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Terryl A. Wallace
Ronald K. Clark
Karl E. Wiedemann

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Langley Research Center
Hampton, Virginia 23665

OXIDATION CHARACTERISTICS OF BETA-21S IN AIR IN THE TEMPERATURE RANGE 600 TO 800°C

T. A. Wallace*, K. E. Wiedemann**, and R. K. Clark*

*NASA Langley Research Center
Mail Stop 194, Hampton, Virginia 23665-5225

**Analytical Services and Materials, Inc.
107 Research Drive, Hampton, Virginia 23666

Abstract

The metastable β-Ti alloy Beta-21S, Ti-15Mo-2.7Nb-3Al-.2Si (weight percent), has been proposed as a candidate for use in metal matrix composites in future hypersonic vehicles. The present study investigated the oxidation behavior of Beta-21S over the temperature range 600 to 800°C. Oxidation weight gain was evaluated using thermogravimetric analysis. Oxidized specimens were evaluated using x-ray diffraction techniques, scanning electron microscopy, energy dispersive x-ray analysis, and electron microprobe analysis to identify oxidation products and evaluate oxidation damage to the alloy.

Introduction

Current designs for future hypersonic vehicles call for the use of titanium-matrix composites for many components, consituting as much as fifty percent of the structural weight. This will require a titanium alloy which has good oxidation resistance, is easily producible as foil, and has good high temperature properties in the temperature range 600 to 800°C. This has required the development of new titanium alloys with an acceptable balance of these properties. One alloy developed for use in this application is the metastable β-Ti alloy Beta-21S, Ti-15Mo-2.7Nb-3Al-.2Si (wt. %).

The purpose of the present study was to characterize the oxidation behavior of Beta-21S in the temperature range 600 to 800°C. Oxidation weight gain was determined by oxidizing samples in air using a thermogravimetric apparatus (TGA). Selected samples were analyzed metallographically to characterize the oxide composition and morphology and the microstructural changes in the metal.

Experimental Procedures

Specimens and Materials. The as-received Beta-21S material was produced from a triple melted ingot by forging to a 12.7 cm (5 inch) slab, hot rolling to a nominal thickness of 0.406 cm (0.160 inch), and cold rolling to 0.051 cm (0.02 inch) thickness using intermediate vacuum anneal steps. The chemical analysis of the Beta-21S materials in weight percent was 15.8 Mo, 2.95 Al, 2.88 Nb, 0.23 Si, 0.026 C, 0.114 O, and 0.005 N with the balance being Ti.

TGA samples were machined to a width of 1 cm, and a length of 1.5 cm with a 0.16 cm diameter hole through the thickness at one end for suspending the sample during the test. Sample surfaces were ground to a uniform finish using silicon carbide paper through 1200 grit. Samples were first detergent cleaned, then ultrasonically cleaned in acetone and ethyl alcohol, and finally air dried. The dimensions of finished samples were measured to the nearest 0.0001 inch and weights were recorded before and after exposure to the nearest 0.01 mg.

Oxidation Tests. Oxidation tests were conducted in high purity air (true hydrocarbon content less than 0.1 ppm) from 600 to 800°C for times up to 100 hr. The sample weight change was recorded continuously during exposure using a Cahn C2000 microbalance with an accuracy of 1 μg. Samples were suspended by quartz fibers in a mullite tube inside a vertical tubular furnace, and the temperature was monitored continuously with an R-type thermocouple located just below the suspended specimen. A low flow of air (1 cc/sec) through the mullite tube was maintained during the test. Duplicate or triplicate tests were performed at each temperature.

Characterization Studies. Specimens were examined before and after oxidation using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) to characterize the microstructure and identify oxide phases. The distribution and morphology of the oxide phases were determined by examining cross-sectioned specimens using SEM, EDS, and electron microprobe analysis. These specimens were cross-sectioned after mounting in epoxy, then polished and lightly etched using Kroll's reagent (2 % HNO_3, 1 % HF), and finally coated with a thin layer of gold to minimize charging.

Results

Oxidation Kinetics. Table 1 summarizes the results for the oxidation exposures of Beta-21S over the temperature range 600 to 800°C. The total weight gains were obtained from comparing initial and final specimen weights. Analysis of the weight gain data obtained from the TGA showed that the weight gain increased parabolically with respect to the time of exposure, as would be expected for a titanium alloy in this temperature range (1). This means that the weight gain can be expressed as $w^2 = k_p t$ where w is the weight gain per unit area, k_p is the parabolic rate coefficient, and t is the time of exposure. Calculated values of k_p for Beta-21S are presented in table 1.

Figure 1 is an Arrhenius plot of the parabolic rate coefficients calculated for Beta-21S. The activation energy for oxidation was calculated to be 41.2 kcal/mol from the parabolic rate coefficients. Also shown for reference is data for commercially pure (c.p.) titanium (2), and the Ti_3Al-based alloy Ti-14Al-21Nb (wt %) (3). This analysis shows that over the temperature range investigated, Beta-21S has better oxidation resistance than c.p. titanium but oxidizes more rapidly than Ti-14Al-21Nb.

Oxidation Products. The results from XRD analysis of as-received and oxidized Beta-21S specimens are shown in table 2. The as-received material consisted exclusively of β-Ti, while some α-Ti was identified after all oxidation exposures. TiO_2 (rutile) was the primary

Table 1. Thermogravimetric Analysis Results For Beta 21-S

Exposure Conditions		Total Weight Gain,	Parabolic Rate Coefficient
Temp,°C	Time,hr	mg/cm^2	$mg^2/cm^4/hr$
600	72.5	0.204	0.000575
650	70.8	0.364	0.00187
700	71.8	0.762	0.00801
700	111.5	1.01	0.00922
750	24.1	0.809	0.0271
800	29.8	1.55	0.0808
800	100.1	2.92	0.0852

oxide identified after exposure at all temperatures examined. Trace amounts of Al_2O_3 were also identified after exposure at temperatures above 600°C.

Figure 2 is an SEM micrograph of the cross-section of a specimen exposed 100 hr at 800°C. The surface oxide consists of two regions; a discontinuous top layer, and a relatively thick compact (void-free) layer. EDS analysis of the top layer showed the presence of Ti, Al, and O; while analysis of the middle layer showed the presence of Ti, O, and a small amount of Nb. Combined with the XRD analysis results (table 2), these scans suggest that the surface oxide is primarily TiO_2, with a mixture of Al_2O_3 and TiO_2 at the surface.

The oxidation of titanium alloys, however, is known to proceed by the dual processes of oxygen dissolution and oxide formation. The total weight gain, therefore, represents the sum of the oxygen consumed in the formation of the surface oxide and the oxygen that diffuses into the metal. Metallurgical analysis of the oxidized specimens is necessary to allocate the total weight gain between these two processes.

Measurement of oxide thicknesses can be used to estimate the amount of oxygen consumed in oxide formation. Since the oxide on Beta-21S has been shown to be primarily TiO_2, the oxide thickness can be used to estimate a weight gain per unit area using the theoretical density of oxygen in TiO_2 (1.7 g/cm^3). Subtracting this weight from the total measured oxygen weight gain also allows an estimation of the amount of oxygen that has diffused into the substrate.

The results of this analysis for several oxidized Beta-21S specimens are presented in table 3. These results show that there is measureable weight gain due to oxide formation. Comparison with the total weight gain data, however, shows that oxide formation only accounts for 70 percent of the total oxygen reacting with the metal. This means that there is also an appreciable amount of the oxygen diffusing into the metal.

Metallurgical examination of the oxidized Beta-21S specimens should confirm the fact that

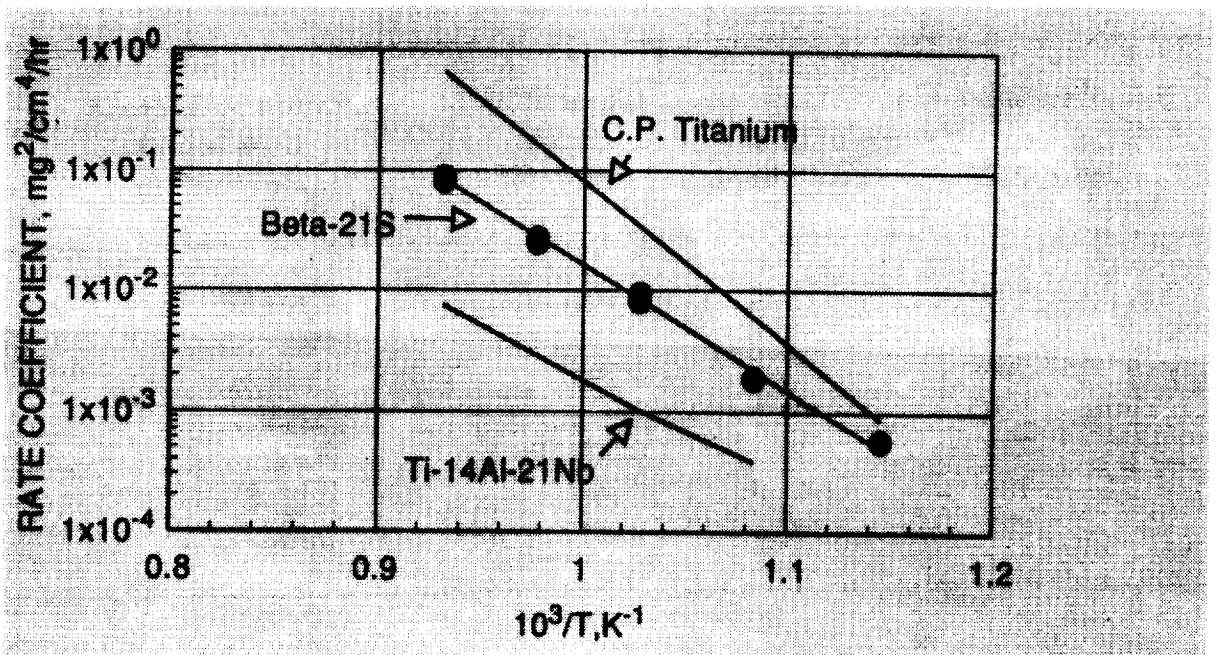

Figure 1 - Arrhenius Plot of Oxidation Rates for Beta-21S

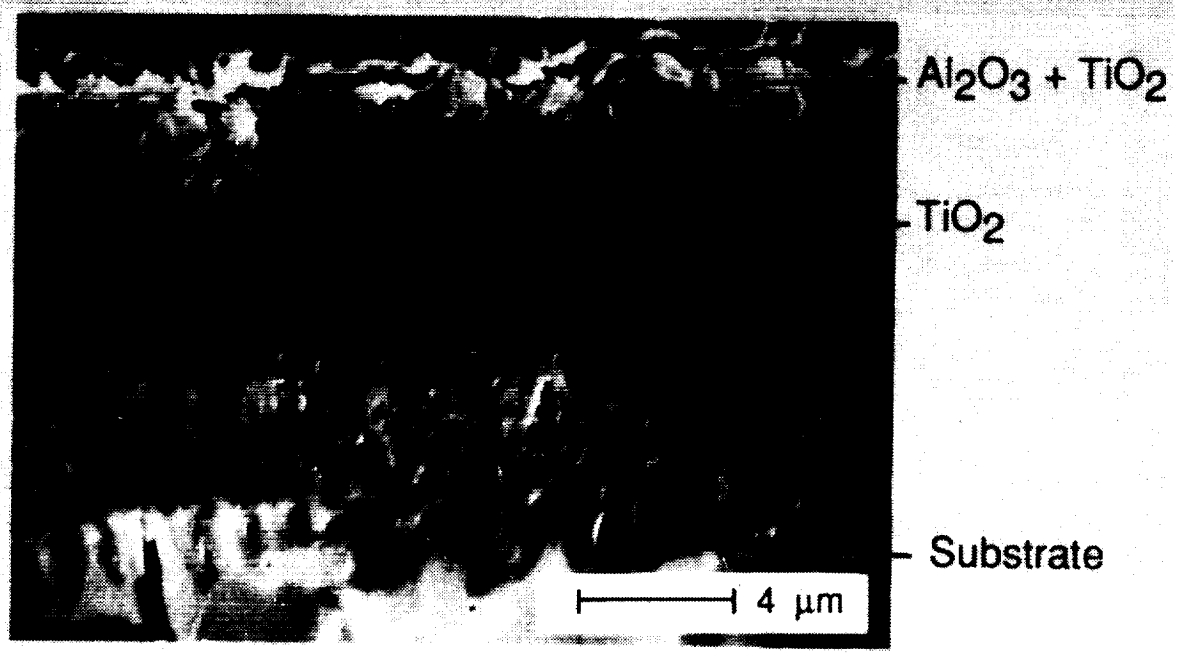

Figure 2 -SEM Micrograph of Beta-21S Exposed at 800°C for 100 hr

Table 2. Oxide Composition Of Beta-21S From XRD

Exposure	Measured Intensities[1] β-Ti	α-Ti	TiO_2	Al_2O_3
as-received	VS	-	-	-
600°C, 72.5 hr	VS	VS	W	-
700°C, 71.8 hr	S	S	VS	W
800°C, 29.8 hr	W	W	VS	W
800°C, 100.1 hr	W	W	VS	W

[1] VS=very strong, S=strong, W=weak

Table 3. Oxide Thickness and Partitioning of Oxygen

Exposure Condition		Oxide Thickness,	Weight Gain, mg/cm^2	
Temperature, °C	Time, hr	μm	Oxide	Metal
600	72.5	0.84	0.14	0.061
700	71.8	3.2	0.54	0.22
800	29.8	5.8	0.99	0.56

[1] VS=very strong, S=strong, W=weak

oxygen diffusion is occuring since oxygen is a known α-Ti stabilizer and should produce some microstructural changes. Figure 3 shows the resulting microstructure after various oxidation exposures. Figure 3(a) shows the microstructure after exposure at 800°C for 30 hr, (b) 800°C for 100 hr, (c) 700°C for 70.8 hr, and (d) 600°C for 72.5 hr. All specimens consist of a mixture of α-Ti and β-Ti, with an increase in the tendency to form Widmanstatten α-Ti as the temperature is decreased. Separation of the affects of oxygen and thermal exposure in this temperature range is difficult, however, since the β-Ti transus for Beta-21S is roughly 815°C (4).

Close examination of these cross-sections, however, does indicate an increased concentration of α-Ti near the metal surface, particularly after exposures at 700°C and 800°C. Figure 4 plots the fraction percent α-Ti (calculated using the point count method: ASTM E562) as a function of distance from the oxide-metal interface for specimen exposed 30 hr

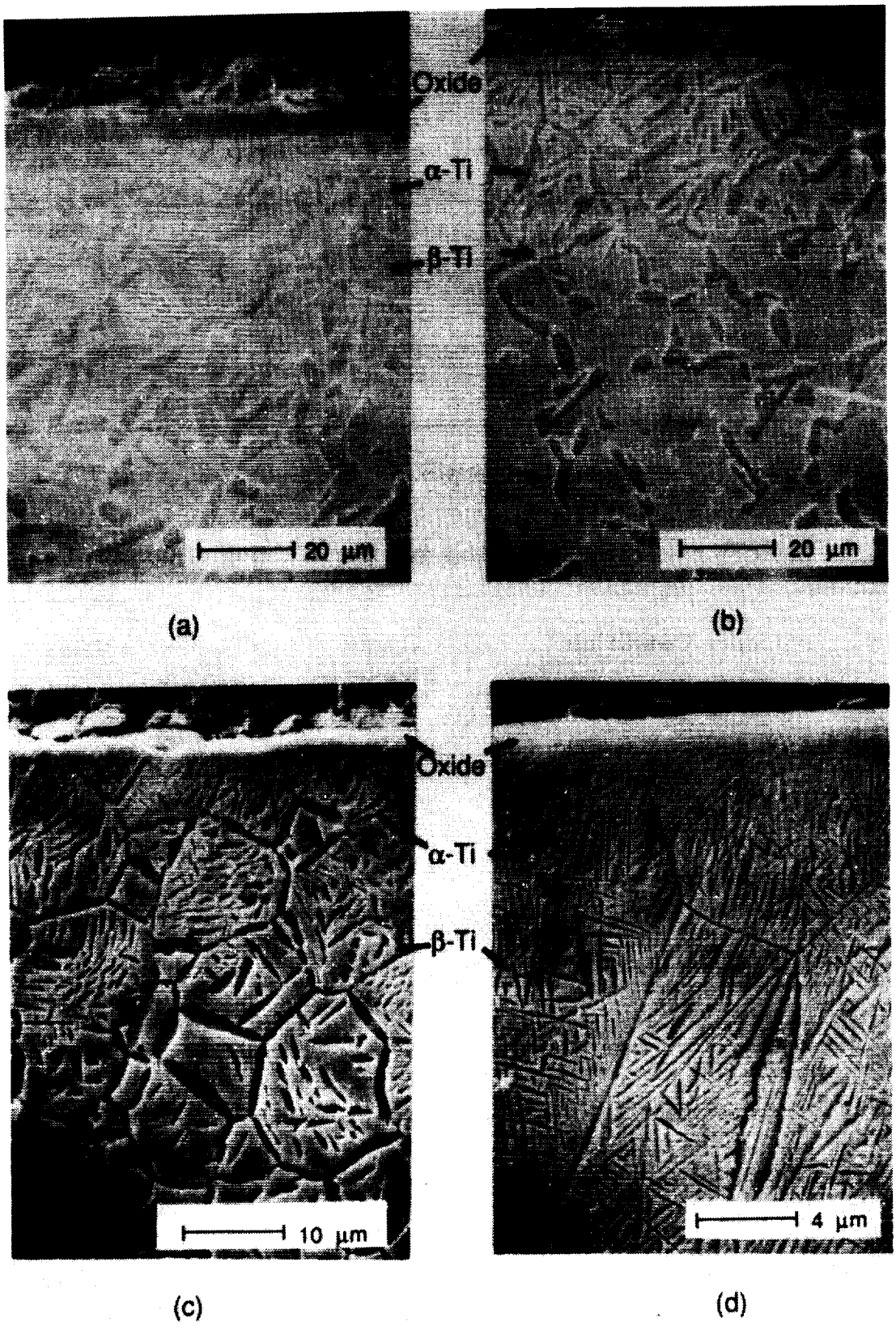

Figure 3 - SEM Micrographs of Beta-21S Exposed at (a) 800°C for 30 hr, (b) 800°C for 100 hr, (c) 700°C for 72 hr, and (d) 600°C for 72.5 hr.

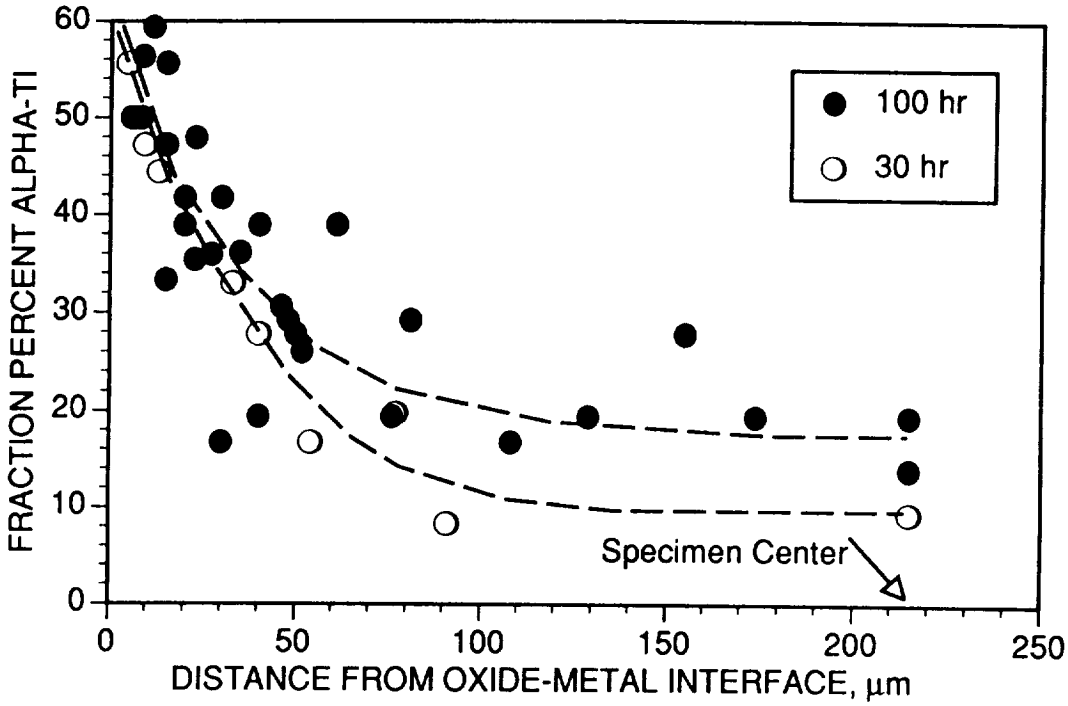

Figure 4 - Fraction Percent α-Ti as a Functions of Distance from the Oxide-Metal Interface for Beta-21S Exposed at 800°C.

and 100 hr at 800°C. For the specimen exposed for 30 hr there is approximately 50 percent α-Ti at the specimen surface decreasing to a constant value of approximately 10 percent 100 μm from the oxide-metal interface. After 100 hr exposure at 800°C, however, the percentage of α-Ti is higher throughout the entire specimen, decreasing to about 20 percent α-Ti at the center of the specimen. Although percent α-Ti is not a direct measurement of oxygen content, the increased levels of α-Ti near the surface do indicate that there is a concentration gradient of oxygen into the metal, extending across the entire specimen after longer term exposures.

Discussion

The oxidation behavior of Beta-21S, like that of other titanium alloys, is difficult to define precisely due to the number and complexity of operative oxidation mechanisms. For instance, for c.p. titanium it has been shown that oxidation proceeds by simultaneous growth of a surface oxide of TiO_2 and oxygen dissolution into the metal. At low temperatures (below 650°C) the oxidation rate is controlled by the growth rate of the TiO_2, producing an activation energy between 25.4 kcal/mol and 27.4 kcal/mol. At higher temperatures, the activation energy changes to that required for diffusion of oxygen into the metal (2,5).

Analysis of the oxidation kinetics and metallurgical characterization for Beta-21S, however, does allow some important insights. For instance, if the surface oxide layer of TiO_2 that

forms on Beta-21S was rate controlling, the activation energy should be similar to that for c.p. titanium and other titanium alloys. The activation energy for the oxidation of Beta-21S, however, was calculated from the parabolic rate coefficient to be 41.2 kcal/mol. This indicates that oxide formation does not control the oxidation kinetics, and suggests that oxygen dissolution into the metal also must be considered.

The fact that measureable oxygen dissolution occurs is confirmed by metallurgical examination of the oxidized Beta-21S specimens. Figure 3 and figure 4 indicates that there there is an increase in the percent of α-Ti near the specimen surface after oxidation exposure, suggesting the presence of an oxygen concentration gradient in the metal. In fact, after 100 hr exposure at 800°C, the percent alpha is increased even at the center of the specimen, suggesting that oxygen has diffused throughout the entire specimen thickness.

This analysis of the oxidation behavior of Beta-21S has shown that, although oxidation rates for that alloy are lower than that for other titanium alloys, there are still measureable oxidation weight gains in the investiaged temperature range. While some of this weight gain is due to oxide formation, an appreciable amount of this oxygen weight gain is due to oxygen diffusing into the metal. The increase in amount of α-Ti as a result of this oxygen diffusion could have significant effects on the mechanical properties of Beta-21S.

Conclusions

Analysis of the oxidation behavior of Beta-21S over the temperature range 600 to 800°C shows that it does have better oxidation resistance than c.p. titanium, but poorer resistance that titanium aluminides. While Beta-21S forms a compact layer of TiO_2, the data suggests that oxygen dissolution into metal is appreciable. Examination of the microstructures after exposure showed an increase in the amount of α-Ti with length of exposure, which should be linked directly with the diffusion of oxygen into the metal. This means that in the temperature range 600 to 800°C, exposure to air may severely degrade the mechanical properties of Beta-21S.

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Terryl A. Wallace
Ronald K. Clark
Karl E. Wiedemann

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