Ti-2007 Science and Technology, edited by M. Ninomi, S. Akiyama, M. Ikeda, M. Hagiwara, K. Maruyama
The Japan Institute of Metals (2007)

Creep Properties of Near Alpha Titanium Alloys at Elevated Temperatures Higher Than 600°C

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TIMETAL®834 (Ti5.8A1-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C) and TIMETAL®1100 (Ti-6A1-2.7Sn-4Zr-0.4Mo-0.45Si) were developed in 1980's to maximize creep resistance with adequate strength and fatigue performance in aircraft jet engine applications. These alloys are recognized as the best near alpha alloys that are available commercially even now. The service temperatures for the alloys were considered to be lower than 600°C or 1100°F, however, these alloys can be used at much higher temperatures depending on the conditions such as stress levels and environment. TIMETAL®1100 has been used for motorcycle engine exhaust valves for last several years. Careful selection of material conditions and optimization of processes are necessary to maximize properties at elevated temperatures. This paper will compare properties of commercial near alpha alloys at elevated temperatures below and above 600°C. Ti-6242S and Ti-811 will be included in the comparison. Chemical compositions of alloys including impurity elements, phases present and microstructure have significant influence on the properties of near alpha alloys at elevated temperatures. Metallurgical factors that control key properties at elevated temperatures such as creep and oxidation resistance will be discussed. ("TIMETAL ®" will be abbreviated as "Ti-" hereafter in the text.)

Keyword:Ttitanium (Ti), Near alpha titanium alloy, Ti-1100, Ti-834, Ti-6242S, Ti-811, Elevated temperature, Creep, Oxidation resistance, Engine valves

1. Introduction

Near alpha titanium alloys have been used for disks and blades of compressor of jet engines for decades. Creep resistance at elevated temperatures is considered to be one of the critical properties in the application. The highest extended service temperature for titanium alloys has been considered as approximately 600°C or 1100°F.

A review of published work on near alpha titanium alloys suggests that stresses for hot rotating parts in jet engine applications can be higher than 250 MPa. Actual design stresses are proprietary and not available. At these stress levels extended exposure above 600°C cannot be tolerated by conventional titanium alloys due to a combination of oxidation, alpha case formation and metallurgical stability. Thus research for advanced high temperature alloys has focused on titanium aluminides with more inherent oxidation resistance and stability. Significant progress towards practical use of titanium aluminides has been made with some parts finding service in specialty applications. However widespread use has been limited due in large part to manufacturing issues[1-5)].

More recently the potential for conventional titanium alloys to operate at temperatures above 600°C in automotive engine exhaust valve applications was evaluated.[6-9)] Advantages of applying conventional alloys are that the process to produce titanium mill products has already been established and a similar parts manufacturing process to steels or nickel base alloys can be used for titanium alloys. High temperature capability of near alpha alloys may not be as attractive as gamma titanium aluminide or TiB MMC[10)], however, the use of conventional titanium alloys may be less risk and economical.

2. Commercial Near Alpha Alloys

Commercial alpha/beta and near alpha alloys developed and used for medium and high temperature applications are shown in Figure 1 [11)]. Several new alloys have been developed in the last 20 years, however, yet Ti-834

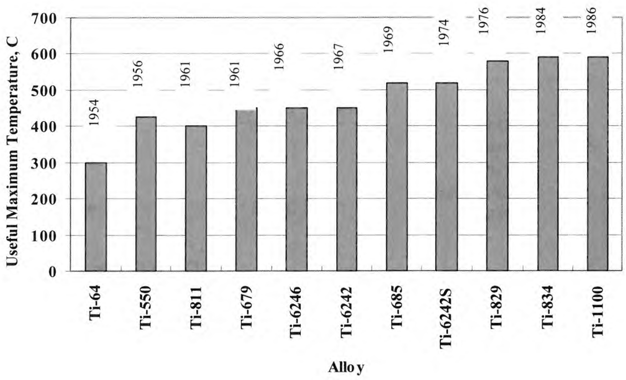

Figure 1. Commercial alpha/beta and near alpha alloys used for med to high temperature applications.

(Ti-5.8A1-4Sn-3.5Zr-0.7Nb-0.5Mo-0.35Si-0.06C) and Ti-1100 (Ti-6A1-2.7Sn-4Zr-0.4Mo-0.45Si) are considered to be the most capable titanium alloys for high temperature applications[12-15)].

3. Application of Near Alpha Alloys in Engine Valves

Ti-6242S (Ti-6A1-2Sn-4Zr-2Mo-0.1Si) is one of the most common near alpha alloys. The alloy has been used for rotating parts of jet engine compressor and readily available compared with more advanced near alpha alloys such as Ti-1100 and Ti-834. The application of Ti-6242S to automotive exhaust valves was first attempted for racing vehicles almost 25 years ago[16)], and the alloy is still used for exhaust valves of Infinity Q-45 (or Nissan Cima) as well as in numerous racing and after market applications.

AISAN Industries had requirement for motorcycle exhaust valves and found Ti-1100 to be the optimum solution. AISAN Industries has established the process for valve manufacturing and heat treatment conditions to optimize microstructure and surface hardening[7,8)]. Over 200 metric tons of Ti-1100 have been melted and converted to mill products for valve manufacturing. Development activities targeting newer and more demanding automotive engine valve applications are currently in progress.

4. Oxidation Resistance

In the application of titanium alloys at temperatures higher than 600°C, oxidation resistance may become a critical property depending on the environment of parts to be applied for service. Although titanium and its alloys have excellent environmental properties against corrosive media in general, oxidation resistance at high temperature is not as good as that of counterparts such as stainless steels or nickel base super alloys. Figure 2 shows weight gains of selected commercial alloys tested at 760°C. Oxidation resistance of near alpha alloys is generally better than other titanium alloys as they contain alloying elements, such as Si and Al, which suppress oxidation of titanium alloys. Among three near alpha alloys, Ti-1100 shows the best results as it contains high amount of Si. Ti-811 resulted in the worst oxidation performance. This is attributed to the presence of V[17].

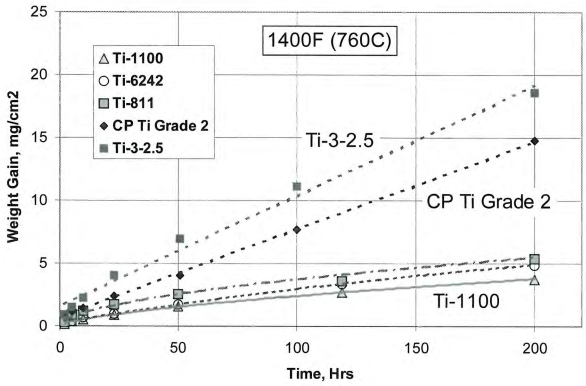

Figure 2. Weight gain of various titanium alloys after exposure at 760°C.

5. Controlling Factors of Elevated Temperature Creep

Al equivalent (Al Eq.) given by equation (1) is an empirical formula to provide the stability of alpha phase in titanium alloy. The higher Al Eq. is, the higher the strength of alpha phase becomes. Al Eq. lower than 9 was suggested to avoid manufacturing difficulty due to the formation of ordered phase; alpha 2 or DO_{19}[18].

$$\text{Al Eq.(wt\%)} = \text{Al} + \text{Sn}/3 + \text{Zr}/6 + 10(\text{O} + \text{N} + \text{C}) \qquad (1)$$

There will be several metallurgical factors that may control elevated temperature creep of near alpha alloys[19,20]. Al equivalent may reflect some of these factors in the equation.

Microstructure --- It is well understood that transformed beta structure that consists of alpha and beta laths show significantly superior creep resistance than equiaxed alpha/beta structure[21]. This is due to the difference of effective slip length as lath width determines slip length in alpha beta lamellar structure[22]. It is shown that smaller beta grain size is beneficial for creep as smaller beta grains consist of smaller colonies resulting thinner laths[22].

Solid Solution Hardening --- The effect of solid solution hardening is partially included in Al equivalent equation. These alloying elements are known to strengthen alpha phase, Al being the most effective.

Ordered Phase --- Alpha 2 (Ti_3A1 or DO_{19}) precipitates in alpha phase depending on heat treatment and chemistry. Al is the most influential element on the formation of alpha 2. Alpha 2 may potentially exist depending on heat treatment when Al is higher than about 7wt% in Ti-Al binary system. Ordered phase is considered to prevent dislocation from cross-slip and climb.

Stacking Fault Energy --- There is little information on the stacking fault energy of practical titanium alloys. It is demonstrated that Al decreased stacking fault energy in Ti-Al binary alloy[23]. Therefore, near alpha alloys with higher aluminum content may have lower stacking fault energy. As a result, higher Al alloys have less mobility in cross-slip and climb of dislocations during elevated temperature creep.

Silicides Precipitation --- Silicon forms silicide, Ti3Si or Ti5 Si3, depending on the amount of silicon and temperature. It is known that $(TiZr)_5Si_3$ type silicides forms when Zr is present[24]. The presence of dispersion of silicides is influential on creep strength by retarding dislocation glide.

Equilibrium phase diagrams for four commercial alloys were calculated using PANDAT software. Nominal chemistry was used for the calculation excluding interstitials. Table 1 shows calculated volume % of DO_{19} and silicide Ti_3Si. The calculation provides some interesting features among four alloys. Al equivalent of four alloys is approximately 9 to maximize creep strength. Ti-811 may contain the highest volume of alpha 2 precipitates at 565°C, while none of these alloys contain it at 760°C. This does not consider short range ordering which may also be a factor. Ti-1100 and Ti-834 contain 2-3 percent of silicides at both temperatures.

Table 1. Calculated phase volume % of DO_{19} and Ti_3A1 for commercial near alpha alloys. (Al Eq with wt%)

ALLOY	AL EQ	565°C		760°C	
		DO_{19}	Ti_3Si	DO_{19}	Ti_3Si
Ti-811	8.7	19.8	0	~ 0	0
Ti-6242S	8.7	6.1	0.1	~ 0	0.1
Ti-1100	8.6	5.0	3.0	~ 0	3.0
Ti-834	9.2	6.9	2.3	~ 0	2.3

Effect of Transition Metals --- It is known that impurity level of Ni and Fe deteriorates creep resistance of titanium alloys[25-30,9]. These transition metals have unusually high diffusion coefficient in hcp Ti as well as in bcc[31,32]. Although an exact mechanism of the influence on elevated temperature creep is not fully understood yet, it is critical to control these impurity elements as low as possible to meet the requirement.

Seven arc melt button ingots containing different amount of Fe and Ni were made as Ti-1100 as a base composition. After beta forge and beta anneal, creep tests were conducted at 565°C/275MPa and 760°C/69MPa. A multiple regression analysis on the creep results indicated that secondary creep rate at either creep condition was determined primarily by the combination of Fe and Ni content, the effect of Ni being more pronounced at 565°C/275MPa condition. This observation suggests a diminishing importance of fast diffusing elements.

6. Comparison of Creep Behaviors of Near Alpha Alloys

Creep tests for four commercial near alpha alloys, shown in Table 2, were conducted with two creep conditions in air, i.e. 565°C/275MPa and 760°C/69MPa. All coupons were beta-annealed followed by mill anneal at 760°C to create an equivalent transformed beta structure to reduce a microstructural effect.

Creep curves for four alloys are given in Figure 3. It is evident from the results that Ti-834 and Ti-1100 exhibit superior creep resistance to Ti-811 or Ti-6242S. Creep strain at 50 hours and steady state creep rate for each test was summarized in Table 3. As can be seen in the table both creep strain and creep rate of Ti-811 and Ti-6242S are more than 10 times greater than Ti-834 or Ti-1100.

Oxidation can be a factor when creep test is carried out at temperatures higher than 600°C. Surface appearance of the cross-section is quite different by alloy. Figure 4 shows the cross-section of Ti-6242S and Ti-1100 tested at 760°C for 50 hours. Ti-6242S revealed thicker scale with sizable cracks, while Ti-1100 does not show any indication of cracks, although thin scale and oxygen enriched layer with the depth of approx. 50~60 µm is present. These cracks appeared to have created early stage of creep judging from

Table 2. Chemical composition of near alpha alloys used for creep tests. (wt%)

ELEM.	TI-811	TI-6242S	TI-834	TI-1100
Al	7.67	6.11	5.70	5.91
V	1.01	-	-	-
Mo	0.93	2.03	0.50	0.39
Sn	-	1.99	3.99	2.60
Zr	-	4.07	3.59	3.98
Nb	-	-	0.70	-
Si	0.01	0.08	0.28	0.35
C	0.01	0.02	0.06	0.04
O	0.09	0.11	0.10	0.08

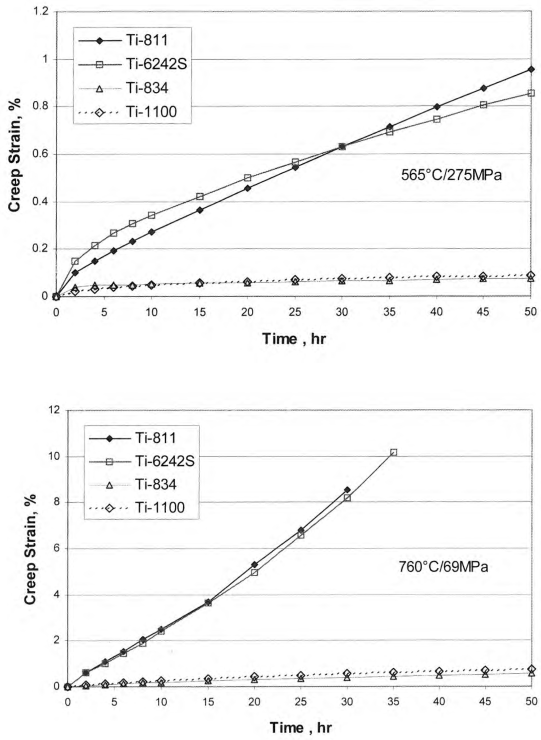

Figure 3. Creep curves of four near alpha alloys at two creep conditions.

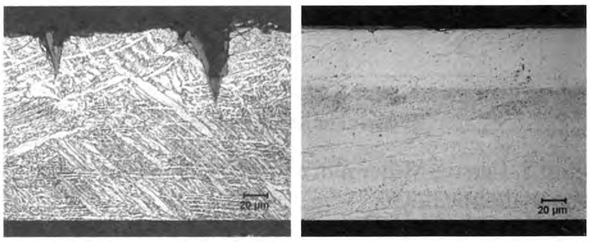

Figure 4. Cross-section of the middle portion of creep specimens tested at 760°C for 50 hours. (a) Ti-6242S, (b) Ti-1100.

Table 3. Summary of creep tests for four alloys.

ALLOY	565°C/275MPA		760°C/69MPA	
	Strain at 50 hrs %	Creep Rate 10^{-6}/h	Strain at 50 hrs %	Creep Rate 10^{-6}/h
Ti-811	0.959	163	9.66	2400
Ti-6242S	0.857	111	>11	2500
Ti-1100	0.075	5.2	0.571	85
Ti-834	0.087	7.2	0.768	105

the presence of thick scale inside of the cracks and their openings.

Figure 5 shows Larson-Miller Plot of the creep test results, where 0.2% creep strain was used as a criterion. It is evident from the figure that Ti-1100 and Ti-834 exhibits superior creep resistance at either condition. The combination of elements in these Ti-1100 and Ti-834 was optimized for creep resistance at around 600°C. At this temperature, diffusion controlled dislocation climb and perhaps solute drag of silicon are considered to be important rate controlling mechanisms[33]. Thus minimizing beta phase content and fast diffusing elements such as nickel and iron whilst maintaining high aluminum equivalent generally provides the optimum solution. From this work, however, two key factors have emerged. One is that the importance of Ni at 760°C is relatively diminished compared to 565°C and the second is that there may be a correlation between the volume fraction of silicides precipitates and creep performance. It is suggested that this effect may be more pronounced at 760°C. From these two observations, it may be inferred that there is a change in dominant creep mechanisms towards a dislocation glide mechanism. This would be expected but does suggest that a different alloy development philosophy for higher

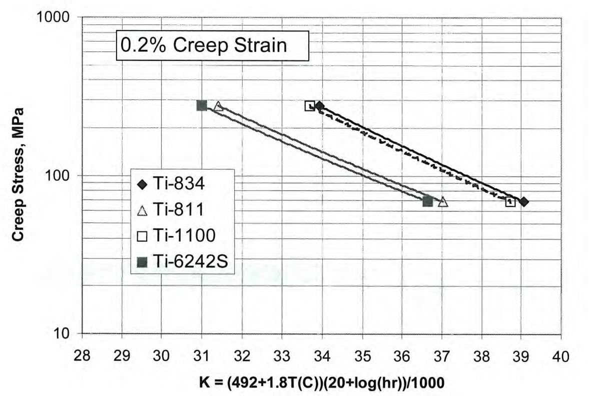

Figure 5. Larson-Miller plot of creep tests for four near alpha titanium alloys.

temperature applications compared to traditional jet engine compressor applications may be appropriate.

7. Conclusions

Factors that control creep behavior at temperatures higher than 600°C was discussed. Adverse effects on Ni and Fe in Ti-1100 were observed at both 565°C/275MPa and 760°C/69MPa conditions. Creep tests for four commercial near alpha titanium alloys under beta anneal condition were conducted. Ti-1100 and Ti-834 exhibited superior creep resistance to Ti-6242S or Ti-811 at either test condition. Oxidation resistance may become important for creep at temperatures higher than 600°C.

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