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# Increase Energy Efficiency of Cogeneration Gas Turbine by Means of New, Advanced Titanium Base Materials and Surface Coatings Development- State-of-Art

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## Abstract

*The present paper presents considerations on a „new field” unexplored with respect to our country and Europe researches, that of advanced titanium aluminide intermetallic alloys. We focused on two titanium aluminides alloys, base for our studies, underling chemical composition, heat treatments and microstructure issues, as well as some mechanical behaviour data. Further, we point the approaches of the Romanian research team, by applying a viable and achievable flow: optimal chemical composition researches, casting process parameters, ingot elaboration, forging process, mechanical and chemical surface treatments, new coatings systems, in order to achieve new advanced titanium aluminide alloys configurations for gas turbine applications.*

*Offering the possibility of performing hot parts by using this light alloys will modify both designers and constructors thinking and will influence clearly the energetic efficiency of gas turbines.*

**Key words:** *titanium aluminides, turbine, turbo- compressor*

## Introduction

If next-generation gas turbine engines are to achieve substantially improved thrust-to-weight ratios, they will have to burn hotter than today's turbines. To withstand these higher fuel-combustion temperatures, however, higher, performance heat-resistant materials will be needed. Likewise, if future aircraft are to routinely fly at hypersonic velocities, their airframes will need the same materials to withstand the heat generated during flight. Compared to conventional aerospace alloys, titanium aluminides-ordered titanium aluminide intermetallic alloys provide an attractive combination of good elevated-temperature strength and creep properties, improved environmental resistance, and relatively low density (about half that of superalloys, more exactly 3.9-4.2 g/cm<sup>3</sup>, depending on their composition). In particular, the lower density

contributes to significant engine weight reduction and reduced stresses on rotating components such as low-pressure turbine blades. For these reasons, titanium aluminides are prime candidates to replace conventional titanium alloys (which lose their strength at about 1000 °F) and lower-temperature nickel-base superalloys. In addition, metal-matrix composites using reinforced titanium aluminide alloys appear to have the potential to surpass the monolithic titanium aluminide alloys in several important areas. "Of all the titanium materials, titanium aluminides have the highest temperature capabilities," said Terence Ronald, head of materials technology for the National Aero-Space Plane (NASP) Joint Program Office at Wright-Patterson Air Force Base, Ohio. Though access to the latest developments in titanium aluminide research is protected by Defence Department export-control laws and industrial secrecy, it is becoming increasingly apparent that significant advances are beginning to occur. For example, a new high-strength titanium-aluminum-niobium alloy has been manufactured that has reasonable ductility and fracture toughness. In addition, other low-ductility titanium aluminides have been successfully cold-rolled into sheets and foils, indicating that it may be possible to produce the material at a reasonable cost. Nevertheless, materials researchers stress that these alloys are still in the exploratory stages. In general, aerospace engineers are interested in transition metal-aluminide alloys such as titanium aluminide because they can maintain good mechanical properties at higher temperatures.

Besides titanium aluminides, metallurgists are investigating nickel aluminides, which have higher melting points and oxidation resistance coupled with low density but are more brittle at lower temperatures. Also under study are iron aluminides, which are more ductile at lower temperatures than titanium aluminides but are heavier. Titanium aluminide (an intermetallic compound known by the chemical formula of TiAl (this substance will be referred to as "TiAl" hereinafter) is drawing attention as an advanced light weight and heat resisting material. This is because the high specific strength of TiAl at elevated temperature is better than those of the nickel-base heat-resisting alloys, and the heat resistance, oxidation resistance and hydrogen embrittlement resistance of TiAl are better than those of the titanium alloys. Since TiAl alloys possess these and other admirable properties, there are demands to make aircraft jet engine parts such as blades and vanes out of this material. On the other hand, however, TiAl has low ductility at ambient temperature and a strong dependency on the strain rate even at high temperatures (even at 700° C or more) where sufficient toughness develops. This makes the machining or processing difficult. Therefore, TiAl cannot be used as a practical material up to now. Solving these difficulties contributes a lot to next generation aircraft Jet engines and the like and therefore research is being conducted from crystal structural and physical metallurgical viewpoints. As a result of such research, methods of improving the low ductility by strengthening the grain boundaries and causing the plastic deformation by deformation twinning have been proposed in, for example, Japanese Patent Application Nos. 61-41740, 1-255632, 1-287243 and 1-298127. In spite of these efforts, however, misrun and cracks occur during the casting operation when TiAl is used to produce thin and complicated castings such as shrouded turbine blades. The solution proposed in the present work by the romanian research team, is based on the achievement and use of special titanium based alloys, of absolute novelty for our country: "titanium aluminide intermetallic alloys", for turbine blades manufacturing in combination with the use of surface coating based on the latest techniques specially adapted, and using new materials designed for this type of application. Temperature rise, we believe the normal operating temperature will be around for 1000°C, correlated with the drastic reduction of weight (in aprox.50%) will experience a significant increase turbine performance and so of its energy efficiency.

## **Achievement of high temperature titanium heat resistant alloys turbine blades - Romanian research team goals**

Currently, the turbine blades are made of nickel and cobalt based superalloys having good mechanical properties at high temperatures *but high specific weight*. At very high speed (an indicator of turbine efficiency, performance), because the specific weight, in the blade material one can notice the development of high forces that can not be bear. Are international level efforts are made to achieve new titanium alloys (material with specific gravity of approximately half that of Ni and Co based alloys), which can be used at high temperatures and high speeds, thereby increasing the turbine performance. Attention of the most recent research studies is focused on  $\gamma$ -alloys and orthorhombic alloys. The development but especially the integration of these types of advanced alloys for vital parts of the gas turbines is very recent (since 2000). The only country which mastered the technology of making such materials is the U.S.A., testing at this time various types of titanium aluminide alloys. Prestigious companies, like General Electric, U.S.A. tackled with huge interest these alloys for turbine blades manufacturing (TiAl LPT, made by precision casting Precision Corp. CastParts.), and their integration into GENx engine (of aircrafts Boeing 787, Boeing 747-8) being the first use at large scale of this alloys, for commercial aircraft engine. At European level, research institutes of high reputation make special efforts to build consortia able to engage in the research of this issues. Our team propose to address this problem in a viable and achievable flow in our country: fundamental research – industrial research (establishing the alloy able to meet the pre-established requirements), the elaboration of ingots/billets - forging at half finished manufacturing level – five axes mechanical machining - surface treatment, special surface coating - integration and testing of turbine discs on testing bench devices available at INCDT COMOTI – Bucharest. The elaboration–manufacturing process system for turbine blades made of high temperatures resistant "titanium aluminide intermetallic alloys" promoted by researchers is based on: achieving basic material (ingots having the desired chemical composition)- repeated remelting stages (using proper technologies) in order to achieve ingots capable of being forged - forging ingots (after special technology – which do not resemble those of the usual materials titanium) in order to obtain products capable of being mechanical manufactured for blades - turbine rotors - achievement of blades, rotors by five axis machining - application of both special mechanical and chemical processing on surface blades - special surface coating on the blades - the control and certification of blades and rotors obtained- testing the blades and rotors on testing devices.

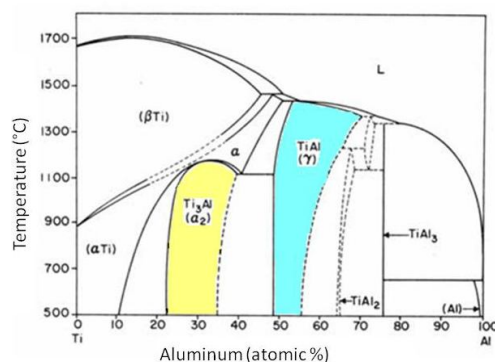
As we already mentioned before, this system is new and original, promoted for the first time (at least for Europe, we don't know exactly the American system), occidental researchers have proposed and want to achieve a system to perform the blades by casting, field where no partner able of such a performance, was found. Romanian researchers aims to address two types of alloys in the range "titanium aluminides " more exactly an alloy of the system"  $\alpha_2$  aluminide" generic named Ti - 14 Al - 21 Nb alloy and an  $\gamma$  aluminide alloy generic named Ti – 33 Al- 6 Nb - Ta 1.4 to determine the structure and chemical composition influence on the structural and mechanical behaviour at high temperatures.

Mastering these alloys require testing and certification of own theories not only for elaboration development but also for forging one, heat treatments, chemical surface treatments, coatings and even mechanical surface processing. The novelty of solutions to be proposed is undeniable, not only for our country but also for the European scientific community.

## Considerations on titanium based intermetallic alloys

### Titanium Aluminides – intermetallic compounds

Titanium aluminide alloys came from a large family of intermetallic chemical compounds, generally known for their previously reported low density ( $3.9 - 4.2 \text{ g/cm}^3$ ) and good oxidation, mechanical resistance at high temperatures [1, 2]. This intermetallic compounds are generally metallic solid solutions which exhibits different structures from their base constitutive crystals. They are formed because the power connection between different atoms is greater than that between atoms alike [3]. Gamma phases (TiAl) and alpha-2 (Ti<sub>3</sub>Al) titanium aluminide (as shown in Figure 1) were carefully studied in recent decades for their application as potential high performance materials.

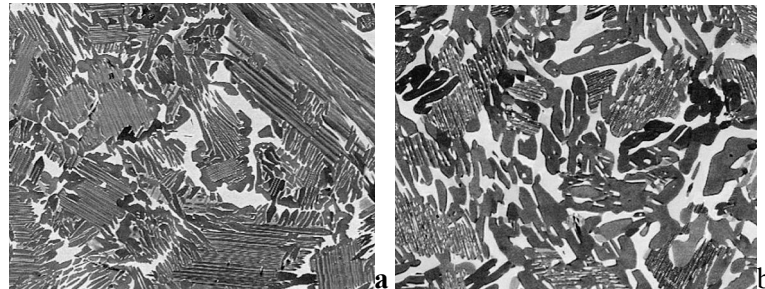


**Fig. 1.** Phase diagram of titanium aluminides

Titanium based intermetallic alloys containing  $\gamma$ -TiAl and  $\alpha_2$ -Ti<sub>3</sub>Al phases have significant potential for applications as structural materials at high temperatures. Basic obstacle to their widespread at large scale introduction is their low technological properties due to directional interatomic bonds with strong covalent component. In case of ingots/billets, especially large one, additional limiting factors are: coarse granulated structure, chemical inhomogeneity, lack of casting precise texture [6, 7, 8]. To refine the structure of alloys  $\gamma$ ,  $\alpha_2$  and improving their technological properties, usually are used expensive processing methods such as extrusion or hot pressing in forms.

Technological properties of  $\gamma + \alpha_2$  intermetallic alloys can be effectively improved by rational selection of alloy composition and a special "metallization" of interatomic bond due to the introduction of proper alloying elements. It is therefore of interest to use a new class of  $\beta$ -solidifying alloys  $\gamma + \alpha_2$  with the Ti-(43-45) Al - X (Nb, Mo, B) (%), where X reaches some atomic percent, this cast structure is characterized already, by small colonies and the absence of a pronounced texture, due to the  $\beta$ -stabilizing elements Mo and Nb, contains a certain amount of  $\beta$  (B2); phase B2 phase is ordered, based on TiAl, from the  $\beta$  phase during cooling after solidification. The presence of an additional intermetallic phase  $\beta$  (B2) at high temperatures provides a new opportunity for action on ingot structure using heat treatment, as now, the phase transformations connected with  $\beta$  phase (B2) may occur, for instance a selection of grains or changes in the structure morphology. In this paper, we continued the study of new classes of  $\beta$ -alloys solidified  $\gamma + \alpha_2$  on Ti-43Al-7 (Nb, Mo)-0.2B (%) alloy, mainly studying the influence of heat treatment on microstructure of cast material, then their effect (heat-treated alloy) on tensile mechanical tests.

Figure 2 presents a typical microstructure of Ti-43Al-7 (Nb, Mo)-0.2B (%) as cast alloy, composed mainly in lamellar colonies,  $\gamma + \alpha_2$ , with an average size of  $d = 20\text{-}40\ \mu\text{m}$ , rough coarse structure of  $\beta$  (B2) +  $\gamma$  lamellar structure, shiny layers of  $\beta$  phase (B2) saturated with Mo and N, in proportion about 11.3 %, and  $\gamma$  grain (closed) along colony boundaries.



**Fig. 2.** a) Microstructure of as cast Ti-43Al-7(Nb,Mo)-0.2B alloy; b) Microstructure of a) after heat treatment at temperature lower than the eutectic limit ( $T=1130^\circ\text{C}$ ,  $t=20\text{h}$ ) followed by furnace cooling

Generally the size of structural components in cast alloy microstructure have not exceeded 50  $\mu\text{m}$ . Heat treatment, consisting primarily of a series of repeated annealing followed by a cooling in the oven followed by an heat treatments in the oven at a temperature slightly lower than the eutectoid point ( $T = 1130^\circ\text{C}$ ) favoured the formation of  $\beta$  structure (B2) +  $\gamma$  to the detriment of  $\gamma + \alpha_2$  lamellar component, figure 2, b). Heat treatment also favoured increasing the volume phase  $\beta$  (B2) to 19.7%. The growth of  $\beta$  (B2) phase takes place first because of the  $\alpha_2 \Rightarrow \beta$  (B2) phase transformation, which explains their close chemical composition. The  $\beta$  (B2) phase development leads to destabilization of lamellar colonies ( $\gamma + \alpha_2$ ) which transform in one globular structure ( $\gamma + \beta$  (B2)).  $\alpha_2$  phase destabilisation can be explain by the supersaturating in Mo which induce a strong stabilisation of  $\beta$  phase.

After this overview of the main approaches of our research team, we will continue with a short analyse of the possibilities of using titanium aluminides for high temperature applications in turbine blades for energetic industry. Two aspects will be pointed issues regarding: chemical composition, microstructure, heat treatments aspect and the mechanical behaviour.

## **Analysis of possibilities to use high temperature titanium aluminides alloys for turbines in the energy industry**

### **Issues regarding: chemical composition, microstructure, heat treatments**

If the Ti-Al alloys system, the influence of major or minor alloying elements is not negligible. High temperature resistance, creep resistance and environmental resistance is favoured by a high content of aluminum, a moderate content of  $\beta$ -stabilizing elements, relatively low vanadium content. In the following lines we describe the influence of alloying elements in these alloy systems. Increasing Nb content leads to increased performances except the creep resistance. Niobium, which substitute titanium atoms and increase the number of slip systems can be replaced with elements: Mo, Ta, Cr to increase strength, with Mo to increase resistance; Mo to increase creep resistance and Ta and Cr for oxidation resistance [4]. Oxygen content is particularly important in terms of ductile-brittle transition temperature alloys, a reduction in oxygen content from 0.186 to 0.081 wt.% in an Ti-Al-Nb system alloy, leads to a increased of elongation at rupture (in tensile regime) from 1.1% to 4.8%. Alloying elements like Y and B (up to 0.5 wt.%) are introduces for grain size control. Si and Zr increase creep resistance, but the highest growth is achieved by increasing the aluminium content up to 25 wt. % and limitation of

$\beta$ -stabilising elements at around 12 %wt. As mentioned before the microstructure depends on all this chemical composition issues. The heat treatments and casting processing parameters are also of great importance [5]. The base alloys for the research studies are: Ti-43Al-7 (Nb, Mo)-0.2B (%), shortly described before and Ti-14Al -21Nb (wt%) which comes from intermetallic  $Ti_3Al$  where Nb was added to stabilize  $\beta$  phase, and to retard the kinetics of ordering and reduce flatness slip, all these, leading to improved ductility at room temperature. Alloy microstructure is stable and consists of  $\alpha_2$  equiaxed grains with a low content of orthorhombic phase and  $\beta$  phase at triple points and grain boundaries. The surface chemical composition variation in Ti-14Al-21Nb alloys depending on the temperature in high vacuum conditions is studied because of the effect on structural/mechanical behaviour. Sulphur segregations, hydrogen embrittlement, low room temperature ductility, fatigue crack growth (FCG) are still issues to improve starting from data base. For both Ti-43Al-7 (Nb, Mo)-0.2B (%), Ti-14Al -21Nb (wt%) and the improved new alloys based on these compositions, the research team propose the study of new heat treatments (exposure in well established regime of temperature-atmosphere) to control the surface segregation of minor elements (like sulphur) which can reduce hydrogen permeability, thus limiting the disastrously effect of embrittlement. Starting from a microstructure configuration that we considered capable of achieving the mechanical performance imposed in terms of creep and fatigue resistance, oxidation resistance, we controlled the chemical composition by introducing alloying elements in clear limits. From this iteration we developed furthermore the researches for obtaining the optimum balance to obtain physical-chemical and mechanical properties desired for our application.

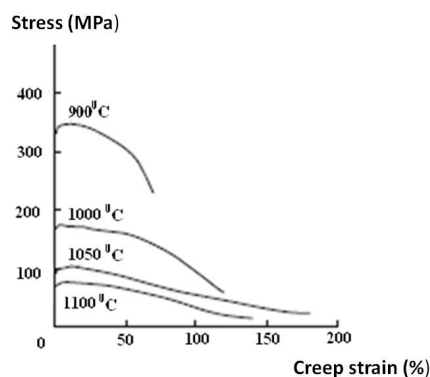
#### Issues regarding the mechanical behaviour

A short and general comparison of mechanical behaviour of titanium aluminides with the conventional alloys and the nickel base superalloys is presented in the table below.

**Table 1.** Properties of titan aluminides, conventional Ti base alloys and of superalloys (HT-high temperature; RT-room temperature; UTS- ultimate tensile strength)

Properties	Ti base	$Ti_3Al$ base ( $\alpha_2$ )	TiAl base ( $\gamma$ )	Superalloys
Density ( $g\ cm^{-3}$ )	4.5	4.1 -4.7	3.7-3.9	8.3
Modulus (GPa)	96-100	100-145	160-176	206
Force(MPa)	380-1150	700-990	400-650	-
UTS (MPa)	480-1200	800-1140	450-800	-
Creep limit ( $^{\circ}C$ )	600	760	1000	1090
Oxidation limit ( $^{\circ}C$ )	600	650	900	1090
Ductility at RT (%)	20	2-10	1-4	3-5
Ductility HT (%)	high	10-20	10-60	10-20
Structure	A3/A2	DO <sub>19</sub>	L1 <sub>0</sub>	f.c.c/L1 <sub>2</sub>

In the figure 3 are presented the  $\sigma - \epsilon$  creep curves obtained on Ti-43Al-7 (Nb, Mo)-0.2b alloy specimens, annealed at  $T = 1130^{\circ}C$  and tested at several temperatures in the range  $T = 900 - 1100^{\circ}C$ , with a creep strain rate of  $\dot{\epsilon} = 1,6 \times 10^{-4}\ s^{-1}$ .



**Fig. 3.** Creep curves obtained on Ti-43Al-7(Nb, Mo)-0.2B specimens annealed at  $T = 1130^{\circ}\text{C}$  tested at several temperatures  $T = 900\text{--}1100^{\circ}\text{C}$  with a creep strain rate of  $\dot{\epsilon} = 1.6 \cdot 10^{-4} \text{ s}^{-1}$

The curve shape is characteristic for the high temperature deformation of intermetallic  $\gamma + \alpha_2$  alloys, which is accompanied by dynamic recrystallization. Increasing the temperature, the flow stress decreases. At  $1050^{\circ}\text{C}$  and  $1100^{\circ}\text{C}$ , the creep strength is low (lower than 100 MPa), which is characteristic for the superplastic flow. The microstructure observations made on Ti-43Al-7(Nb, Mo)-0.2B alloy specimens, after creep rupture ( $T = 1050^{\circ}\text{C}$ ,  $\dot{\epsilon} = 1.7 \cdot 10^{-4} \text{ s}^{-1}$ ,  $\delta = 205\%$ ) showed deformation induced a complete recrystallized microstructure. Regarding the tensile tests performed we have noticed that the relative elongation depends on the volume fraction of the lamellar component. In order to conclude, we can see that the resistance of titanium aluminide Ti-43Al-7(Nb, Mo) - 0.2B alloy can be raised by applying a special heat treatment which leads to a minimum of  $\beta(\text{B}_2)$  and a maximum of lamellar component.

All structural and mechanical issues presented above, as well as all our preliminary results shows clearly that we can obtain a optimised alloy, chosen from the titanium aluminides system alloys, that can be used efficiently in the temperature and stress domains exhibit in service by the energetic industry turbine that is the aim of our study.

## Conclusions

The study will not only contribute to develop the knowledge in the advanced materials field by involving research domains unexplored yet in our country and few in Europe like: the elaboration of titanium base aluminides ( $\alpha_2$  and  $\gamma$ ) alloys, forging and manufacturing parts for turbine blades, surface chemical treatments, surface coatings.

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## Creșterea eficienței energetice a turbomotoarelor utilizate în ciclul cogenerativ dezvoltând materiale avansate noi cu baza titan și acoperiri de suprafață speciale

### Rezumat

*Lucrarea prezintă considerații asupra unui “nou câmp” neexplorat în țara noastră și în Europa, acela al aliajelor intermetalice avansate, aluminidele de titan. Ne concentrăm pe două aluminide de titan, și analizăm aspectele legate de compoziția chimică, tratamentele termice, aspectele microstructurale și comportamentul mecanic. Mai mult, punctăm orientările studiilor echipei de cercetare românești, prin aplicarea unui flux viabil și realizabil: cercetări optime cu privire la compoziția chimică, parametrilor de turnare, elaborarea lingourilor, procesul de forjare, tratamente mecanice și chimice de suprafață, noi sisteme de acoperire, pentru a realiza noi configurații de aliaje de aluminide de titan avansate pentru aplicații turbinei cu gaz. Oferind posibilitatea de a realiza părțile calde prin utilizarea acestor aliaje ușoare se va modifica atât gândirea proiectanților și constructorilor și va influența în mod clar eficiența energetică a turbinelor cu gaz.*