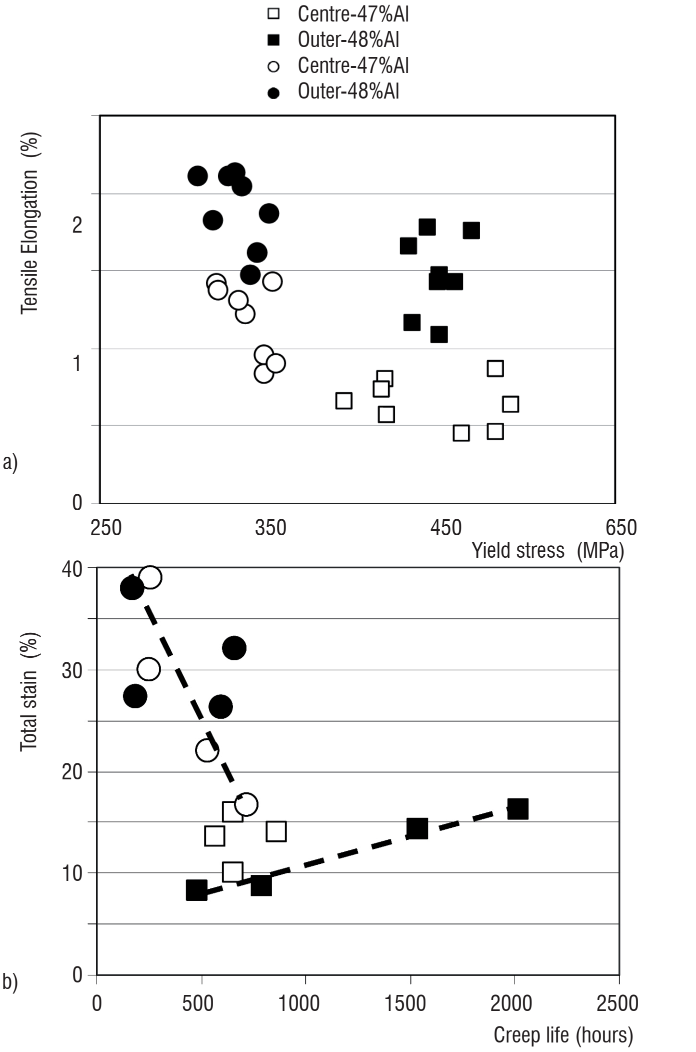


Figure 1 - Effect of Al content and location of the test specimen for heat treated TiAl-2Cr-2Nb alloys. (a) Tensile behavior (after reference 25) and (b) Creep behavior (after reference 26).

Casting is a difficult process to optimize. On one hand, columnar cast structure and chemical inhomogeneities have to be reduced through heat treatments to yield more attractive mechanical properties. On the other hand, property scatter is larger when subsequent heat treatments are carried out in the sub-transus field region, which is indicative of some return to chemical equilibrium counterbalancing a kind of solidification "memory" with cast structural features. To reduce property scatter, the recommended procedure is to then directly optimize the casting conditions with regard to property requirements, i.e. without post-heat treatments. Furthermore, current cast alloys tend to suffer from the inherent lack of strength associated with the cast structure. Recent cast alloy development efforts have focused on the addition of minor elements (B, C, Si) and of β-stabilizing strengtheners for a better performance [21,22]. Nevertheless, it should be stressed that the centrifugal casting process has already demonstrated that sound parts of a difficult configuration such as low-pressure turbine blades can be obtained [23,24]. On the industrial side, centrifugal casting is sufficiently mature to offer the possibility to manufacture complex shape components.

In order to alleviate inherent crystallographic and morphological texture factors of the γ-TiAl lamellar structure, other processing routes such as PM were explored at Onera. Several main advantages can be stressed regarding the PM route. Full consolidation was obtained for sub α-transus HIP conditions with no evidence of macrosegregation or directionality. Powder compacts exhibit a refined microstructure and are less sensitive to the Al content than cast bars. The next step with PM parts was to establish microstructure-property relationships. For this purpose, an expanded range of microstructures, typically near-γ equiaxed, duplex and fully lamellar, was tailored in samples by varying heat treatment conditions. The tensile behavior was compared for γ-equiaxed and lamellar microstructures by plotting the plastic elongation as a function of the work hardening rate [25]. From figure 2, it is clear that the strategy to improve the tensile ductility is different in both microstructures. It can be seen that the best ductilities are obtained for intermediate work hardening. For lamellar microstructures, the steeper the curves in the plastic domain, the higher the flow stress which rapidly overcomes the critical transgranular cleavage stress and the lower the plastic elongations. This strong work hardening rate dependence of tensile ductility is governed by a homogeneous deformation through the lamellar microstructure. In contrast, γ-equiaxed microstructures exhibit significant strain localization during plastic deformation.

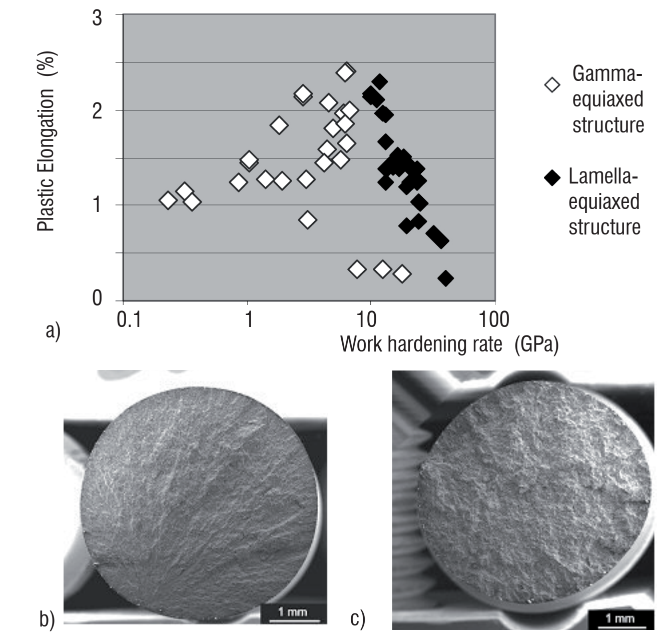


Figure 2 - Tensile behavior for γ-equiaxed and lamellar structures:
(a) dependence of tensile ductility on work hardening rate,
(b) heterogeneous deformation mode for γ-equiaxed structure,
(c) homogeneous deformation mode for lamellar structure (after reference 25).

Phase transformations and microstructural changes

The uniform microstructure obtained for powder compacts after HIPing gave the opportunity to further investigate some microstructural evolutions and related phase transformations in the 47-2-2 alloy. By using specific heat treatment conditions, Onera has identified novel phase transformations in the well-known 47-2-2 alloy [27]. In parallel, coarsening mechanisms for the grain size and lamellar spacing were clarified and are now examined. As already documented in the literature [28,29], heat treatments above the α transus temperature result in fully-lamellar microstructures. Moreover, the holding time is found to control the lamellar colony size while the cooling rate controls the lamellar spacing. However, more unusual is the fact that the lamellar colony size appears to be also cooling rate dependent, whereas the lamellar spacing is also time dependent [27].

Several authors [30-33] have already pointed out the fact that the final grain size is time dependent and not cooling rate dependent since grain coarsening should only occur above the α-transus. However, our quantitative analyses [27] show that over-aged samples still exhibit a significant effect of the cooling rate on grain coarsening. Some authors [34,35] have already noticed that, despite the fact that additional time during cooling seems to be negligible with respect to the holding time, different cooling rates nevertheless lead to significant differences in colony size. However, they assumed that the lamellar colonies produced at a higher cooling rate had a size similar to that of prior α grains, and that slow cooling would enhance some lamellar impingement at colony boundaries leading to substantial colony coarsening.

In the work performed at Onera, Icy Water Quenching (IWQ) provides information about the initial grain size just before cooling. In more detail, the number of small lamellar colonies is higher in the Furnace Cooled (FC) sample than in the IWQ sample and the FC sample has the greatest amount of large colonies in the 400-650 μm range, indicating that larger grains also exhibit coarsening. But, the Intermediate sand Cooled (IC) sample is the one with small grains as the most representative grain size fraction. The overall grain size distributions can then be interpreted by two distinct mechanisms: (i) a nucleation of new grains leading to small lamellar colonies with cooling rate dependence and (ii) a moderate grain growth during furnace cooling. The nucleation of new grains is likely to occur before the onset of lamellar formation, since there cannot be more than one lamellar colony per prior α grain. Continuous Cooling Transformation (CCT) experiments have reported that an undercooling of at least 70°C below the α-transus temperature is necessary for nucleation of lamellae, even for very slow continuous cooling [34]. It is then reasonable to assume that new α grains are formed within this sub-transus temperature range, even though no in-situ experiment was carried out to confirm such a nucleation process. We may assume that a relaxation phenomenon of internal stresses takes place by promoting new α grains, in particular at triple point junctions.

Looking now at the lamellar spacing, Yang [36] suggested that a relationship can be established with the grain size which is controlled by the holding time, the lamellar spacing λ being proportional to $D^{-1/2}$. In the Onera study, the first interpretation given for the inverse relationship between D and λ is related to a decrease in the total grain boundary area per unit volume, owing to grain coarsening. Therefore, larger prior α grains tend to reduce the number of primary γ nucleation sites and then to decrease the rate of the lamellar transformation. The lamellar transformation is expected to be shifted to lower temperatures with a sufficiently large undercooling to provide the internal energy required to overcome the excess strain energy resulting from the lamellar formation. The second interpretation is related to a difference in interfacial energy at prior α grain boundaries. After only 5 minutes of annealing, the interfacial energy would remain sufficiently high to trigger the lamellar transformation at a relatively high temperature in the sub-transus temperature range. Further, a holding time of 120 minutes would then drastically reduce the interfacial energy through grain coarsening, thus leading to a dramatic delay of the lamellar transformation. Such a lower-temperature homogeneous transformation of fine lamellae is also consistent with the relatively planar morphology of colony boundaries.

Mechanical properties

Heat treatment studies were conducted to optimize the mechanical properties. A relationship has been established between twin and dislocation densities, grain size and interlamellar spacing, and mechanical properties. The microstructure could then be optimized via process parameters in order to meet industrial requirements in terms of tensile, creep, and fatigue. For instance, the yield stress is affected by the lamellar colony size (Φ) and by the interlamellar spacing (λ), which can be described by the following Hall-Petch expression :

$$\sigma_e = \sigma_0 + k_\Phi.\Phi^{-1/2} + k_\lambda.\lambda^{-1/2} \tag{1}$$

with σ_e the slip system strength, σ_0 the lattice friction stress related to the Peierls-Nabarro stress and solute hardening, and the two empirical constants k_Φ and k_λ related to the critical stresses required for a dislocation to cross a grain boundary and a lamellar interface, respectively. Fatigue behavior and resonant mode behavior are also important properties for component design. In particular, the response from such a material to cyclic deformation during transitional engine speed was found to involve considerable work hardening, which could become deleterious for the component life due to the quite moderate intrinsic ductility of the γ-TiAl alloy.

Onera developed an optimized microstructure that exhibits a significantly lower work hardening rate while preserving the fatigue life of the material. The Cyclic Stress-Strain (CSS) behavior at 20°C and at 500°C of the 47-2-2 alloy showed that an increasing amount of lamellar colonies, a finer lamellar spacing and a smaller γ grain size, can markedly decrease the cyclic strain hardening rate [37]. This is due to enhanced twinning development and then to reduction of the dislocation mean free path which delay the formation of a fully-developed vein-like structure. At 500°C an increased dislocation activity takes place at the expense of mechanical twinning. This replacement of twins by dislocation walls and networks favors the formation of the vein-like structure. Therefore, the CSS behavior at 500°C can be described by two regimes, the first one involving strong hardening which is related to the vein-like structure formation, and the second one which is a saturation regime where a braid-like structure is formed. Finally, the fine fully lamellar microstructure appears to be the optimized microstructure for achieving a lower cyclic strain hardening and a longer fatigue life. For engineering applications, such microstructures are known to be adequate for enhanced creep resistance and fracture toughness properties.

Alternative PM processing routes

Extensive work was carried out by using the Spark Plasma Sintering process (SPS) to consolidate different γ-TiAl alloys. Indeed, the advanced "PM + SPS" processing route is competitive for TiAl implementation in aerospace and automotive applications by reducing the production cost to affordable levels and by ensuring parts with enhanced homogeneity, pore-free microstructures and with suppressed cast mis-runs, melting defects or hot forging cracks. Since the heat inside the material is generated by a Joule effect, whereas the die remains relatively cold, thermal gradients are observed in the parts which involve significant radial structural inhomogeneities. However, uniform microstructures can be achieved either by sintering at elevated temperatures, typically above the α-transus, or by using a boron-containing alloy [38]. In the latter case, the as-SPS alloy displayed the same duplex and uniform microstructures which consist of a mixture of lamellar colonies and γ grains, for sintering temperatures in the 1190-1250°C temperature range. Looking now at the tensile properties, the overall set of tensile data shows a very low scatter for duplicate tests together with a nice balance of yield strength – tensile ductility for the two alloys investigated of the compositions Ti-47Al-2Cr-2Nb and Ti-44Al-2Cr-2Nb-1B [38].

A direct manufacturing technology was employed to produce fully dense parts of 47-2-2 by means of Direct Metal Deposition (DMD). This Onera study was aimed at demonstrating the feasibility of manufacturing TiAl components without hard tooling. In practice, a Computer-Aided Design (CAD) file is used to index the laser and/or the powder supply which is aimed at building 3D parts. DMD is a technique which consists of injecting the powder through a nozzle with helium gas onto the substrate to be molten layer by layer. Because of the high power density used, which leads to very high cooling rate in the order of 10^3 up to 10^4 °C/s, ultra fine and metastable structures are generated. In order to build up dense 3D parts with a good geometrical quality using DMD, a number of key parameters have to be controlled, i.e. the laser power, the powder feeding rate, and the displacement rate. However, when using a single heating source, tensile residual stresses cannot be overcome completely by strong thermal gradients. In order to slow dovn the cooling rate and relieve the residual stresses, pre-heating of the substrate at a temperature of 300°C and gradual post-heating from external heat source with a low energy density were successfully used to yield crack-free samples [39]. A concomitant reduction of the feeding rate and a power increase were found to lead to a better dilution and a better coupling with the substrate.

Thermal-induced inhomogeneities were successfully reduced by annealing treatments. A sub α-transus solution anneal at 1250°C appears to be successful in providing a quite uniform duplex microstructure which was then selected for tensile testing. Tensile test results of laser formed 47-2-2 alloy were encouraging since the tensile ductility was even better than that of HIP casting, which is indicative of the fact that post heat-treatments can be successfully used to restore the structural homogeneity and to relieve the residual stresses (figures 3a,b). Comparison of building directions X and Z reveals in average a 30% difference in tensile elongations which is indicative of a moderate anisotropy.

Current status on temperature limitations

Thermal stability after long term exposure

The thermal stability of high-temperature applications of γ-TiAl-based alloys after long term exposure needs to be studied. In the literature, a significant reduction in ductility was reported to occur after exposure at service temperatures such as 650-700°C. Different interpretations were proposed for this material embrittlement: surface oxidation [40] – loss of residual machining stresses [41] – structural instabilities [42,43] – more in-depth interstitial contaminations [44,45] – hydrogen and moisture embrittlement [46,47] – aluminum depletion [48,49] – formation of brittle phase particles [41,50] – nitrogen effect [51].

Attempts were made at Onera to discover the predominant factors causing this reduction in the tensile ductility of the 47-2-2 alloy [52]. Gas atomized powder compacts were used in the as-HIPed condition to yield a near-γ microstructure for the major part of this study because the location of the initiation fracture site is enhanced with such a microstructure, as shown in figure 2. Despite different machining procedures for the unexposed test specimens, YS and UTS values were found to be very close to each other, with tensile elongations between 1.5 and 2%. The deformation mechanisms which were investigated by TEM include a twinning propagation stage through the entire

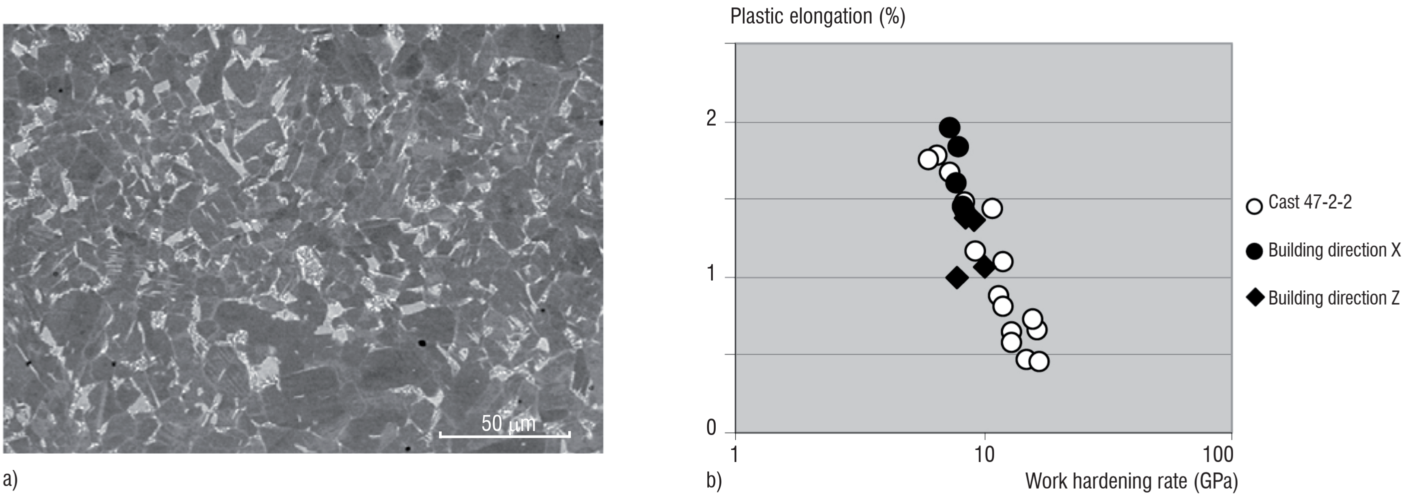
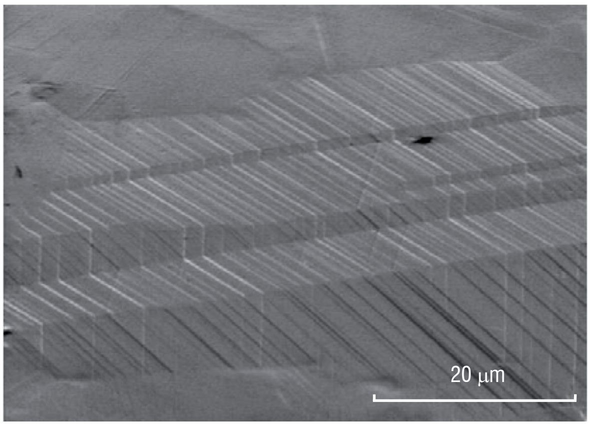


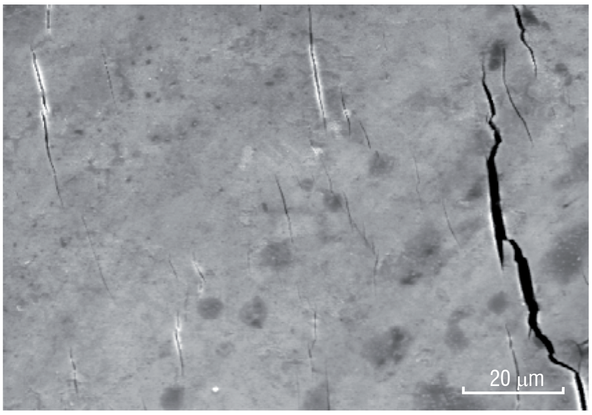
Figure 3 - DMD laser formed 47-2-2 alloy: (a) SEM micrograph of the duplex microstructure, (b) Work hardening rate dependence of tensile ductility for cast and both building directions.

gage length of the specimen, followed by the motion of ordinary dislocations and a build-up of dislocation tangles. Electro-polished gage length surfaces revealed deformation-induced instabilities which can be ascribed to mechanical twinning, as emphasized in Figure 4a. The topographical features which result from cross twinning at the surface do not appear to induce any micro-cracks which might lead to the premature failure of the test specimen.

Blanks and machined test specimens were exposed at 700°C for 400 hours in ambient air, followed by air cooling. When machining the blanks afterwards, the room temperature tensile properties did not seem to differ much from the as-received condition. On the other hand, the exposed test specimens exhibited a pronounced reduction in tensile elongation irrespective of the machining procedure. In our near-γ microstructure, the difference in tensile ductility between surface-removed and surface-retained specimens can definitely be ascribed to a surface-related embrittlement. SEM examinations confirmed this statement since the four specimens actually failed from the surface. The exposure time at 700°C was long enough to enhance the formation of a fine alumina scale with an Al-depletion layer, the composition of which is close to Ti_3Al, both having lower deformation capability than the TiAl subscale.



a)



b)

Figure 4 - SEM micrographs of the electro-polished gage length surface after testing for the near-γ microstructure: (a) unexposed test specimen, (b) test specimen exposed 2 hours at 700°C (after reference 52).

Moreover, a short exposure at 700°C for 2 hours already had a detrimental effect on ductility with strain values between 0.2 and 0.9%, with a fracture originating at the surface. However, no oxide layer was detected at the surface. It was interesting to detect some sub-surface cracks which could be indicative of a residual stress gradient from the surface towards the interior of the sample generated by air cooling (figure 4b). Moreover, mechanical twinning was not evidenced at the surface, suggesting that a twinning arrest mechanism occurs in the upper layer. It can be concluded that deformation is not accommodated at the surface, thus leading to the build-up of stress concentrations in the sub-scale. Eventually, cracks were found to be generated either from this sub-scale or from the surface. Surface machining was undertaken after short term-exposure to confirm the surface-related embrittlement. When the surface was removed dovn to 10 μm by mechanical polishing, room temperature tensile elongations were recovered.

Oxidation, corrosion, protection of TiAl

For high temperature applications, such as turbine blades, the oxidation resistance of binary γ-TiAl and also low-alloyed γ-TiAl-based alloys above 700°C still needs to be improved. Indeed at high temperature in air, layers of mixed oxides grow by competitive oxidation of the Ti and Al alloying elements, which prevents the formation of a continuous and dense α-alumina layer that would provide an effective oxidation barrier [53]. On the contrary, γ-TiAl alloys form a continuous alumina scale in pure oxygen up to 1000°C [54].

An XPS and AES investigation of the early stages of oxidation of γ-TiAl (111) surfaces at 650 °C under low O_2 pressure has been carried out at Onera [55,56]. The results show a mechanism of formation of the oxide layers exhibiting three stages [55]. Stage I is a pre-oxidation stage characterized by the adsorption and absorption of oxygen species. When the sub-surface is saturated with dissolved oxygen, the selective oxidation of the alloy leads to the nucleation and growth of ultra-thin ($\sim$1.2 nm on γ-TiAl) alumina layers characterizing Stage II. The growth of the alumina layers is limited by the transport of Al in the alloy. An Al-depleted metallic phase is formed underneath the oxide. When a critical concentration is reached (Ti_{82}-Al_{18} on γ-TiAl), titanium oxidation occurs characterizing Stage III. Ti(III) and Ti(IV) oxide particles are formed at the surface of the still growing alumina layer, which indicates the transfer, possibly promoted by defects, of titanium cations through alumina layer. The direct atomic-scale observations of the interface between the ultrathin protective alumina grown on a γ-TiAl(111) enabled us to observe, for the first time, nanocavities resulting from the self-assembling of atomic vacancies injected at the interface by the growth mechanism of the protective oxide [56].

The poor oxidation behavior in air, as compared to pure oxygen, is commonly referred as the “nitrogen effect”. Dettenwanger [51] and Lang [57] proposed that the inability of binary γ-TiAl alloys to develop a continuous alumina scale is related to the formation of TiN during the initial stages of oxidation. The formation of these titanium nitrides interrupts the alumina formed at the metal/scale interface and hinders the formation of a continuous and protective alumina layer. As oxidation proceeds, the TiN is subsequently oxidized to form TiO_2. The process results in the formation of an intermixed Al_2O_3/TiO_2 scale rather than a continuous scale of alumina.

Efforts to improve the oxidation resistance of γ-TiAl alloys have concentrated on different approaches. The first one was based on alloying additions that favored the formation of a highly protective alumina surface layer. Ternary or higher order alloying additions can reduce the rate of oxidation of γ-alloys. In particular, additions of tungsten, tantalum, zirconium, molybdenum, chromium, manganese, silicon, yttrium, rhenium and/or niobium improve the oxidation resistance by decreasing the growth rate of the intermixed Al_2O_3/TiO_2 [58]. Proposed explanations include the decrease of the oxygen vacancies in TiO_2 by doping (valence control rule) [54], an increase of Al/Ti activity to favor Al_2O_3 layer formation [54], the formation of a diffusion layer [58] and the suppression of internal oxidation by reducing oxygen solubility [59]. Niobium effects at the onset of oxidation of α_2-$Ti_{3-x}AlNb_x$ alloys were studied at Onera and Chimie Paris Tech by XPS after exposure to pure oxygen and oxygen/nitrogen mixture at 650°C ($P=1.0.10^{-7}$ mbar). Niobium contents were observed to be linked to a poisoning of the entry of $N_{adsorbed}$ and a decrease of the nitrogen mobility in the alloys, both being supposed to be responsible for the improvement of the oxidation resistance of these niobium doped alloys [60]. Although further experimental confirmation is needed, these data suggest that niobium addition may reduce the "nitrogen effect" that exists during the γ-TiAl oxidation.

Microalloying with small amounts of halogens can improve the oxidation resistance up to 1000°C [61] which may avoid the potential negative effects on mechanical properties by bulk addition of ternary or quaternary elements. Halogen can be applied in many ways: treatment with diluted halogen liquid or gas, ion implantation. This improvement of the oxidation resistance is based on the selective transport of aluminum via the gas phase from the substrate metal to the oxide scale through pores and micro-cracks by gaseous halogen gas. This leads to the formation of a continuous scale of growing Al_2O_3. But this positive halogen effect only works in a certain halogen concentration window. A lower value of halogen gas pressure is needed to ensure that the beneficial halogen effect is obtained via the AlCl gas formation, and an upper value must not be exceeded in order to avoid the titanium chloride formation which prevents the select formation of an alumina layer [62]. These limiting values depend on the nature of the halogen.

Other solutions for improving the oxidation/corrosion resistance consist of using surface-modification techniques. Overlay coatings as MCrAlY, CrAlYN or TiAlCr [63] have been studied although with unsatisfactory results due to thermal mismatch between coating and substrate which often resulted in spallation during cyclic oxidation.

Numerous studies in this field have been conducted with pack-cementation processes – such as siliconizing or aluminizing – to improve oxidation resistance [64-66]. But only a small number of studies concern the corrosion issues [67-69] and the influence of oxidation/corrosion mechanisms on the mechanical properties [41,70,71].

Exposures of TiAl alloys to corrosive atmosphere at temperatures higher than 700-750°C reduced the high temperature tensile strength [70,72]. The corrosion mechanisms of γ-TiAl are complex. It is believed [73] that the sulfur released from the sulfate reacts with the alumina layer formed on the alloy surface at the beginning in an O_2-containing atmosphere according to the following reactions called basic fluxing:

$$SO_4^{2-} \text{ (from } Na_2SO_4) \rightarrow 1/2\, S_2 + 3/2\, O_2 + O^{2-} \quad (2)$$

The O^{2-} ions produced in the condensed salt react with the oxide leading to the formation of a porous and non protective alumina layer.

$$Al_2O_3 + O^{2-} \rightarrow 2\,(AlO_2)^- \quad (3)$$

$$2\,(AlO_2)^- \rightarrow Al_2O_3 \text{ (porous layer)} + O^{2-} \quad (4)$$

Chromium inhibits the basic fluxing by decreasing the O^{2-} ions concentration in the salt.

$$Cr_2O_3 + 3/2\, O_2 + 2O^{2-} \rightarrow 2CrO_4^{2-} \quad (5)$$

In the opposite sense, the presence of an excess of niobium may increase the corrosion rate. In the presence of oxygen, niobium forms an acid oxide Nb_2O_5 that increases local acidity and then induces the acidic dissolution of oxides (particularly chromia) as follows [73]:

$$Al_2O_3 \rightarrow 2\,Al^{3+} + 3\,O^{2-} \quad (6)$$

$$Cr_2O_3 \rightarrow 2Cr^{3+} + 3\,O^{2-} \quad (7)$$

The presence of niobium is detrimental during the corrosion process while chromium is beneficial. For alloys containing both chromium and niobium, effects of these two elements cancel each other and there is no internal corrosion while in the case of alloys only containing niobium generalized internal corrosion occurs [70].

Adding NaCl to the sulfate increases the corrosion process. According to [68] the reaction of sodium chloride with titanium and aluminum from the alloy, or their oxides from the scale leads to the formation of $TiCl_2$, $AlCl_3$, ($TiCl_2$ formation being favored up to 750°C) and Na_2TiO_3.The titanium and aluminum chlorides oxidize in mixed layer of titanium oxide and alumina by releasing HCl and Cl_2 gases. These gases go through pores and channels in the oxide scales down to the metal-oxide interface and lead to the formation of new halides $TiCl_2$ and $AlCl_3$ by releasing H_2 gas which attacks preferentially the α_2-phases present at the grain boundaries leading to an intergranular corrosion. This mechanism implies a self-propagating corrosion process that explains why the corrosion phenomenon is more extensive when the NaCl salt content increases [70] (figure 5).

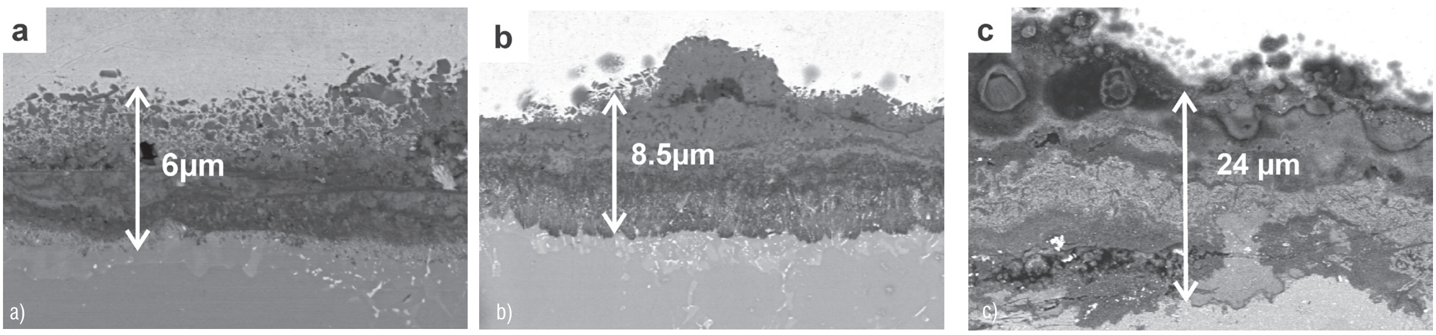


Figure 5 - SEM cross section micrograph of the layers formed at 750°C on corroded Ti46.5Al4 (Cr, Nb, Ta, B) after (a) 1000 1-hour cycles with 97.3 wt% Na_2SO_4 and 2.7 wt% NaCl (b) 1000 1-hour cycles with 75 wt% Na_2SO_4 and 25 wt% NaCl (c) 550 1-hour cycles with pure NaCl, (fig 5b and c after reference 70).

Onera developed coatings to protect γ-TiAl alloys against corrosion [64,72,74]. A typical pack cementation treatment was used to improve the corrosion resistance of the alloy G4 with the composition Ti-47Al-1Re-1W-0.2Si (at%) alloy. Cyclic corrosion tests were performed at 800°C in air up to 800 cycles with a mixture composed of 97.3 wt% of Na_2SO_4 and 2.7 wt% of NaCl. It was shown that the cyclic corrosion resistance of the coated TiAl was improved by aluminizing. The coated specimen firstly exhibited the lowest mass variation but finally cracks appeared during the cyclic corrosion, which were filled with oxide that led to spallation. Nevertheless, at the end of the test, the total corroded bulk area is less developed for the coated specimen than for the uncoated one. No particular creep degradation was observed in terms of mechanical behavior of the different test specimens, neither from the pack cementation treatment nor from the corrosion. It can then be concluded that the alloy G4 is suitable, even without coating, for turbine applications in corroded atmospheres at least up to 800°C.

An Au-based specific coating designed to prevent pure NaCl corrosion of a Ti-48Al-2Cr-2Nb alloy has also been investigated at Onera [72,74]. A two $TiAlAu_2$ and TiAlAu layers coating, obtained after vacuum heat treatment, was effective in improving NaCl salt corrosion resistance of the coated specimens at 600°C. This good resistance is attributable to the formation of an Al_2O_3 scale on the surface of the coated specimen. During oxidation, or NaCl salt corrosion, the upper $TiAlAu_2$ layer of the coating transformed in an Al_2O_3 layer on a $TiAu_2$ layer. The slightly lower creep properties exhibited by the coated specimens are presumably linked to new phases that segregate at grain boundaries during the vacuum heat treatment. The degradation of creep properties after coating and corrosion is believed to be brought about either by the formation of the brittle $TiAu_2$ phase or by corrosion or oxygen diffusion through the upper scale.

The main factors that can cause the degradation of mechanical properties of the coated γ-TiAl alloys are brittleness of the coating layers and differences in the coefficient of thermal expansion between the coating and the substrate. Onera is involved in the optimization of high corrosion resistance through a “coating by design” approach. Based on microstructural and mechanical characterizations of the different coating layers, and on diffusion and mechanical models, the aim of this work in progress is to optimize the coating process in order to improve the corrosion resistance of the coated alloy whilst minimizing the mechanical property degradation.

Conclusions

The status of Onera’s work on alloy development, microstructural evolution through heat treatments, mechanical properties and different manufacturing technologies for γ-TiAl-based alloys has been reviewed. Assessment of improved mechanical properties with respect to conventional near-γ alloys was demonstrated with alloy G4. In contrast to the commonly practiced sub-transus heat treatment applied to conventional gamma aluminides to achieve nearly lamellar microstructure, a modified heat treatment condition leading to a duplex microstructure was found to considerably increase the creep resistance and the fatigue behavior of this alloy. Centrifugal casting of γ-TiAl-based alloys appears to be sufficiently mature to offer the possibility of manufacturing complex shaped components. On the other hand, a better repeatability of mechanical properties was successfully achieved by using other processing approaches such as pre-alloyed powder metallurgy which is more tolerant to the alloy chemistry and to the microstructure. The investigation of static and cyclic tensile behaviors in gas atomized powder compacts indicate that three parameters (lamellar colonies, lamellar spacing and γ grain size) are the most relevant microstructural variables that directly influence tensile and fatigue properties. A model of the mechanism of the formation of vein-like structure based on how they are influenced by three microstructural parameters has also been developed. For the different microstructures involved, a correlation between the ability to develop a vein-like structure and the cyclic strain hardening rate has been established. The more prone the microstructure is to develop a vein-like structure, the higher the cyclic strain hardening rate. In another respect, attractive mechanical properties can be achieved by applying alternative Spark Plasma Sintering and laser forming powder technologies. In particular, the feasibility of applying laser forming to the manufacture of γ-TiAl parts has been evaluated on the basis of good geometrical quality, satisfactory metallurgical integrity and the possibility of achieving an optimized microstructure. Finally, tensile ductility degradation after long term exposure is directly related to the brittleness of the surface layers (oxide scales – Al-depletion layer – Nb-rich precipitates). On the other hand, after short term exposure, embrittlement comes from the interactions between several factors: an oxygen-enriched surface, a mechanical twinning propagation which is hindered towards the surface as well as a residual stress gradient generated by air cooling. In terms of environmental durability the titanium aluminides look promising as there are solutions for improving their resistance. In particular, tailored coatings were designed to protect them against oxidation and salt corrosion while retaining good mechanical properties ■

Acknowledgements

The authors are grateful to O. BERTEAUX, P. JOSSO, G. HENAFF, A. COURET and C. COLIN for helpful discussion. Thanks are addressed to J.L. RAVIART, A. BACHELIER-LOCQ, F. POPOFF for their technical contribution. The authors are also indebted to J.L. LUNEL, D. REGEN, A. RAFRAY and A. MOREL for material preparation and testing.

References

[1] T. TETSUI - *Development of a New TiAl Turbocharger for High Temperature Use*. Third International Workshop on γ-TiAl Technologies, Bamberg, Germany, 29-31 May 2006 (unpublished).
[2] R.E. SCHAFRIK - *A Perspective on Intermetallic Commercialization for Aero-Turbine Applications*. Structural Intermetallics 2001, edited by K.J. Hemker et al, TMS, pp. 13-17, 2001.
[3] M. YAMAGUCHI, and H. INUI - *TiAl Compounds for Structural Applications*. Structural Intermetallics 1993, edited by R. Darolia et al, The Minerals, Metals & Materials Society, pp. 127-142 ,1993.

[4] N. BIERY, M. DE GRAEF, J. BEUTH, R. RABAN, A. ELLIOTT, T.M. POLLOCK and C. AUSTIN - *Use of Weibull Statistics to Quantify Property Variability in TiAl Alloys.* Metall. Mater. Trans. A, vol. 33A, pp. 3127-3136, 2002.
[5] T. TSUJIMOTO and K. HASHIMOTO - *Structures and Properties of TiAl-Base Alloys Containing Mn.* High-Temperature Ordered Intermetallic Alloys III, edited by C.T. Liu et al, MRS, Pittsburgh, vol. 133, pp.391-396, 1989.
[6] S-C. HUANG - *Titanium Aluminum Alloys Modified by Chromium and Niobium and Method of Preparation*. US. Patent 4,879,092, Nov. 7, 1989.
[7] G.L. CHEN, Z.C. LIU, J.P. LIN and W.J. ZHANG - *Strengthening Mechanism in High Nb Containing TiAl Base Alloys.* Structural Intermetallics 2001, edited by K.J. Hemker et al, Warrendale PA: TMS, pp.475-482, 2001.
[8] V. IMAYEV, R. IMAYEV and A. KUZNETSOV - *Thermomechanical Processing and Tensile Mechanical Properties of β-Solidifying γ-TiAl+α_2-Ti_3Al Alloys*. Gamma Titanium Aluminides 2003, edited by Y-W. Kim et al, Warrendale, PA: TMS, pp.311-318, 2003.
[9] F. APPEL, J.D.H. PAUL, M. OEHRING and C. BUQUE - *Recent Developments of TiAl Alloys Towards Improved High-Temperature Capability*. Gamma Titanium Aluminides 2003, edited by Y-W. Kim et al, Warrendale, PA: TMS, pp.139-152, 2003.
[10] W.E. VOICE, M. HENDERSON, E.F.J. SHELTON and X. WU - *Gamma Titanium Aluminide, TNB.* Intermetallics, vol. 13, pp. 959-964, 2005.
[11] M.A. MUNOZ-MORRIS, I. GIL and D.G. MORRIS - *Microstructural Stability of γ-Based TiAl Intermetallics Containing β Phase.* Intermetallics, vol.13, pp. 929-936, 2005.
[12] X. WU – *Review of alloy and process development of TiAl alloys* - Intermetallics, vol. 14, pp.1114-1124, 2006.
[13] H.F. CHLADIL, H. CLEMENS, H. LEITNER, A. BARTELS, R. GERLING, F.-P. SCHIMANSKY and S. KREMMER – *Phase Transformations in High Niobium and Carbon Containing γ-TiAl Based Alloys*. Intermetallics, vol. 14, 1194-1198, 2006.
[14] J. LAPIN, Z. GABALCOVÁ, T. PELACHOVÁ andO. BAJANA – *Microstructure and Mechanical Properties of a Cast Intermetallic Ti-46Al-8Ta Alloy*. Materials Science Forum Vols. 638-642, pp. 1368-1373, 2010.
[15] S. NAKA, M. THOMAS, C. SANCHEZ and T. KHAN - *Development of Third Generation Castable Gamma Titanium Aluminides: Role of Solidification Paths.* Proc. of 2nd Symposium on Structural Intermetallics, edited by M.V. Nathal et al, Seven Springs, PA (USA), September 21-26, pp. 313-322, 1997.
[16] M. GRANGE, J.L. RAVIART and M. THOMAS - *Influence of Microstructure on Tensile and Creep Properties of a New Castable TiAl-based Alloy*. Met. Trans. vol. 35A, pp. 2087-2102, 2004.
[17] V. LUPINC, M. MARCHIONNI, G. ONOFRIO, M. NAZMY and M. STAUBLI - *Microstructural Effects on Creep, Low Cycle Fatigue and Crack Propagation Behavior of Ti-47Al-2W-0.5Si*. Gamma Titanium Aluminides 1999, edited by Y-W. Kim et al, The Minerals, Metals & Materials Society, pp. 349-356, 1999.
[18] A. PONCHEL - *Champs de déformation locaux autour d'éléments d'addition en solution solide dans les alliages ordonnés TiAl+X (X=Cr, Mn, Ni, Zr, Nb). Déterminations expérimentales et théoriques : Application à l'étude de l'interaction soluté-dislocation*. Thèse de doctorat, Université Pierre et Marie Curie Paris VI, 30 octobre 2001.
[19] Y.L. HAO, D.S. XU, Y.Y. CUI, R. YANG and D. LI – *The Site Occupancies of Alloying Elements in TiAl and Ti_3Al Alloys*. Acta mater. Vol. 47, N° 4, pp. 1129-1139, 1999.
[20] S. NISHIKIORI, S. TAKAHASHI, S. SATOU, T. TANAKA and T. MATSUO – *Microstructure and Creep Strength of Fully-Lamellar Ti_3Al Alloys Containing Beta-Phase.* Materials Science and Engineering, vol. A329–331, pp. 802–809, 2002.
[21] M. KRISHNAN, B. NATARAJAN, V.K. VASUDEVAN and D.M. DIMIDUK – *Microstructure Evolution in Gamma Titanium Aluminides Containing Beta-Phase Stabilizers and Boron Addition.* Proc. of 2nd Symposium on Structural Intermetallics, edited by M.V. Nathal et al, Seven Springs, PA (USA), September 21-26, pp. 235-244, 1997.
[22] J. LAPIN, T. PELACHOVA - *Microstructural Stability of a Cast Ti-45.2Al-2W-0.6Si-0.7B Alloy at Temperatures 973-1073K.* Intermetallics, vol.14, pp.1175-1180, 2006.
[23] M. PANINSKI – *Development of a Casting Technology for Complex TiAl Components.* Third International Workshop on γ-TiAl Technologies, Bamberg, Germany, 29-31 May 2006 (unpublished).
[24] Y. CHEN,Y. CHEN, F. KONG and S. XIAO – *Fabrication and Processing of Gamma Titanium Aluminides -a Review.* Materials Science Forum Vols. 638-642, pp. 1281-1287, 2010.
[25] M. THOMAS - *Robustness Versus Performance Assessment for Different Gamma-TiAl Processing Routes*. MRS Boston 2010, to be published.
[26] M. THOMAS, J-L. RAVIART and F. POPOFF - *Composition and Microstructural Effects upon Creep Strength of Gas Atomized TiAl Alloy Powder Compacts*. Thermec'09, Berlin, 2009 (unpublished).
[27] O. BERTEAUX, F. POPOFF and M. THOMAS - *An Experimental Assessment of the Effects of Heat Treatment on the Microstructure of Ti-47Al-2Cr-2Nb Powder Compacts*. Met. Trans. A, vol. 39A, n°10, pp. 2281-2296, 2008.
[28] V. SEETHARAMAN and S.L. SEMIATIN - *Analysis of Grain Growth in a Two-Phase Gamma Titanium Aluminide Alloy.* Metall. Mater. Trans. A, vol. 28A, pp. 947-954, 1997.
[29] Y. BHAMBRI, V.K. SIKKA, W.D. PORTER, E.A. LORIA and T. CARNEIRO - *Effect of Composition and Cooling Rate on the Transformation of α to γ Phase in TiAl Alloys.* Mater. Sci. Eng. A, vol.424, Issues 1-2, pp. 361-365, 2006.
[30] G.X. GUO FU'AN - *Influence de la microstructure sur des propriétés mécaniques et des contraintes internes d'un alliage intermétallique biphasé à base de TiAl.* Thèse de doctorat de l'ENSAM Paris, 20 juin 2001.
[31] G.X. CAO, L.F. FU, J.G. LIN, Y.G. ZHANG and C.Q. CHEN - *The Relationships of Microstructure and Properties of a Fully Lamellar TiAl Alloy.* Intermetallics, vol.8, pp. 647-653, 2000.
[32] C.E. WEN, K. YASUE, J.G. LIN, Y.G. ZHANG and C.Q. CHEN - *The Effect of Lamellar Spacing on the Creep Behavior of a Fully Lamellar TiAl Alloy.* Intermetallics, vol.8, pp. 525-529, 2000.
[33] G.W. QIN, G.D. W. SMITH, B.J. INKSON and R. DUNIN-BORKOWSKI - *Distribution Behaviour of Alloying Elements in $\alpha_2(\alpha)/\gamma$ Lamellae of TiAl-Based Alloy*. Intermetallics, vol.8, pp. 945-952, 2000.
[34] M. CHARPENTIER, D. DALOZ, A. HAZOTTE and E. AEBY-GAUTIER - *Toward a Better Understanding of Chemical and Microstructure Heterogeneities Inherited from Solidification and Solid State Phase Transformations in the Ti-48Al-2Cr-2Nb Alloy*. Matériaux & Techniques, N°1-2, pp. 39-50, 2004.
[35] T. NOVOSELOVA, S. MALINOV and W. SHA - *Experimental Study of the Effects of Heat Treatment on Microstructure and Grain Size of a Gamma TiAl Alloy*. Intermetallics, vol.11, pp. 491-499, 2003.
[36] R. YANG - *A Theory of the Formation and Growth of Primary Gamma/Alpha2 Lamellae in Fully-Lamellar Gamma-TiAl Based Alloys.* International Titanium Aluminide Workshop, Birmingham, UK , 5-7 July 2004 (unpublished).
[37] O. BERTEAUX, F. POPOFF, M. JOUIAD, G. HENAFF and M. THOMAS - *Microstructure Dependence of the Strain Hardening Rate in a PM Ti-48Al-2Cr-2Nb Alloy*. Third International Workshop on γ-TiAl Technologies, Bamberg, Germany, 29-31 May 2006.
[38] A. COURET, G. MOLENAT, J. GALY and M. THOMAS - *Microstructures and Mechanical Properties of TiAl Alloys Consolidated by Spark Plasma Sintering*. Intermetallics, vol. 16 n° 9, pp. 1134-1141, 2008.

[39] T. VILARO, V. KOTTMANN-REXERODT, M. THOMAS, P. BERTRAND, L. THIVILLON, C. COLIN, S. ABED, V. JI, P. AUBRY, T. MALOT and P. PEYRE - *Direct Fabrication of a Ti-47Al-2Cr-2Nb Alloy by Selective Laser Melting and Direct Metal Deposition Processes*. Adv. Mater. Res., 89-91, p. 586, 2010.
[40] S.L. DRAPER, B.A. LERCH, I.E. LOCCI, M. SHAZLY and V. PRAKASH - *Effect of Exposure on the Mechanical Properties of Gamma MET PX*. Intermetallics, vol. 13, pp. 1014-1019, 2005.
[41] R. PATHER, W.A. MITTEN, P. HOLDWAY, H.S. UBHI, A. WISBEY and J.W. BROOKS - *The Effect of High Temperature Exposure on the Tensile Properties of γ TiAl Alloys.* Intermetallics, vol. 11, pp.1015-1027, 2003.
[42] Z.W. HUANG, W. VOYCE and W.P. BOWEN - *Thermal Stability of a Fine-Grained Fully Lamellar TiAl-Based Alloy*. Structural Intermetallics 2001, edited by K.J. Hemker et al, Warrendale, PA: TMS, pp. 551-560, 2001.
[43] M. BESCHLIESSER, H. CLEMENS, H. KESTLER and F. JEGLITSCH - *Phase Stability of a γ-TiAl Based Alloy Upon Annealing: Comparison Between Experiment and Thermodynamic Calculations*. Scripta Mater, vol. 49, N°4, pp. 279-284, 2003.
[44] Y-W. KIM - *Recent Advances in Gamma Titanium Aluminide Alloys*. High Temperature Ordered Intermetallic Alloys IV, , edited by J.O. Stiegler et al, MRS, pp. 777-794, 1991.
[45] T. KAWABATA, M. TADANO and O. IZUMI - *Effect of Purity and Second Phase on Ductility of TiAl.* Scripta Met, vol.22, N°11 pp.1725-1730, 1988.
[46] C.T. LIU, Y-W. KIM - *Room-Temperature Environmental Embrittlement in a TiAl Alloy*. Scripta Met, vol. 27, n°5, pp. 599-603, 1992.
[47] A. ZELLER, F. DETTENWANGER and M. SCHÜTZE - *Influence of Water Vapour on the Oxidation Behaviour of Titanium Aluminides.* Intermetallics, vol. 10 pp. 59-72, 2002.
[48] S.L. DRAPER, G. DAS, I. LOCCI, J.D. WHITTENBERGER, B.A. LERCH and H. KESTLER - *Microstructure and Mechanical Properties of Extruded Gamma MET PX*. Gamma Titanium Aluminides 2003, edited by Y-W. Kim et al, Warrendale, PA: TMS, pp. 207-212, 2003.
[49] V. MAURICE, G. DESPERT, S. ZANNA, P. JOSSO, M.-P. BACOS and P. MARCUS - *The Growth of Protective Ultra-Thin Alumina Layers on γ-TiAl(111)Intermetallic Single-Crystal Surfaces.* Surface Science, vol. 596, pp. 61-73, 2005.
[50] G. SCHUMACHER, F. DETTENWANGER, M. SCHÜTZE , A. IBERL and D. REIL - *XRD Investigations of the Phosphorus Effect on the Oxidation of TiAl Alloys by High-Resolution Methods*. Oxidation of Metals, vol. 54 n° 3-4, pp.317-37, 2000.
[51] F. DETTENWANGER , E. SCHUMANN, M. RÜHLE , J. RAKOWSKI and G.H. MEIER - *Microstructural Study of Oxidized γ-TiAl*. Oxidation of Metals vol. 50 n° 3-4, pp. 269-305, 1998.
[52] M. THOMAS, O. BERTEAUX, F. POPOFF, M.-P. BACOS, A. MOREL, B. PASSILLY and V. JI - *Effects of exposure at 700°C on RT Tensile Properties in a PM γ-TiAl*. Intermetallics, vol. 14, pp. 1143-1150, 2006.
[53] J.M. RAKOWSKI, F.S. PETTIT, G.H. MEIER – *The Effect of Nitrogen on the Oxidation of γ-TiAl.* Scripta Metall. et Mater. Vol. 33, n°6, pp. 997-1003, 1995.
[54] N.S. CHOUDHURY, H.C GRAHAM, J.W.HINZE - *Properties of high temperature alloys*. Edited by Z.A.Fouroulis and F.S.Pettit (Pennington,N): the Electrochemical Society, pp. 668-680, 1976.
[55] V. MAURICE, G. DESPERT, S. ZANNA, P. JOSSO, M.-P. BACOS and P. MARCUS - *XPS Study of the Initial Stages of Oxidation of* α_2*-*Ti_3Al *and γ-TiAl Intermetallic Alloys.* Acta Materialia, vol. 55, pp. 3315-3325, 2007.
[56] V. MAURICE, G. DESPERT, S. ZANNA, M.-P. BACOS and P. MARCUS - *Self-Assembling of Atomic Vacancies at an Oxide/Intermetallic Alloy Interface.* Nature Materials, vol. 3, pp. 687-691, 2004.
[57] C. LANG, M. SCHÜTZE - *TEM Investigations of the Early Stages of TiAl Oxidation*. Oxidation of Metals, vol. 46 n° 3-4, pp. 255-285, 1996.
[58] S. TANIGUCHI, T. SHIBAT - *Influence of Additional Elements on the Oxidation Behaviour of TiAl.* Intermetallics, vol. 4 supplement 1, pp. S85-S93, 1996.
[59] Y. SHIDA, H. ANADA - *Role of W, Mo, Nb and Si on Oxidation of TiAl in Air at High Temperatures*. Materials Transactions, JIM vol. 35, n° 9, pp. 623-631, 1994.
[60] V. MAURICE, A-G. NOUMET, S. ZANNA, P. JOSSO, M.-P. BACOS and P. MARCUS - *Dual Surface and Bulk Control by Nb of the Penetration of Environmental Elements in TiAl Intermetallic Alloys.* Acta Mater., vol. 56, pp. 3963-3968, 2008.
[61] A. DONCHEV, E. RICHTER, M. SCHÜTZE and R. YANKOV - *Improvement of the Oxidation Behaviour of TiAl-Alloys by Treatment With Halogens*. Intermetallics, vol. 14, n°10-11, pp. 1168-1174, 2006.
[62] A. DONCHEV, B. GLEESON and M. SCHÜTZE - *Thermodynamic Considerations of the Beneficial Effect of Halogens on the Oxidation Resistance of TiAl-Based Alloys.* Intermetallics, vol. 11 n°5, pp. 387-398, 2003.
[63] R. BRAUN, F. ROVERE, P.H. MAYROFER and C. LEYENS - *Environmental Protection of γ-TiAl Based Alloy Ti-45Al-8Nb by CrAlYN Thin Films and Thermal Barrier Coatings.* Intermetallics, vol. 18, n°4, pp. 479-486, 2010.
[64] M.-P. BACOS, M. THOMAS, J-L. RAVIART, A. MOREL, S. NAVEOS and P. JOSSO - *Influence of Surface Modification and Long Term-Exposure on Mechanical Creep Properties of γ-TiAl G4*. Materials at High Temperatures, vol. 26, n°4, pp. 339-346, 2009.
[65] V. GAUTHIER, F. DETTENWANGER, M. SCHÜTZE, V. SHEMET and W.J. QUADAKKERS - *Oxidation-Resistant Aluminide Coatings on γ-TiAl.* Oxidation of. Metals, vol. 59, n°3/4, pp. 233-255, 2003.
[66] Z.D.XIANG, S.R.ROSE and P.K. DATTA - O*xidation Resistance of Diffusion Coatings Formed by Pack-Codeposition of Al and Si on γ-TiAl.* J. Mat. Sci., vol. 39, n°6, pp. 2099-2106, 2004.
[67] Z. TANG, F. WANG, W. WU - *Hot-corrosion Behavior of TiAl-Base Intermetallics in Molten Salts*. Oxidation of Metals vol. 51, n°3-4, pp. 235-250, 1999.
[68] J.R. NICHOLLS, J. LEGETT and P. ANDREWS. - *Hot Salt Corrosion of Titanium Aluminides*. Materials and Corrosion vol. 48, pp. 56-64, 1997.
[69] Z. YAO, M. MAREK - *NaCl-Induced Hot Corrosion of a Titanium Aluminide Alloy*. Materials Science and Engineering A; vols. 192-193 part 2, pp. 994-1000, 1995.
[70] M-P. BACOS, A. MOREL, S. NAVEOS, A BACHELIER-LOCQ, P. JOSSO and M. THOMAS - *The Effect of Oxidised and Corroded Long Term Exposure on Tensile Properties of Two Gamma-TiAl Alloys*. Intermetallics, vol. 14, n° 1, pp. 102-113, 2006.
[71] X.Y. LI, S. TANIGUCHI - *Correlation of High Temperature Oxidation with Tensile Properties for Ti-48Al-2Cr-2Nb and Ti-48Al-2Cr-2Fe Alloys.* Intermetallics, vol. 13, n°7, pp.683-693, 2005.
[72] M.-P. BACOS, M. THOMAS, J.-L. RAVIART, A. MOREL, S. MERCIER and P. JOSSO - *Influence of an Oxidation Protective Coating Upon hot Corrosion and Mechanical Behaviour of Ti-48Al-2Cr-2Nb Alloy*. Intermetallics, vol. 19 , pp.1120-1129, 2011.
[73] R. MORBIOLI, P. STEINMETZ and C. DURET - *Mechanisms of Hot Corrosion of NiAl-Type Aluminide Coatings in Aeronautical Conditions.* Materials Science and Engineering, vol. 87, pp. 337-344, 1987.
[74] M.-P. BACOS, P. JOSSO - *Procédé pour protéger la surface d'un substrat en alliage intermétallique à base d'aluminiure de titane contre la corrosion.* Patent 2918672, 9 July 2007.

Acronymes

AES (Auger Electron Spectroscopy)
CAD (Computer-Aided Design)
CCT (Continuous Cooling Transformation)
CSS (Cyclic Stress-Strain)
DMD (Direct Metal Deposition)
FAR (Federal Acquisition Regulation)
FC (Furnace Cooled)
HCF (High Cycle Fatigue)
HIP (Hot Isostatic Pressing)
IC (Intermediate sand Cooled)
IWQ (Icy Water Quenching)
LCF (Low Cycle Fatigue)
PM (Powder Metallurgy)
SEM (Scanning Electron Microscopy)
SPS (Spark Plasma Sintering)
TEM (Transmission Electron Microscopy)
UTS (Ultimate Tensile Strength)
XPS (X-ray Photoelectron Spectroscopy)
YS (Yield Stress)

Authors

Marc Thomas received his Doctorate (Ph.D) from Sussex University (UK) in 1983. He received his HDR (Research Director Authorization) diploma in 2005, for his research activities on titanium aluminides over the last twenty years. He is currently in charge of the development of structured multifunctional materials at Onera and of additional research projects dealing with powder manufacturing and using innovative processes such as Spark Plasma Sintering and Laser Forming.

Marie-Pierre Bacos graduated from the «Ecole Nationale Supérieure de Chimie de Paris" Paris (1981) and received a PhD degree in Applied Chemistry from University Paris VI (1983). She joined Onera in 1983 where she has been involved in oxidation and corrosion mechanisms and in the development of innovative coatings and brazing technologies. She is the Head of the Materials and Architecture Research Unit at Onera Chatillon.