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Cyclic oxidation of copper doped Ti-48Al-2Cr-2Nb

J. W. FERGUS, V. L. SALAZAR, C. J. LONG, N. L. HARRIS, T. ZHOU, W. F. GALE
Material Research and Education Center, 201 Ross Hall, Auburn University, Auburn, AL 36849

The widespread use of titanium aluminide alloys will require effective joining techniques for primary fabrication and repair. One such technique is Transient Liquid Phase (TLP) bonding, which has been used to join titanium aluminide alloys. A successful TLP bonding process uses a copper-containing composite interlayer and thus introduces a small amount of copper into the alloy. Although even relatively small alloying additions can be detrimental to the oxidation resistance of titanium aluminide alloys, the amount of copper added to the alloy during the TLP bonding process has previously been shown to be neutral or beneficial to the isothermal oxidation resistance of the alloy. In this paper, a small amount of copper introduced during TLP bonding is shown to have no detrimental effect on the cyclic oxidation of Ti-48 at% Al-2 at% Cr-2 at% Nb.

1. Introduction

Titanium aluminide alloys are candidate materials for a number of high-temperature applications. However, use of these alloys requires techniques for joining the alloys during primary fabrication or for repair. One joining technique, which has been used successfully to join titanium aluminide alloys, is Transient Liquid Phase (TLP) bonding [1]. As applied to titanium aluminide alloys, this process involves melting a copper-containing composite interlayer, which then isothermally solidifies by diffusion of copper into the titanium aluminide alloy, resulting in small amounts of copper, typically less than 1 at%, being incorporated into the alloy. Since even small amounts of alloying additions can significantly degrade the oxidation behavior of titanium aluminide alloys [2–4], evaluation of the effect of copper on the oxidation resistance is required for TLP bonding, using copper-containing interlayers, to be adopted for joining titanium aluminide alloys.

Previous studies of the isothermal oxidation of copper-containing titanium aluminide alloys [5] have shown that, while large amounts (2–4 at%) of copper can be detrimental to the oxidation resistance, small amounts (1 at%) are neutral or slightly beneficial to the oxidation resistance. A similar trend was observed for cyclic oxidation [6]. While 1% Cu also did not significantly affect the cyclic oxidation rate, the detrimental effect of 2% Cu was enhanced (as compared to isothermal oxidation) during cyclic oxidation due to spallation of the oxide scale. At 1000°C, alloys with or without copper exhibited weight loss, but with increasing copper content the amount of weight loss increased and the time for onset of weight loss decreased.

Fortunately, the TLP bonding process introduces less than 1% Cu and most potential applications of these alloys are below 900°C, so the TLP bonding process is promising for many practical applications. In this paper, results on the cyclic oxidation of a Ti-48 at% Al-2 at% Cr-2 at% Nb with and without 1% Cu in air at 900°C are reported and discussed.

2. Experimental

2.1. Materials

The base material in the study, Ti-48 at% Al-2 at% Cr-2 at% Nb, was provided by NASA Glenn Research Center and had a typical duplex microstructure consisting of γ grains and lamellar colonies of alternating layers of γ and α_2 platelets. Copper was added by remelting the Ti-48 at% Al-2 at% Cr-2 at% Nb alloy with pure copper in a tungsten arc furnace with a copper hearth. The resulting alloys, and samples of the base alloy, were heated under vacuum from room temperature to 1150°C and held for 10 min and then heated to 1350°C and held for 1 h, which simulates the heat cycle during the TLP bonding process.

2.2. Oxidation experiments

Rectangular samples (10 × 10 × 2 mm) for the oxidation experiments were electrodischarge machined from stock of the as-received material or from the arc-melted and heat-treated buttons. The surfaces of all the samples were mechanically ground with SiC paper to 600 grit finish and ultrasonically cleaned in acetone.

The oxidation experiments were conducted in a box furnace in laboratory air ($\sim 10^5$ Pa) at 900°C. The

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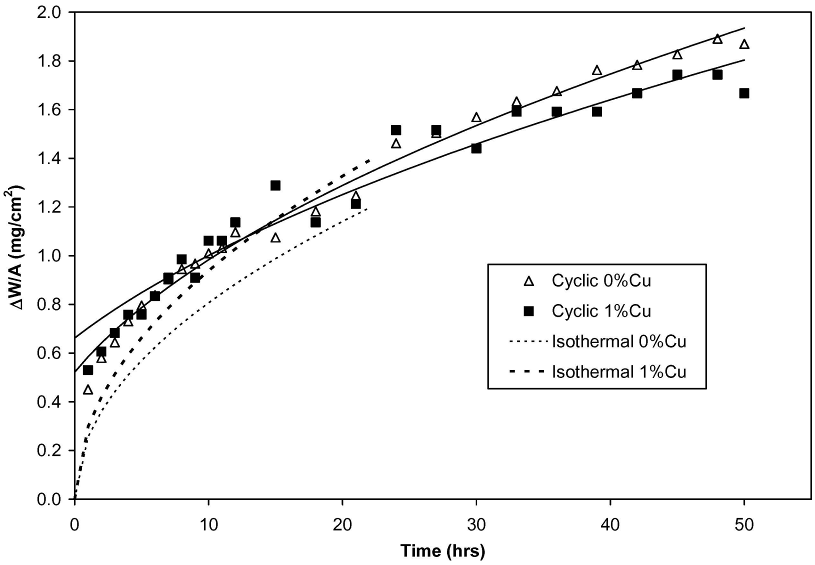

Figure 1 Weight change during isothermal [5] and cyclic oxidation (1-hour cycles) [6] of Ti-48 at% Al-2 at% Cr-2 at% Nb with 0 or 1 at% Cu in air at 900°C.

samples were tested simultaneously by placing each sample in a separate crucible at room temperature and placing the crucibles in the preheated box furnace. After one hour, the crucibles were removed from the furnace. Heating and cooling rates, as determined by welding a thermocouple to a similar-sized sample, showed that the sample reached the furnace temperature in 1–2 min and then reached room temperature in less than 5 min after being removed from the furnace [6]. The samples were allowed to cool for at least 20 min between cycles to ensure that they reached room temperature. For the first few cycles, the samples were weighed (±100 μg) before and after each oxidation cycle. After several cycles, the samples were exposed to up to three cycles between weight measurements. The samples were held in separate crucibles to keep any spalled oxides separated, but the amount of spalled oxide was not measurable for the samples discussed in this paper.

2.3. Characterization

The samples were examined using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). After oxidation, the samples were sectioned and mounted such that the oxidation scale could be observed in cross-section.

3. Results and discussion

The weight changes of the alloys with and without copper additions during cyclic oxidation at 900°C are shown in Fig. 1 [6]. The solid lines in Fig. 1 represent fits using a parabolic rate law (0.6–0.7 $\mathrm{mg^2\ cm^{-4}\ h^{-1}}$), which was followed through 50 h. Haanappel *et al.* [7, 8] observed a decrease in weight after longer exposures to cyclic oxidation of the same alloy at 900°C, with the maximum weight gain prior to weight loss being in the same range as the maximum weight gain observed in this work. The results in Fig. 1 indicate that the addition of 1% Cu does not significantly affect the oxidation rate for up to 50 hr at 900°C. For comparison, the broken lines in Fig. 1 represent the weight gains for the same alloys during isothermal oxidation [5], which, for both 0% Cu and 1% Cu, are in the same range as those for cyclic oxidation.

The scale formed on the alloy without copper addition is shown in Fig. 2. The numbers represent the locations at which EDS spectra were collected, the concentrations from which are summarized Fig. 3. As is typical of titanium aluminide alloys, the scale contains multiple layers. The outer layer is rich in titania and the middle layer is rich in alumina. The concentrations of both chromium and niobium decrease towards the outer scale surface. The scale formed on the alloy containing 1% Cu (Fig. 4) is similar. The concentrations of titanium and aluminum (Fig. 5) show similar trends as for the alloy without copper.

Fig. 6 shows the Al/Ti ratio at various regions in the scale formed in both cyclic and isothermal [5] oxidation. In both cases there is an alumina-rich layer in the middle of the scale. Since transport in alumina is much slower than through titania, this alumina-rich layer is important for good oxidation resistance.

Although copper is not present in the oxide, its presence in the alloy below the scale affects the concentration of other elements in the oxide scale. Specifically, the amount of chromium in the oxide scale is reduced, which is consistent with the results from isothermal oxidation [5]. The effect of copper additions has been attributed to copper tying up the chromium (presumably due to formation of an intermetallic compound containing both copper and chromium in the region that is observed to be rich in these elements, although the formation of such a phase has not been confirmed experimentally) at the alloy/scale interface and thus reducing the detrimental effect associated with small chromium additions [9].

Fig. 7 shows the Cr/Nb ratio at different regions in the scale. Ratios are not shown in the middle and outer layers, because the concentrations in those regions are too low to produce reliable ratios. One notable trend is that the Cr/Nb ratios in the oxide scales for the alloy

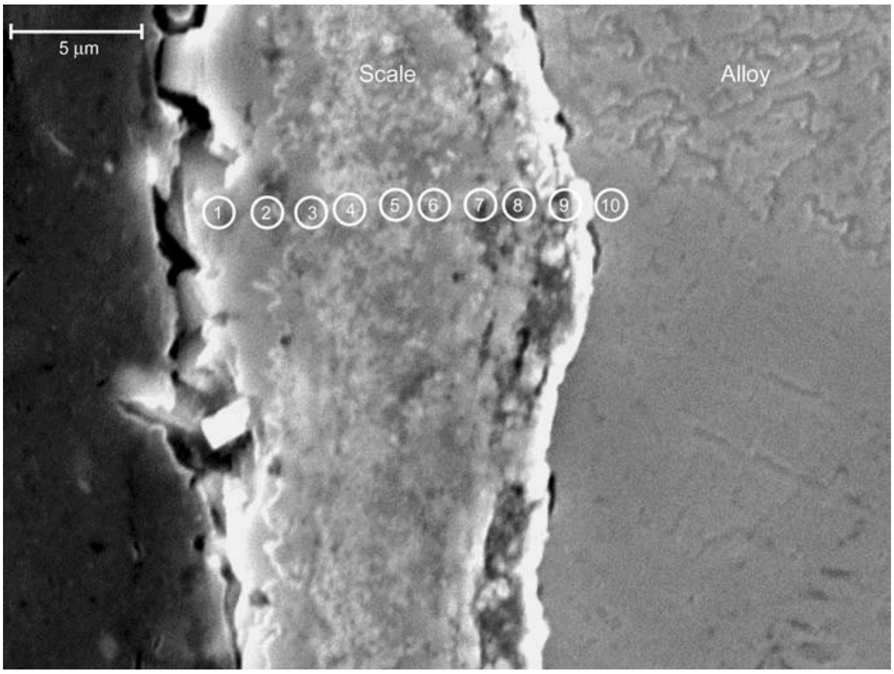

Figure 2 Secondary electron SEM micrograph of scale formed on Ti-48 at% Al-2 at% Cr-2 at% Nb after 50 1-hour cycles in air at 900°C.

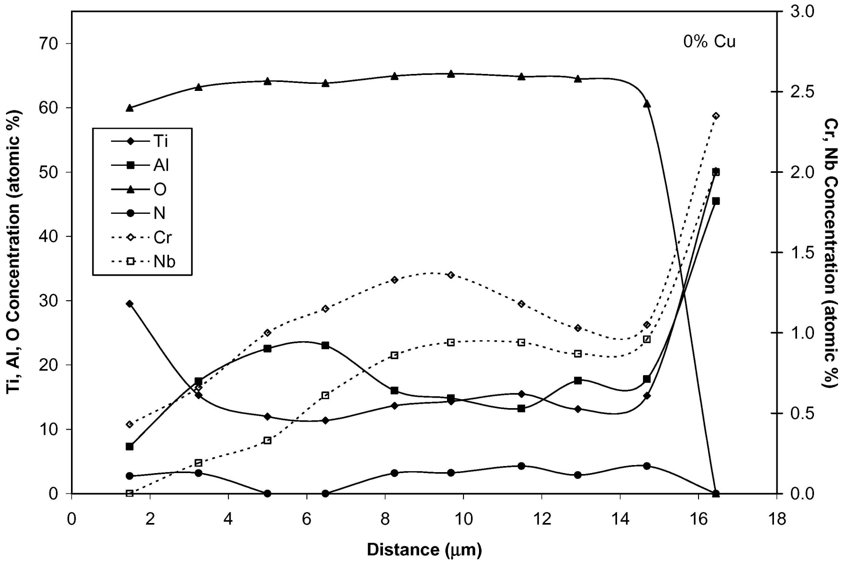

Figure 3 Compositions from EDS of scale formed on Ti-48 at% Al-2 at% Cr-2 at% Nb after 50 1-hour cycles in air at 900°C.

containing 1% Cu for both cyclic and isothermal oxidation are lower than the corresponding ratios for the alloy without copper. Also shown in Fig. 7 are the copper concentrations in each region. There appears to be a positive correlation between the copper content and the Cr/Nb ratio and the copper concentration, which provides evidence for interaction between copper and chromium. The interaction, however, does not appear to be as strong in the samples from cyclic oxidation as for those from isothermal oxidation.

To determine if the interface compositions are representative of the concentration along the alloy-scale interface, EDS spectra were collected at several locations in the interlayer and just below the scale surface. The average concentrations from these measurements (Table I) show that the copper is concentrated in these regions—particularly in the interlayer. Although the variation is large, the chromium and niobium concentrations in the interlayer are also higher than those in the bulk, and there is a strong correlation between the copper concentration and the concentrations of chromium and niobium, as is shown in Fig. 8. To focus on the distribution of metallic elements, and to compare the ratio of these elements to those of the alloy, only metal components (Ti, Al, Cr, Nb, Cu) were used for the concentrations in Fig. 8. Linear regression of the results for

TABLE I Average compositions in interlayer and in alloy below scale at measured by EDS

	Concentration (at%) standard deviation in parenthesis		
Region	Cu	Cr	Nb
Interlayer (20 measurements)	3.1 (1.4)	3.6 (1.6)	2.8 (1.1)
Alloy below scale (9 measurements)	1.7 (0.4)	2.2 (0.4)	2.0 (0.3)

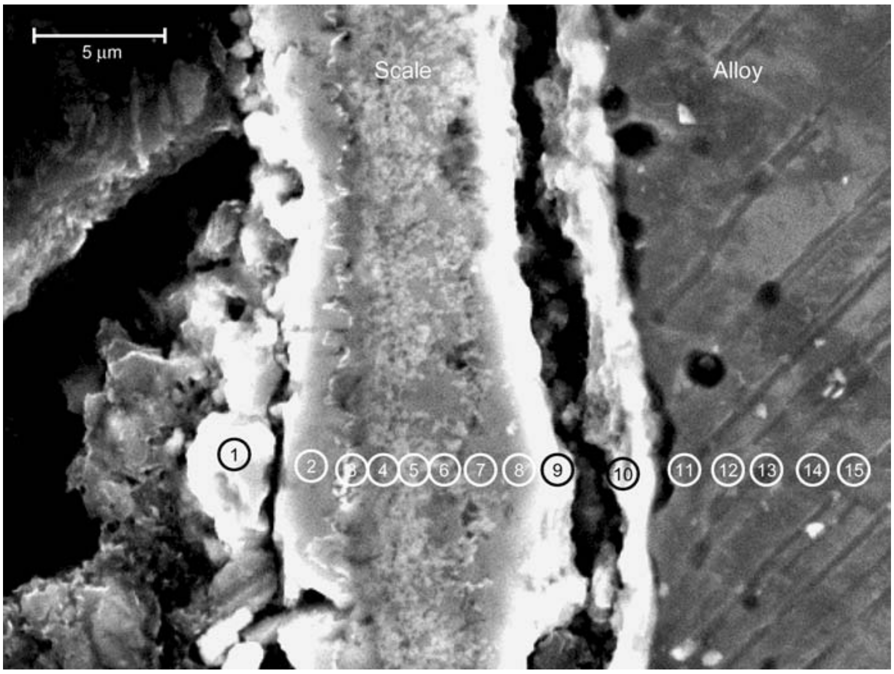

Figure 4 Secondary electron SEM micrograph of scale formed on Ti-48 at% Al-2 at% Cr-2 at% Nb with 1%Cu after 50 1-hour cycles in air at 900°C.

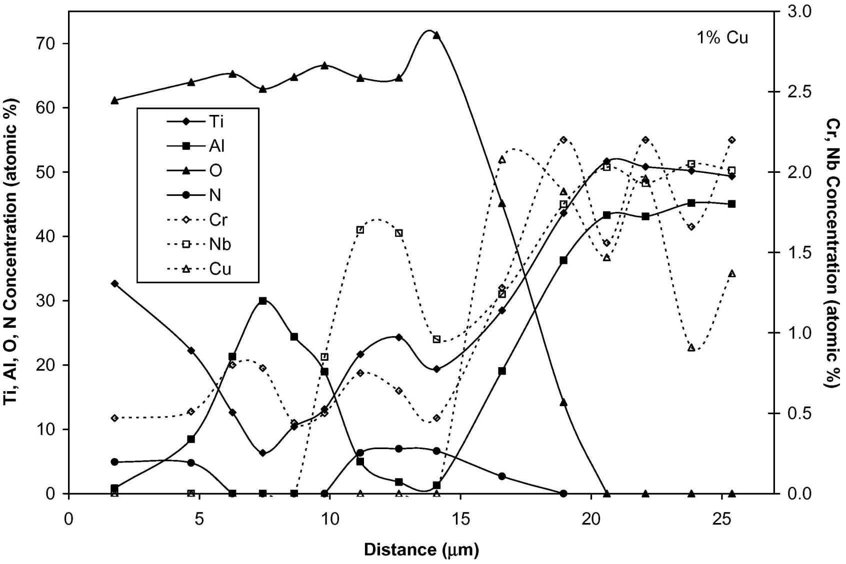

Figure 5 Compositions from EDS of scale formed on Ti-48 at% Al-2 at% Cr-2 at% Nb with 1%Cu after 50 1-hour cycles in air at 900°C.

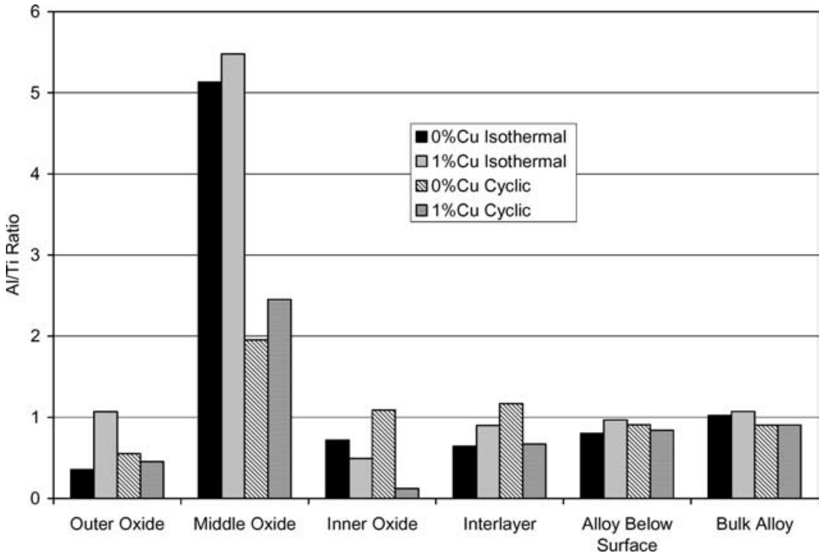

Figure 6 Ratio of Al:Ti from EDS analysis. Isothermal results from [5].

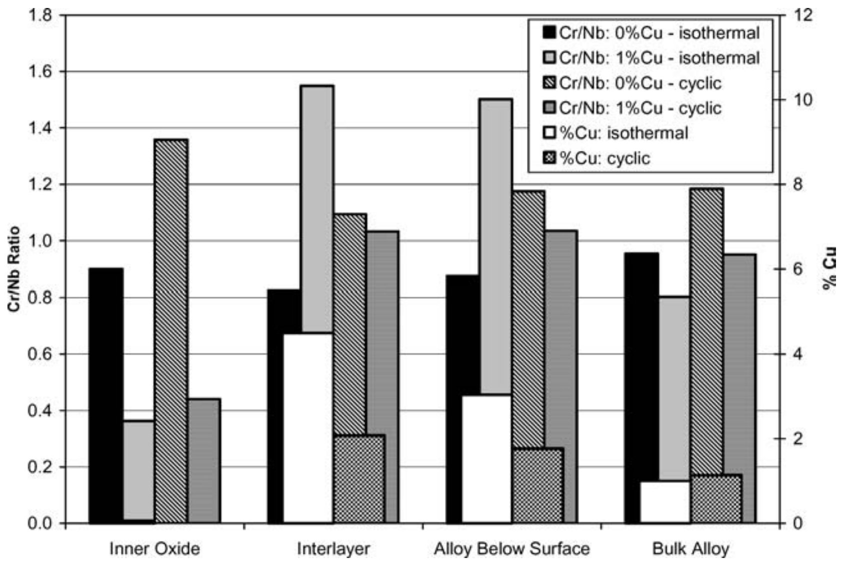

Figure 7 Ratio of Cr:Nb from EDS analysis. Isothermal results from [5].

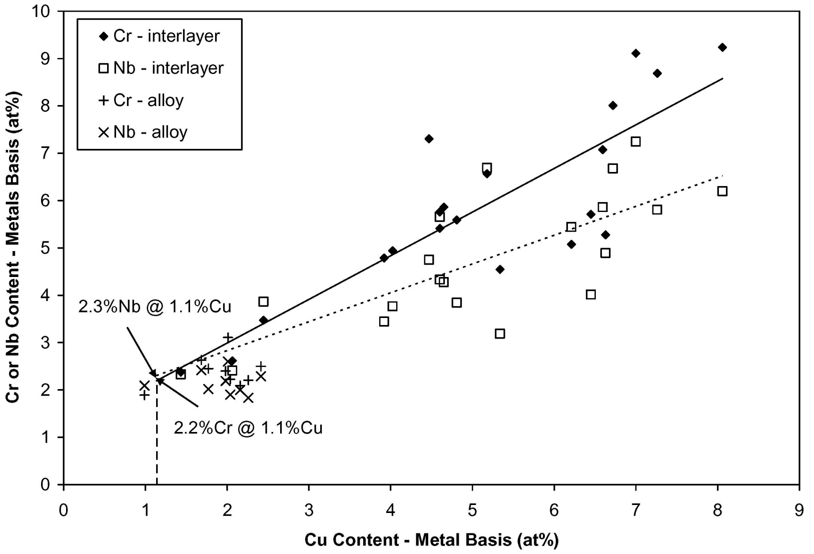

Figure 8 Correlation between Cu content and Cr or Nb content in the interlayer and alloy below scale. Compositions based on metallic elements (Ti, Al, Cr, Nb, Cu) only.

both chromium and niobium (represented by the lines in Fig. 8) extrapolate to near the bulk composition. This correlation suggests that an intermetallic compound, containing chromium and a lesser amount of niobium may exist, in which case the simultaneous increase in the concentrations of the three elements could be due to an increase in the amount of this intermetallic compound within the location from which the EDS spectra is collected.

A recent review of the effect of chromium and niobium on the cyclic oxidation of titanium aluminide alloys [10] shows that small amounts of chromium, although generally detrimental to the oxidation rate, appear to increase the scale thickness at which scale spallation occurs. This suggests that chromium may improve scale adherence or improve the mechanical properties of the scale. The high concentration of chromium in the interlayer observed in this work supports the latter, but additional work is needed to fully understand the effect of alloying additions on morphology, defect structure, strength and adherence of the oxide scale.

4. Conclusions

The amount of copper incorporated in a Ti-48 at% Al-2 at% Cr-2 at% alloy during Transient Liquid Phase (TLP) bonding, with a copper-containing composite interlayer, does not significantly affect the cyclic oxidation resistance at 900°C. The oxidation rate and the distribution of the alloying elements in the scale formed during cyclic oxidation are similar to those for the scale formed during isothermal oxidation. Copper is not present in the oxide scale, but interacts with other elements at the alloy-scale interface, which indirectly affects the composition of the oxide scale.

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