

High temperature oxidation behaviors of Ti-Cr alloys with Laves phase TiCr_2 ^①

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[Abstract] The high temperature oxidation behaviors of Ti-Cr alloys containing 18% ~ 35% Cr with Laves phase TiCr_2 were investigated at 650~ 780 °C for exposure up to 104 h. The results reveal that chromium content has critical significance to the oxidation resistance of the alloys. The scaling rates of the alloys with less than 21% Cr are higher than those measured for pure titanium, but for the alloys with more than 26% Cr their scaling rate is lowered by 1~ 2 times, under the same oxidizing conditions. Both an external and an internal oxidation layers were observed. The oxidation resistance enhancement by chromium alloying is contributed to the formation of a continuous and compact chromic oxide interleaf in the scale. Oxidation temperature significantly affects the scaling rates of Ti-Cr alloys, and the mass gain is doubled with a temperature change from 650 °C to 700 °C or from 700 °C to 780 °C, for the same exposure duration. TiCr_2 shows no negative influence on the high temperature oxidation resistance of the alloys.

[Key words] Laves phase; TiCr_2 ; Ti-Cr alloy; oxidation

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1 INTRODUCTION

With a high melting temperature, chromium is the sole refractory metal element with good high temperature oxidation resistance^[1], so it sounds reasonable that a Ti-Cr alloy with a high Cr content should have an outstanding oxidation resistance at high temperature and is a good candidate of high-temperature titanium alloys applied in aero industries^[2~6]. This work examines the oxidation behaviors of Ti-Cr alloys with Laves phase TiCr_2 in the range of 650~ 780 °C for exposure in air up to 104 h in order to make up a titanium matrix composite with good high temperature oxidation resistance and high mechanical properties in the future.

2 EXPERIMENTAL

The test alloys containing 18% Cr, 21% Cr, 26% Cr, 30% Cr and 35% Cr, with three phases: β -Ti and α -Ti as matrix and intermetallic TiCr_2 both distributed along the grain boundary and dispersed in the matrix, were prepared, respectively, whose fabrication was described in Ref. [7]. The specimens were cut from the as-annealed buttons to the size of 10 mm × 10 mm × 10 mm by electric discharge machining and then ground with Al_2O_3 papers before ox-

idation tests. Elemental Ti (99.8% purity) specimens were also used in all the tests for comparison.

Isothermal oxidation experiments in air were performed in a well resistance furnace at 650, 700 and 780 °C respectively. The specimens were firstly heated to the test temperature and then soaked. A specimen in every different composition was withdrawn from the furnace and cooled down in air to room temperature after the following desired exposure times: 20 h, 41 h, 70 h and 104 h, respectively.

Both the mass and the surface area of every specimen were measured before the tests and the oxidized specimens were weighed again to evaluate their mass gain from oxidation after the test.

The cross-section micrograph and element linear analysis of the scales on oxidized specimens were characterized by a scanning electron microscope (SEM) JSM-5600LV with an X-ray energy dispersive system.

3 RESULTS AND DISCUSSION

The isothermal oxidation kinetics curves of the test alloys at three temperatures are plotted in Fig. 1. The curves reveal that the oxidation resistance of Ti-Cr alloys containing less than 21% Cr is lower than that of pure titanium under the same testing condi-

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tion. The less the Cr content, the worse the oxidation resistance. By contrary, the alloys with Cr content above 26% are oxidized much slowly with only 1/2~ 1/3 of the mass gain per unit area of pure Ti for 104 h exposure, but the efficiency of oxidation resistance improvement by chromium additions becomes lower and lower with the increase of Cr content. On the other hand, the oxidation temperatures show a great influence on the oxidation resistance of all the test alloys, the mass gain is doubled with a temperature change from 650 °C to 700 °C or from 700 °C to 780 °C, for the same exposure duration.

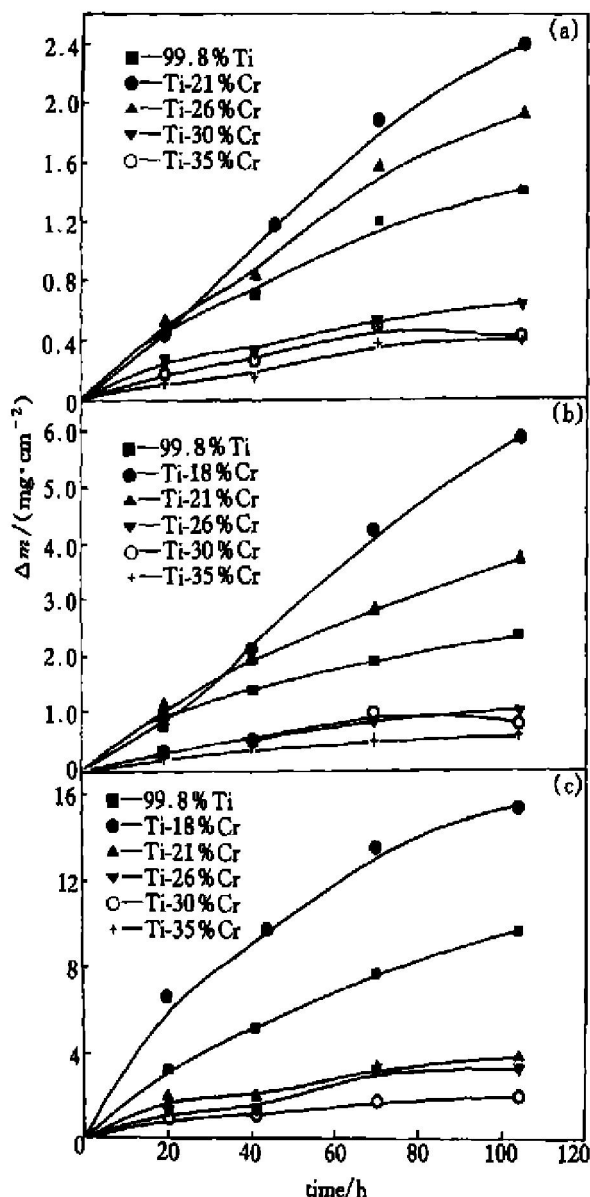


Fig. 1 Isothermal oxidation kinetics curves of alloys
(a) —650 °C; (b) —700 °C; (c) —780 °C

It is very difficult for Cr as an alloying element to form a selective oxidation chromic scale on a Ti-Cr alloy under common conditions because of both its aptency to oxygen and the stability of Cr₂O₃ inferior to titanic aptency to oxygen and the stability of TiO₂^[8,9], respectively. In order to study the high

temperature oxidation mechanism of the test alloys the cross section of the scales on both Ti-18% Cr and Ti-30% Cr alloys oxidized at 700 °C and Ti-30% Cr alloy oxidized at 780 °C, for 104 h exposure, have been examined by SEM-EDS. The cross-section micrographs and the element linear analysis of the scales are shown in Figs. 2 and 3.

Figs. 2 and 3 reveal that both an external and internal oxidations have taken place and the scale is composed of an external oxidation layer and an internal oxidation layer between which there is a distinct interface. The external oxidation layer, almost free from chromium, is only composed of titanic oxides and it can also be seen that there are some white clumps of TiCr₂ in the internal oxidation layer in Fig. 2(a).

The linear analysis of Ti, Cr and O in the scale of Ti-18% alloy in Fig. 2(a) indicates that although there is little difference of the Ti content between the internal oxidation layer and the external oxidation layer whose Ti content is a little higher than the former one's, an apparent change of Ti content occurs around their interface. Considering the above mentioned phenomena and the almost unchanged oxygen content in the external oxidation layer, we can come to a conclusion that the external oxidation layer keeps its growth by the combination of titanium in the form of ions (the radius of Ti⁴⁺: 0.069 nm and 0.149 nm for Ti atom^[8]) diffusing outside to the surface of the specimen with dissolved oxygen in the form of atoms (the radius of oxygen atom: 0.060 nm and 0.140 nm for O²⁻^[8]) diffusing inside through the having existed external oxidation layer at the interface.

In Fig. 2(a) there are some macroscopic holes in the external oxidation layer, providing advantages for the short-circuit diffusion of oxygen atoms, which explains why the oxygen content in the external layer is almost unchanged. The formation of holes in scales is always related to the congregation of supersaturated vacancies^[10]. TiO₂, an oxide with very few point defects, is so sensitive to impurities that its vacancy concentration can be rapidly increased even as a very small amount of alloying elements diffuses into it, and at the same time its protection to the alloy from further oxidation is heavily weakened. In the internal oxidation layer there is a typical bi-directional diffusion gradient of oxygen, which suggests that this layer, to some extent, can obstruct the diffusion of oxygen atoms toward the matrix and the diffusivity of oxygen atoms is the key controlling factor of the whole oxidation procedure. It should be noticed that it is the internal oxidation layer with little resistance to the diffusion of titanic ions that makes itself obviously thinner than the external one as shown in Fig. 2(a).

Both titanic and chromic oxides can be formed in

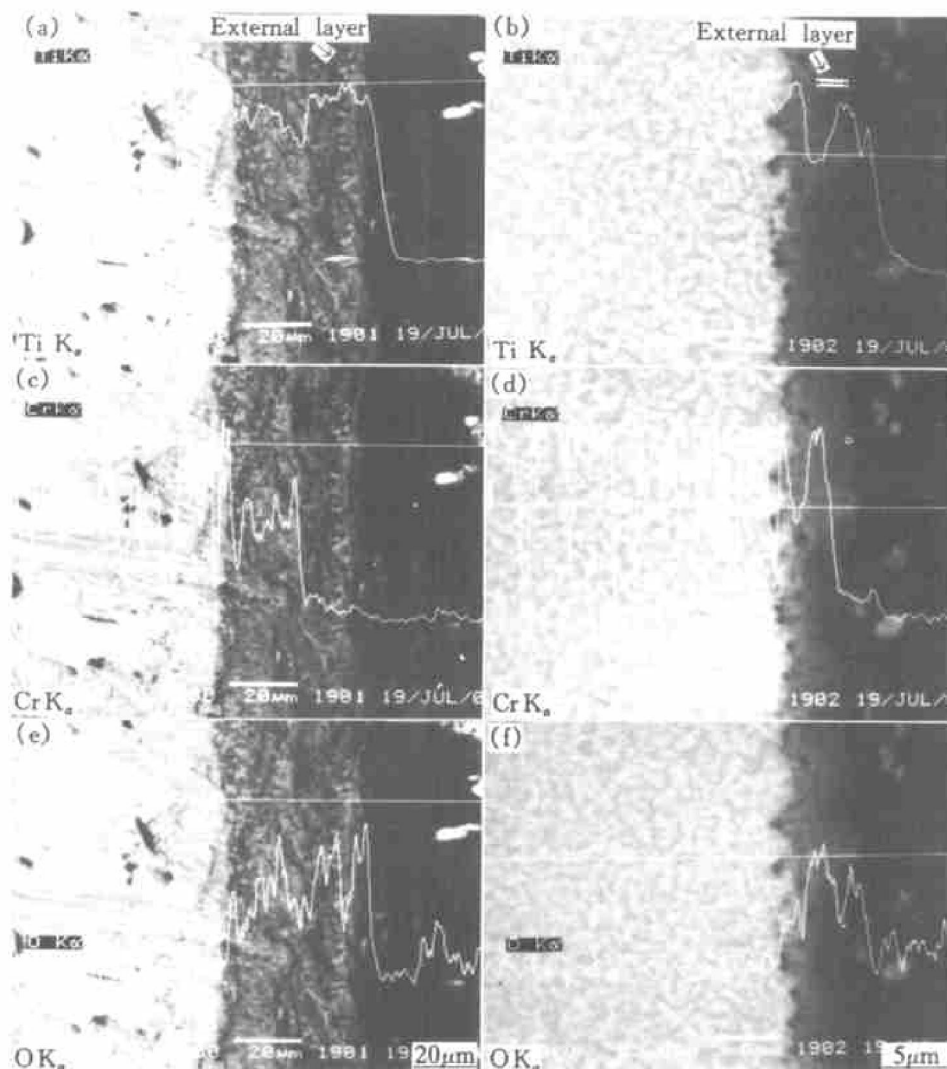


Fig. 2 SEM micrographs and element linear analyses of cross section of scales at 700 °C after 104 h exposure for (a, c, e) Ti-18%Cr alloy and (b, d, f) Ti-30%Cr alloy

the internal oxidation layer due to the coexistence of titanite and chromite ions as well as oxygen atoms. The growth rate of TiO_2 as an oxide with superfluous cations depends on the concentration of the cations in it, so that the alloying of chromium whose valence electrons are less than those of titanium will raise the concentration and make the oxidation speed up. As a result, Ti-Cr alloys, such as those with chromium below 21% in our test, show a poor oxidation resistance because of its too low chromium content to form a continuous and compacted chromite oxide interleaf in the internal oxidation layer.

For a comparison with the scale in Fig. 2(a), there are some distinctive features in the cross-section micrograph and element linear analysis of the scale in Fig. 2(b). At first, although the scale still consists of two layers, they both are thin and uniform and their compactness has been improved markedly. Then there is a jagged metal-scale interface, which implies that the adherence of the scale to the matrix, one of the key factors affecting the oxidation protection to an alloy offered by its scale, has been improved. Finally

the most important feature which determines why Ti-Cr alloys with chromium above 26% has an outstanding oxidation resistance maybe is that there is an apparent interleaf with high chromium and low titanium in the internal oxidation layer, making it possible to form a continuous and compacted Cr_2O_3 interleaf. Cr_2O_3 , an insulating oxide, can intensively retard the diffusion of electrons, furthermore its $\alpha\text{-Al}_2\text{O}_3$ type crystal lattice with extremely few point defects is a strong obstacle to the diffusion of both cations and anions through it^[11].

The cross-section micrographs and linear analysis of the scale on Ti-30%Cr alloy oxidized at 780 °C for 104 h are shown in Fig. 3. The linear analyses of Ti and Cr resemble those shown in the case of Ti-30%Cr alloy oxidized at 700 °C, but the oxygen content appears higher and shows little change across the whole scale, which indicates that the scale is no longer an effective obstacle to the diffusion of oxygen atoms when the oxidation temperature rises to as high as 780 °C. Therefore, as it is shown in Fig. 3, the oxidation of the alloy mainly takes place at the metal

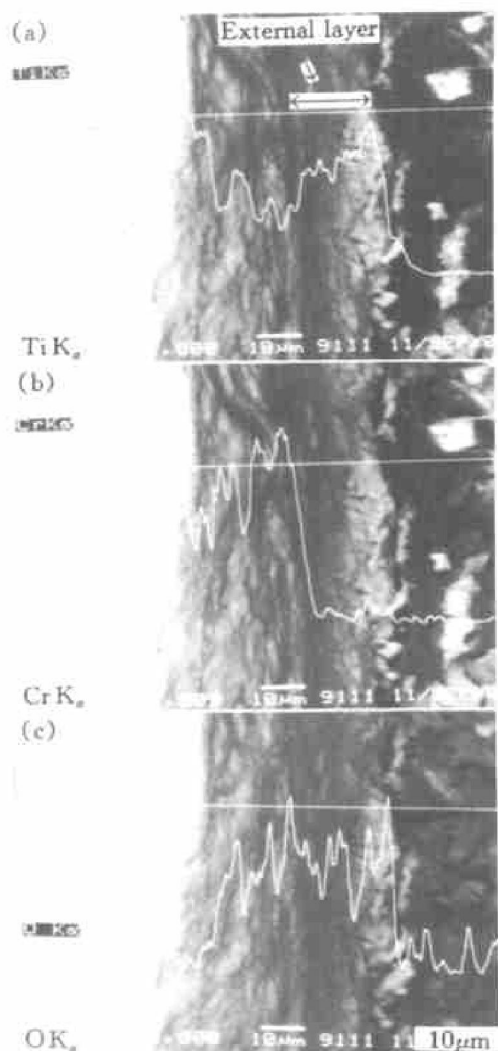


Fig. 3 SEM micrographs and element linear analyses of cross section of scale at 780 °C after 104 h exposure for Ti-30% Cr alloy

scale interface and the internal oxidation layer looks thicker than the external one. The reason why the oxidation resistance of Ti-Cr alloy containing more than 26% Cr becomes poor at 780 °C maybe come down to the following: 1) β -Ti of BCC becomes the main phase in the matrix of the alloy at 780 °C. The diffusivity of ions and atoms in β -Ti is higher than that in α -Ti of HCP^[12] and the higher the temperature, the higher their diffusivity. 2) The concentration of point defects in Cr₂O₃ is rapidly increased as a result of the enhancement of the diffusivity of impurities; so that its obstruction to metallic ions and oxygen atoms, or its compactness, is worsen. 3) Some multiplex oxides with low compactness maybe formed in the internal oxidation layer at 780 °C.

The oxidation of a hypereutectoid Ti-Cr alloy with Laves phase TiCr₂ is a very complicated oxidation procedure of a binary alloy with three phases, in which it becomes difficult for us to observe self-existent white TiCr₂ clumps in the scale as the temperature becomes higher and higher, as shown in Figs. 2 and 3, but we can still make a conclusion, after the comparison of all the isothermal oxidation kinetics curves in Fig. 1, that TiCr₂ has no negative influence on the oxidation resistance of the Ti-Cr alloys in the test.

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