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Effect of Chromium on the Oxidation Resistance of TiAl Intermetallics

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The effect of 10 at.%Cr on the oxidation resistance of TiAl intermetallic compound at 800–1100°C in air was investigated. The results indicated that 10 at.%Cr equally substituting for Ti and Al in TiAl alloy had duplex effects on the isothermal kinetics of TiAl. At lower temperatures (800–900°C), Cr increased the oxidation rates as a result of the doping effect of Cr in the scale and at higher temperatures (1000–1100°C), especially at 1100°C, Cr significantly reduced the oxidation rates as a result of the formation of a continuous Al_2O_3 film on the surface. 10 at.%Cr only substituting for Ti in TiAl alloy remarkably reduced the oxidation rates at all temperatures by about two orders of magnitude. Moreover, 10 at%Cr significantly improved the cyclic-oxidation rsistance of TiAl alloy.

KEY WORDS: TiAl intermetallics; chromium; oxidation kinetics.

INTRODUCTION

TiAl-base intermetallics have received more attention as potential high-temperature structural materials because they have many properties beneficial to high-temperature applications, including low density, good high-temperature strength, and high stiffness especially at high temperature.[1,2] However, to develop these materials for real applications at elevated temperatures, their oxidation resistance must be considered because they possess insufficient oxidation resistance as a result of the formation of TiO_2 scales rather than Al_2O_3 on the surface and this problem has not been solved yet.

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To date, many studies dealing with the effects of ternary alloying elements on the oxidation resistance of TiAl-base alloys have been reported.[3-11] It was found that chromium at low concentrations <4 at.%) has a detrimental effect on the oxidation resistance of TiAl intermetallics and that at high concentrations (>10 at.%) has a beneficial effect.

In this paper, the effect of 10 at.% Cr on the oxidation resistance of TiAl was investigated.

EXPERIMENTAL PROCEDURES

Alloy Preparation

In order to study the effect of chromium on the oxidation resistance of the TiAl intermetallic compound, the following three alloys (nominal compositions, at.% added) were selected: A–Ti–50Al; B–Ti–45Al–10Cr; and C–Ti–50Al–10Cr. In alloy B, 10 at.% of Cr equally substitutes for both Ti and Al and in alloy C, 10 at.% of Cr substitutes only for Ti. The alloys were melted three times in a tungsten-arc furnace with a copper crucible. The specimens were cut from the ingots into pieces $10 \times 10 \times 2$ mm, and then polished through 800-grit SiC paper.

Oxidation Tests

Isothermal-oxidation tests were carried at 800, 900, 1000, and 1100°C in static air. For the Ti–50Al alloy, an electronic thermal-balance was used to measure the weight change continuously, because the severe spallation of scales formed on this alloy occurred during cooling. For the Ti–45Al–10Cr and Ti–50Al–10Cr alloys, the specimens were placed in alumina crucibles oxidized at the various temperatures and cooled to room temperature at regular intervals of 20 hr for weight measurements.

Cyclic-oxidation tests were conducted at 900–1100°C in static air. The specimens were kept at the desired temperature for 1 hr and cooled to room temperature for 10 min per cycle.

Specimen Analysis

After oxidation, the specimens were analyzed using optical metallography (OP), X-ray diffraction (XRD), and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX).

EXPERIMENTAL RESULTS

Isothermal Oxidation

Figure 1 shows the isothermal oxidation kinetics of Ti–50Al, Ti–45Al–10Cr, and Ti–50Al–10Cr at 800–1100°C in air. Ti-50Al shows very high weight gains which are about one order of magnitude higher than those of traditional nickel-base superalloys. Ti–45Al–10Cr possesses a little bit higher weight gains at 800 and 900°C and much less weight gains at 1000 and 1100°C than those of Ti–50Al. However, at all temperatures, Ti–50Al–10Cr shows much lower weight gains than those of Ti–50Al. It is very interesting to note that the weight gain for Ti–45Al–10Cr at 1100°C is much less than the weight gains at 800–1000°C. For Ti–50Al–10Cr, the weight gain at 900°C is higher that at 1000°C.

Figure 2 shows a cross-section of Ti–45Al–10Cr after 100 hr oxidation at 900°C. The scale exhibits a typical layered structure which is similar to that formed on Ti–50Al. The outer layer (I) is rather pure TiO_2, the inner layer (III) is a mixture of $TiO_2 + Al_2O_3$, and the middle layer is Al_2O_3-rich (II). The only difference is that there is chromium doping in the scale formed on Ti–45Al–10Cr. As a result of this, the weight gains of Ti–45Al–10Cr at 900°C or below are slightly higher than those of Ti–50Al. With increasing temperature the content of Al_2O_3 in the scale increased, and when the temperature was increased to 1100°C, pure Al_2O_3 scale formed on the surface of Ti–45Al–10Cr (Fig. 3). So the weight gains of Ti–45Cr–10Al were remarkably reduced at 1100°C.

Figure 4 shows a cross-section of Ti–50Al–10Cr after 100 hr oxidation at 1100°C. Predominate Al_2O_3 scales formed at all test temperatures, thus the weight gains of Ti–50Al–10Cr are much lower than those of Ti–50Al.

Cyclic Oxidation

Figure 5 shows the cyclic-oxidation kinetics of Ti–50Al, Ti–45Al–10Cr, and Ti–50Al–10Cr at 900–1100°C. For Ti–50Al, a weight loss was found only after ten cycles at 900°C, and severe weight losses were found at 1000 and 1100°C. For Ti–45Al–10Cr, the visible weight loss was observed only at 1000°C. For Ti–50Al–10Cr, however, no weight loss was observed. The weight gain of Ti–50Al–10Cr is a little bit higher than that during isothermal oxidation at 900°C and almost the same as that at 1000 and 1100°C.

For Ti–50Al, severe spallation of oxide scales occurred during cooling, so that a large weight loss occurred. For Ti–45Al–10Cr, slight spallation was found only at 1000°C, and for Ti–50Al–10Cr, no spallation was observed at any temperature. Figure 6 shows the surface morphology and a cross-section of Ti–50Al–10Cr after 100 cycles oxidation at 1100°C. The Al_2O_3 scale was very adherent on the substrate.

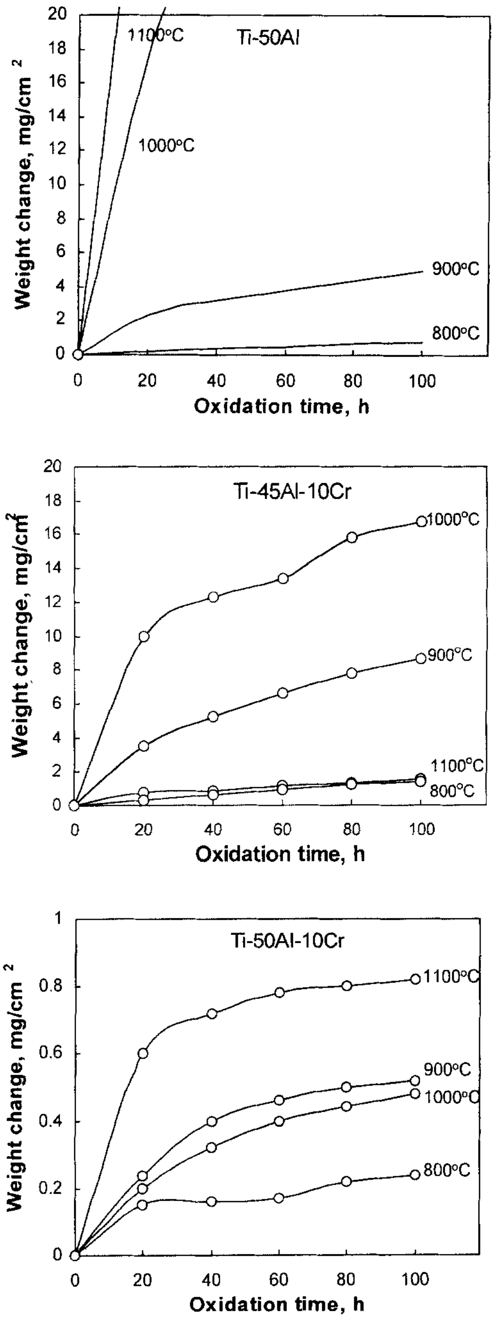

Fig. 1. Isothermal oxidation kinetics of alloys.

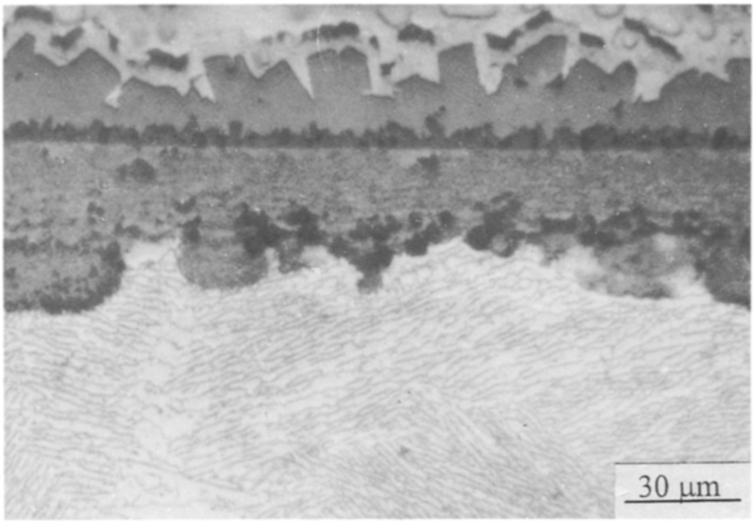

Fig. 2. Cross section of Ti–45Al–10Cr after 100 hr oxidation at 900°C.

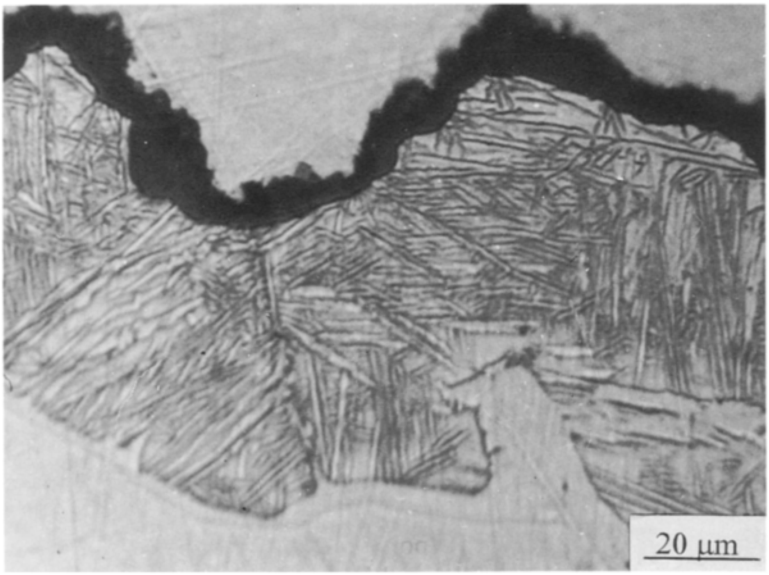

Fig. 3. Cross section of Ti–45Al–10Cr after 100 hr oxidation at 1100°C.

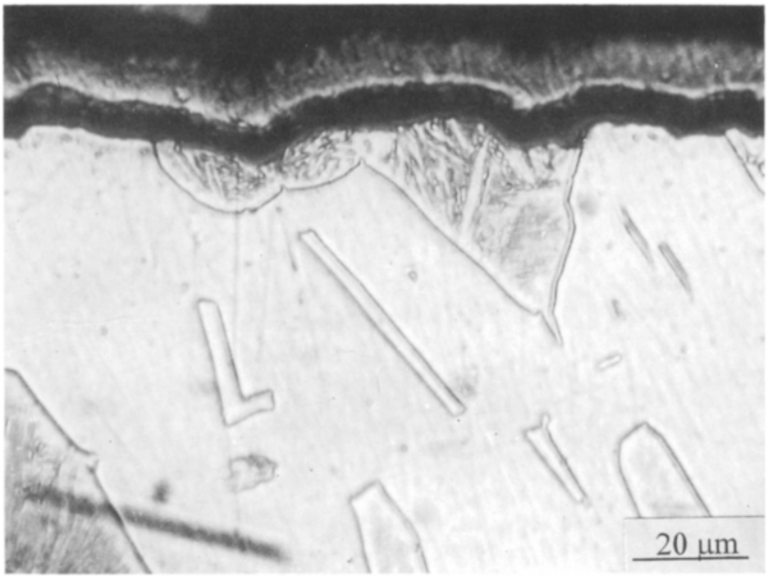

Fig. 4. Cross section of Ti–50Al–10Cr after 100 hr oxidation at 1100°C.

DISCUSSIONS

It is well known that for Ni–Al, Co–Al, and Fe–Al alloys, chromium additions may promote the formation of continuous Al_2O_3 scales on the surfaces, but the Al_2O_3 scales formed on these alloys are not adherent. In order to enhance the scale adhesion in M–Cr–Al systems, reactive elements such as Y, Ce, and Hf should be added. It is very interesting, however, that the Al_2O_3 scales formed on Ti–Al–Cr alloys are very adherent. For Ti–50Al–10Cr, neither cracking nor spalling was observed after 100 cycles from 1100°C to room temperature. The reason for this may come from the low thermal expansion coefficient of Ti–50Al–10Al. The thermal stress in the Al_2O_3 scale can be calculated by the following equation:

$$\sigma = E\frac{\Delta\alpha\Delta T}{1-\gamma}$$

where σ is the thermal stress, E is the Young's modulus of oxide, $\Delta\alpha$ is the thermal coefficient difference between substrate alloy and oxide scale, ΔT is the temperature change, and γ is poisson's ratio. From literature data and the data measured in this study listed in Table I, it is determined that the thermal stress of Al_2O_3 scales formed on Ti–50Al–10Cr alloy is much lower than in scales formed on MCrAlY alloys.

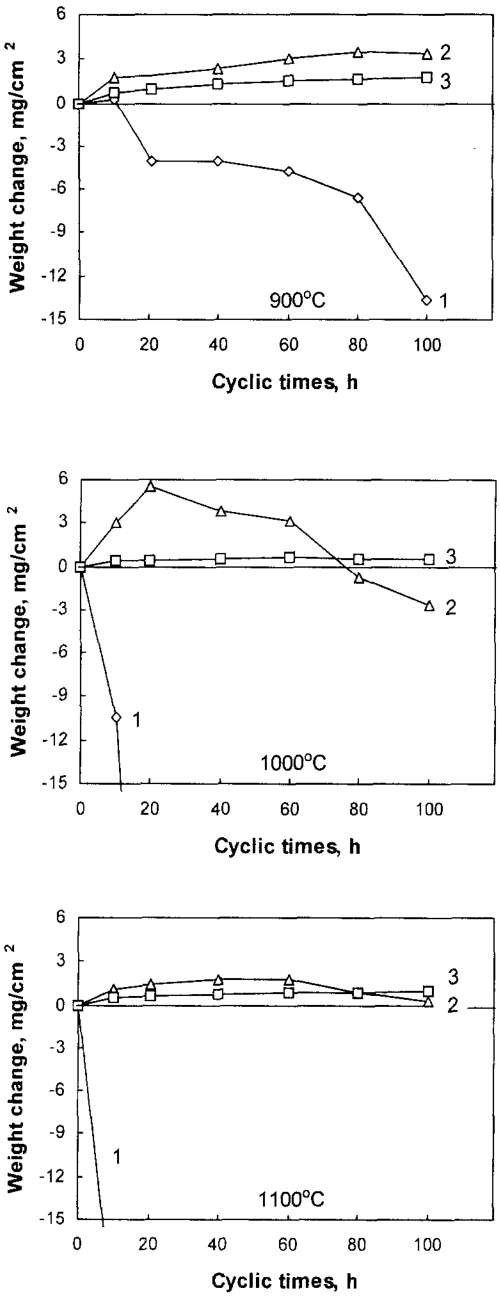

Fig. 5. Cyclic-oxidation kinetics.

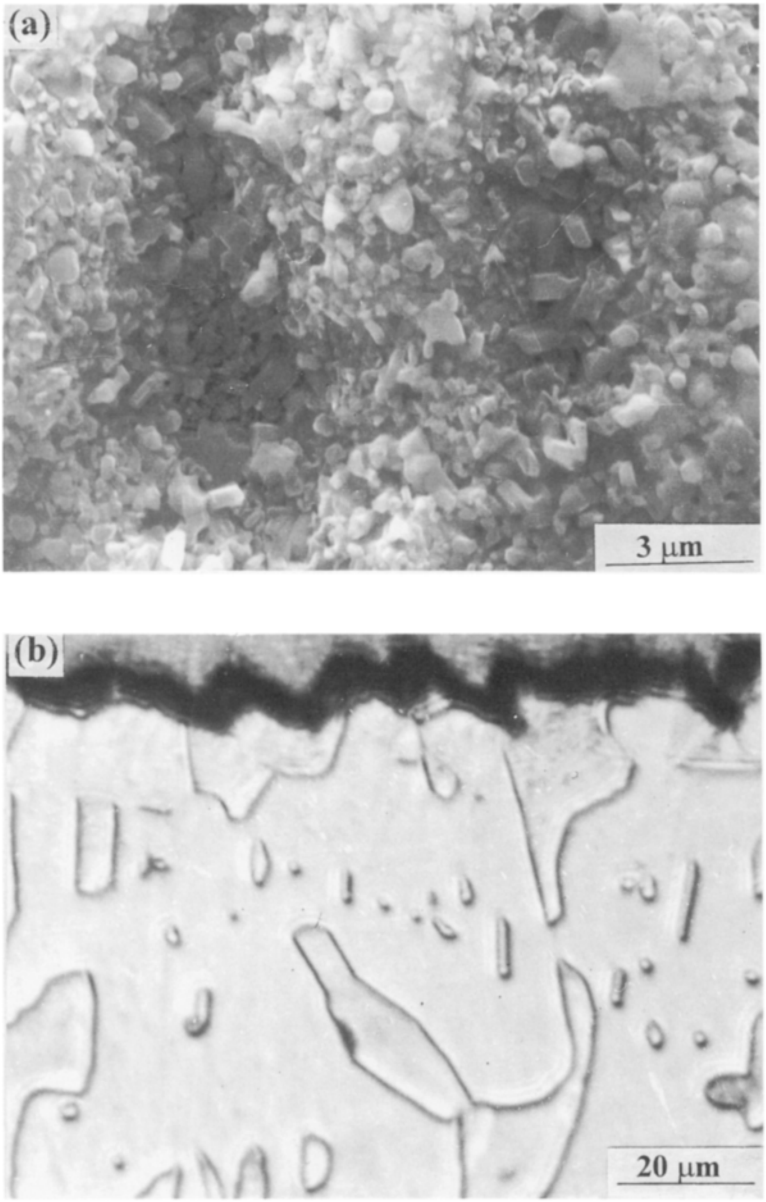

Fig. 6. Surface morphology (a) and cross-section (b) of Ti–50Al–10Cr after 100-cycles oxidation at 1100°C.

Table I. Comparison of Thermal Expansion Coefficients of TiAl, TiAlCr, MCrAlY Alloys and Al_2O_3

Material	Thermal expansion coefficient	Reference
CoCrAlY	$19 \times 10^{-6}\,°C^{-1}$	12
NiCrAlY	$17 \times 10^{-6}\,°C^{-1}$	12
FeCrAlY	$17 \times 10^{-6}\,°C^{-1}$	12
TiAl	$14.4 \times 10^{-6}\,°C^{-1}$	12
Ti–50Al–10Cr	$13.5 \times 10^{-6}\,°C^{-1}$	this study
Al_2O_3	$8.3 \times 10^{-6}\,°C^{-1}$	13

CONCLUSIONS

1. 10 at.%Cr additions substituting equally for both Ti and Al (Ti–45Al–10Cr) have duplex effects on the isothermal-oxidation kinetics. At lower temperatures (800 and 900°C), Cr additions are not enough to help the formation of Al_2O_3 scales, which promote rapid growing TiO_2 and increase the oxidation rates of TiAl alloy. At higher temperatures (1000 and 1100°C), however, Cr additions caused a significant improvement on the oxidation resistance of TiAl alloys due to enhanced formation of Al_2O_3-rich scales. Additionally, 10 at.%Cr additions improve the cyclic-oxidation resistance of TiAl alloys at all temperatures due to enhancement of the scale adhesion.

2. 10 at.%Cr additions substituting only for Ti (Ti–50Al–10Cr) remarkably improve both the isothermal and cyclic-oxidation resistance of TiAl alloys over the entire temperature range due to enhanced formation of Al_2O_3-rich scales which have excellent adhesion.

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