

Properties of Novel High Temperature Titanium Alloys for Aerospace Applications

John Mantione¹, Matias Garcia-Avila¹, Matthew Arnold¹, David Bryan¹, John Foltz¹

¹ATI Specialty Materials

Monroe, NC 28110

Abstract

The attractive combination of strength and low density has resulted in titanium alloys covering 15 to 25% of the weight of a modern jet engine, with titanium currently being used in fan, compressor and nozzle components. Typically, titanium alloys used in jet engine applications are selected from the group of near alpha and alpha-beta titanium alloys, which exhibit superior elevated temperature strength, creep resistance and fatigue life compared to typical titanium alloys such as Ti-6Al-4V. Legacy titanium alloys for elevated temperature jet engine applications include Ti-5Al-2Sn-2Zr-4Mo-4Cr, Ti-6Al-2Sn-4Zr-2Mo-0.1Si and Ti-4Al-4Mo-2Sn-0.5Si. Improving the mechanical behavior of these alloys enables improved component performance, which is crucial to advancing jet engine performance.

As a world leader in supplying advanced alloys of titanium, nickel, cobalt, and specialty stainless steels, ATI is developing new titanium alloys with improved elevated temperature properties. These improved properties derive from precipitation of secondary intermetallics in alpha-beta titanium alloys. ATI has developed several new alpha-beta titanium alloy compositions which exhibit significantly improved elevated temperature strength and creep resistance. This paper will focus on the effects of chemistry and heat treat conditions on the microstructure and resulting elevated temperature properties of these new aerospace titanium alloys.

Introduction

For decades Ti-6Al-2Sn-4Zr-2Mo-0.1Si (Ti-6242Si, UNS R54620) has been the workhorse alloy for high temperature aerospace applications due to its excellent elevated temperature strength, creep resistance and good weldability. Ti-6242Si is an alpha-beta titanium alloy patented in 1967 with a primary claim of creep resistance in excess of 150 hours at 1000°F (538°C) [1]. The primary application for this alloy has been jet engine components including compressor blades, disk and impellers, as well as airframe structure and skins near the engine subject to elevated temperature in service [2].

The creep resistance behaviour of titanium and titanium alloys at high temperature and under sustained loads depends primarily on microstructural morphology and secondary phase compositions. Titanium has two allotropic forms: a beta phase, which has a body centered cubic ("bcc") crystal structure; and an alpha phase, which has a hexagonal close packed ("hcp") crystal structure [2, 3]. Titanium alloys can be categorized depending on the fraction of alpha stabilizers and beta stabilizers in the alloy: alpha alloys, alpha-beta alloys, and beta alloys. Main alpha stabilizers include Al, Sn, Zr, O, N, and C, while main beta stabilizing elements include Mo, V, Fe, Cr, Co, Mn, Nb, Ni, W and Ta. A convenient way to characterize Ti alloys is through Al equivalency (Al_{eq}) and Mo equivalency (Mo_{eq}) using equations found in Figure 1 [2]. The ratio of alpha stabilizing and beta stabilizing elements in an alloy determine constituent phases and kinetics of phase precipitation in a Ti alloy. Typical alpha Ti alloys are commercially pure titanium (CP Ti), which are categorized by grade according to the oxygen content in the alloy. Alpha Ti alloys have excellent workability and weldability, and offer improvements in corrosion resistance compared to stainless steels. Alpha Ti alloys are typically used in petrochemical applications and in heat exchangers and tubing. Higher temperature resistant alpha-beta alloys such as ATI 6-2-4-2™ alloy requires high volume fraction of alpha phase, so they contain higher amounts of alpha stabilizers such as Al, Sn, and Zr. On the other hand, beta alloys such ATI 21S™ alloy and ATI 15Mo™ alloy contain higher amount of beta stabilizers such as Mo, Nb or V and lower amount of alpha stabilizers such as Al, Zr, or Sn. Figure 1 shows aerospace titanium alloys commonly produced at ATI categorized in terms of Al_{eq} and Mo_{eq} . Most high-temperature titanium alloys take advantage of heat treatment to precipitate strengthening secondary alpha phase, and are between $5 < Al_{eq} < 9$ and $1 < Mo_{eq} < 10$.

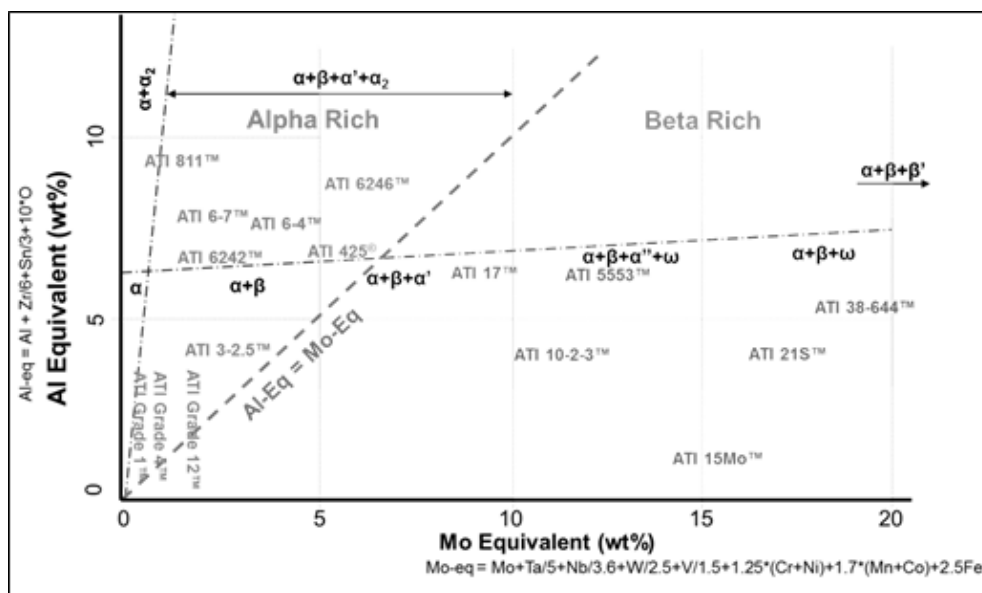


Figure 1: Plot of Al equivalency (Al_{eq}) and Mo equivalency (Mo_{eq}) for titanium alloys commonly produced at ATI.

Predicted titanium phase fields obtained from Ref [4]. Al_{eq} and Mo_{eq} equations obtained from Ref. [2].

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In general, beta titanium alloys exhibit poor elevated-temperature creep resistance due to the significant volume fraction of beta phase present at elevated temperatures. The beta phase does not resist creep due to its body centered cubic structure, which has a lower packing density and a significantly larger number of independent slip systems than the alpha phase [3]. These two aspects together translate often to higher diffusivities in beta phase than alpha phase. In alpha-beta titanium alloys, the volume fraction and size of the primary alpha particles can directly impact creep resistance as the hexagonal close packed structure has greater resistance to dislocation motion by diffusion assisted climb [3]. Additionally, alpha-beta titanium alloys containing silicon in greater than trace amounts will exhibit improved creep resistance due to the precipitation of silicides at the grain boundaries, but the silicides also result in a decrease in room temperature tensile ductility [3]. The reduction in room temperature tensile ductility that occurs with silicon addition limits the concentration of silicon that can be added to alpha-beta titanium alloys; typically to a 0.3% (by weight) maximum [3]. Furthermore, the optimum silicon content for maximum creep resistance in Ti-6242Si has been experimentally determined at 0.09 wt% [5] with higher and lower silicon contents resulting in lower creep resistance.

The ATI team identified the elevated temperature strength and creep resistance of Ti-6242Si as an application-limiting property and executed a series of experiments to improve the elevated temperature strength and/or creep resistance of alpha rich alpha-beta titanium alloys with minor chemistry modifications. Prior research has documented the improvement in creep resistance, first by the addition of silicon and later by the reduction in iron and nickel residual content [3, 5, 6, 7]. Some research using germanium as a solid solution strengthening addition to increase the alpha phase volume fraction has already been explored. Those experiments focused on using germanium as a primary alloying element in the range of 1-4 wt% [8, 9]. The ATI team identified that smaller germanium additions on the order of 0.1 wt%, similar to the optimum silicon addition in Ti-6242Si, were beneficial to elevated temperature properties without the negative effects reported for experiments at higher concentrations (patent applications submitted).

Materials and Experiments

A series of Plasma Arc Melt (PAM) 9 inch diameter electrodes (Figure 2) were produced from 100% virgin raw materials including elemental additions, master alloys and titanium sponge. The heats included baseline Ti-6242Si chemistry and two Ti-6242Si heats with 0.1-0.2 wt% germanium additions. Each electrode was conditioned and Vacuum Arc Remelted (VAR) to produce 10 inch diameter ingots each weighing 450 lb. Each ingot was converted to a 3 inch diameter billet on a 1000 US-ton open die forge press by an upset and draw practice which included a beta grain refinement step and a final alpha-beta draw. The 3 inch diameter billet was cut into 2.5 lb. mullets and upset forged in the alpha-beta regime into a 4.75 inch diameter pancakes for testing (Figure 3). The forged pancakes were solution treated at 1785°F (974°C) for 4 hours, water quenched to room temperature and aged at 1100°F (593°C) for 8 hours followed by an air cool (STA heat treatment).

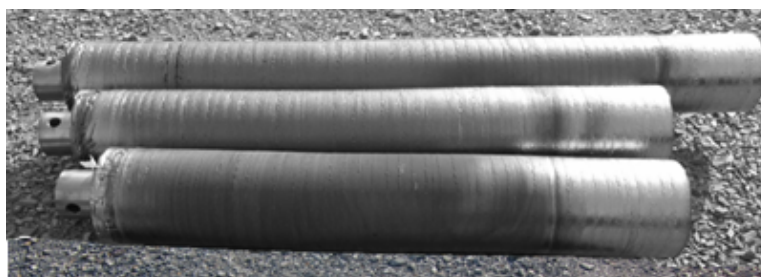


Figure 2: Plasma Arc Melt (PAM) 9 inch diameter electrodes.

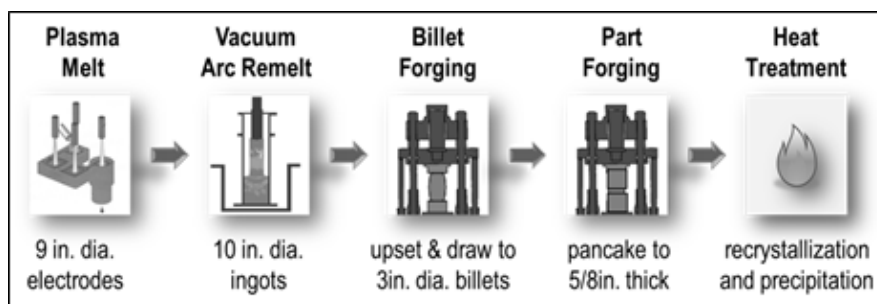


Figure 3: Ingot to test sample manufacturing process.

Mechanical testing of the forged and heat treated pancakes consisted of tensile testing in accordance with ASTM E8 and ASTM E21 and creep testing in accordance with ASTM E-139. Beta transus determination was performed using the DSC-TGA method. Bulk chemistry was analyzed using XRF, ICP-OE, IGF or combustion analysis as applicable. The mechanical and chemical testing was performed at ATI Specialty Materials or an external NADCAP certified laboratory. Microscopy and electron dispersive spectroscopy (EDS) was performed using a Hitachi SU6600 field emission scanning electron microscope (SEM) using a backscattered electron detector used for imaging and chemical analysis of polished and un-etched samples. Quantification of the microstructure was done using 3rd party image quantification tools. Thermodynamic simulation was performed using a commercially available CALPHAD tool (Pandat™ with the PanTitanium database from CompuTherm LLC) to predict the beta transus and equilibrium phases for comparison with experimental data.

Results

Chemistry of the experimental heats was consistent through the length and thickness of the ingot but slightly below the nominal Ti-6242Si chemistry (Figure 4). The Beta Transus predictions were within +/-3°C of the DSC-TGA experimental results (Figure 5) and the slightly elevated transus of heat B5P41 is related to the elevated oxygen content (0.16 wt%) which slightly increased the Al-eq compared with the other two experimental heats. Room and elevated temperature tensile properties were also consistent between the three experimental heats (Figure 6). Elevated temperature creep resistance improved as a function of increasing germanium content; both in total strain at 125 hours and in steady state creep rate (Figure 6). The microstructure of the pancake forging after heat treatment is the typical equiaxed and elongated primary alpha particles in a transformed beta matrix necessary for a good balance of strength, ductility and creep resistance (Figure 7). Examination of the creep test samples after exposure revealed ~1mm diameter precipitates enriched in Zr-Si-Ge and depleted in Ti-Al-Mo within the primary alpha particles (Figure 8).

	Al (wt%)	Sn (wt%)	Zr (wt%)	Mo (wt%)	Si (wt%)	O(wt%)	Ge (wt%)	Al _{eq}	Mo _{eq}
Ti-6242Si Nominal	6	2	4	2	0.1	0.12	0	8.5	2.0
B5P41	5.9	1.8	4.1	1.9	0.07	0.16	0	8.8	1.9
B5P42	5.9	1.9	4.0	1.8	0.06	0.12	0.1	8.4	1.8
B5P43	5.9	1.9	3.9	1.9	0.07	0.13	0.2	8.5	1.9

Figure 4: Chemistry of the experimental ingots.

Beta Transus			
Heat #	DTA (°F)	DTA (°C)	CALPHAD (°C)
Ti-6242Si typical	1825 (+/-25)	990 (+/-15)	-

B5P41	1855	1013	1010
B5P42	1835	1002	1002
B5P43	1840	1004	1002

Figure 5: Beta Transus as determined by differential thermal analysis (DTA) and thermodynamic calculation (CALPHAD).

Temperature	Heat #	UTS (ksi)	YS (ksi)	%Elong (4D)	%RA	%Creep Strain	
						52ksi load 125 hours	Steady State Creep Rate (%/h) x10 ⁻⁴
72°F (22°C)	B5P41	175	158	14	41		
	B5P42	174	153	15	38		
	B5P43	178	157	14	39		
900°F (482°C)	B5P41	126	99	19	63	0.20	7.9
	B5P42	127	95	18	58	0.16	3.5
	B5P43	130	95	17	59	0.13	3.4

Figure 6: Room and elevated temperature tensile and creep properties.

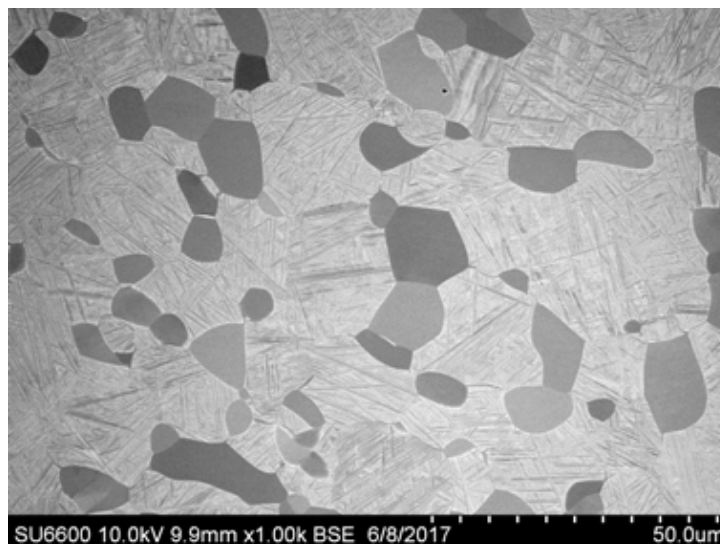


Figure 7: BSE image of alpha particles in a transformed matrix: heat B5P43 after pancake forging and STA heat treatment.

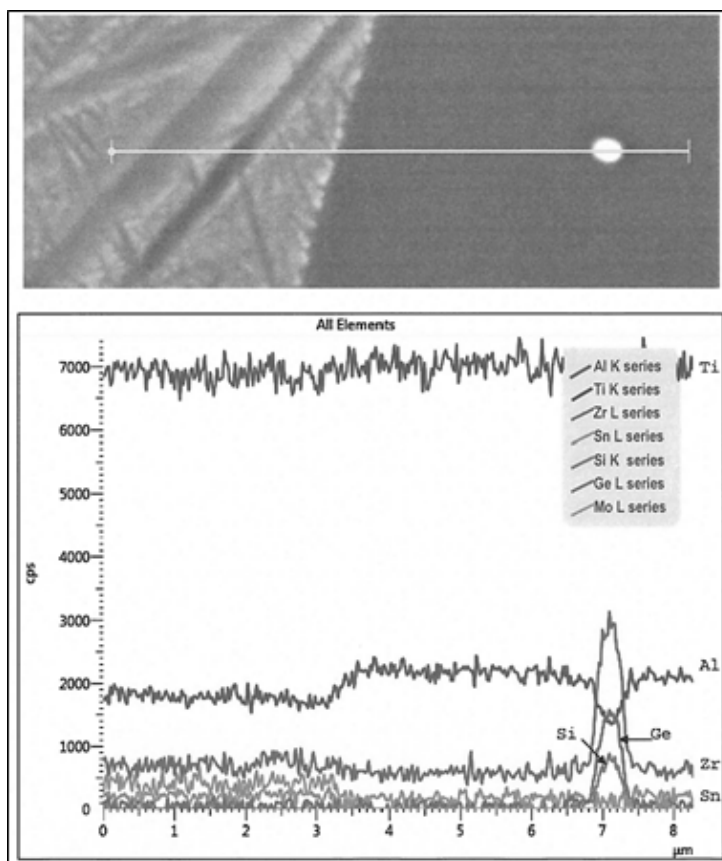


Figure 8: BSE image and EDS line scan of Zr-Si-Ge particle in heat B5P43 after pancake forging, heat treatment and creep testing.

Discussion

The role of $(\text{Ti,Zr})_5\text{Si}_3$ silicide precipitation in reducing the steady state creep rate of alpha-beta titanium alloys has been examined and well documented by Neal, Fox [10] and Paton, Mahoney [11]. The precipitation of a Ti_6Ge_5 or TiGe_2 germanide in a Ti-Ge binary and the precipitation of a $\text{Ti}_6(\text{Si,Ge})_5$ germanide-silicide in a Ti-Ge-Si system have been studied by Thomas [12]. The full range of Ti-Ge compositions including the Ti_5Ge_3 were confirmed by Liu [13]. In this study, the addition of small amounts of germanium to Ti-6242Si resulted in a zirconium germanide-silicide precipitate which is likely in the form $(\text{Ti,Zr})_5(\text{Ge,Si})_3$. Prior work by Kitashima [8] using higher germanium content demonstrated a similar Ti-Zr-Ge-Si precipitate, but the higher Ge content (up to 4 wt%) resulted in a significant increase in tensile strength and ductility which was not evident in the present study with a Ge content less than 1 wt%. The experimental data for Ti-6242Si with Ge additions of 0.1 and 0.2 wt% exhibited significant improvement in steady state creep rate and total creep strain as a function of increasing Ge content. Apparent activation energies for steady state creep were calculated from creep tests performed at 900°F (482°C) and 950°F (510°C) (Figure 9). The calculated activation energy for the baseline Ti-6242Si heat B5P41 is slightly higher than the 304-316 kJ/mol reported by Es-Souni [14], lower than the 360-420 kJ/mol reported by Bania and Hall [15] and agree with the 308-374 kJ/mol reported by Mishra [3] [7]. The experimental activation energy for the Ti-6242Si+Ge heats B5P42 and B5P43 are significantly higher at 425-465 kJ/mol. (Figure 9).

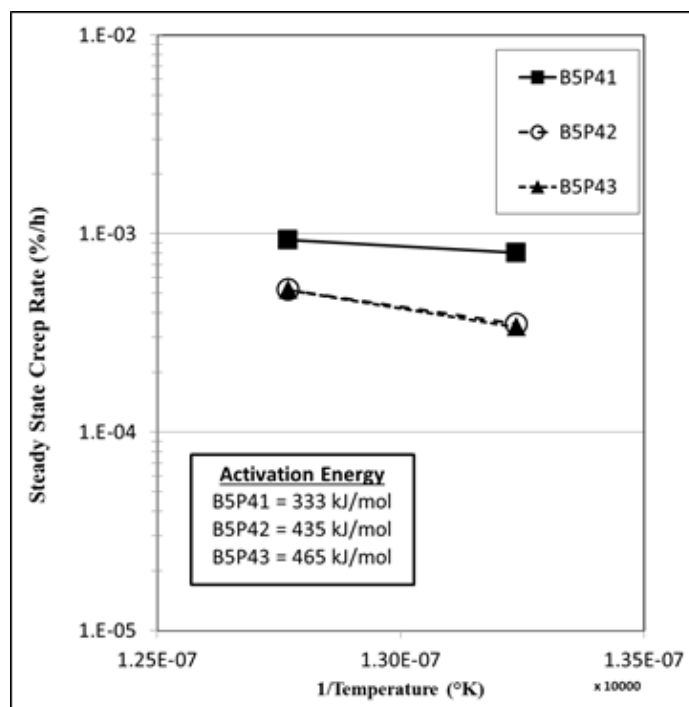


Figure 9: Natural log steady state creep rate as a function of inverse temperature.

Apparent activation energy calculated from the slope.

Conclusions

In this study, systematic addition of germanium to Ti-6242Si alloy was achieved using 450 lb. double melted titanium ingots. These ingots were forged in an open-die press to simulate typical processing of titanium billet and titanium forgings. In all cases, the addition of a small amount of germanium (less than 1 wt%) to the Ti-6242Si alpha-beta titanium alloy resulted in the formation of a Ti-Zr germanide-silicide precipitate which improved creep resistance at 900-950°F (482-510°C) without a negative impact to strength or ductility. Further analysis is warranted to determine the composition of the germanide precipitate and the mechanism of creep resistance enhancement. Nevertheless, application of these improved titanium alloys into jet engine components will translate to an increase in jet engine performance.

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