EFFECT OF OXYGEN ON THE SCALE RESISTANCE OF TITANIUM – TIN ALLOYS

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UDC 669.295'6'787:620.191.32

Alloying of titanium with tin lowers its heat resistance [1, 2]. The heat resistance of titanium alloys with tin (up to 9%) at 700-1000°C was investigated in [1]. It was found that the heat resistance of titanium decreases with the addition of tin, particularly with 9% Sn.

The heat resistance of titanium alloys with tin (up to 20%) was investigated in [2], where it was found that tin lowers the scale resistance of titanium.

An investigation of phase equilibrium in the Ti–Sn–O system showed the presence of a broad range of α solid solutions. Alloys located in this region (up to 5% O) may be of interest as secondary alloys based on oxidized titanium wastes containing tin, and therefore it is of interest to determine the effect of oxygen on the properties of binary titanium alloys with tin, particularly the heat resistance [3]. Preliminary studies of the heat resistance and mechanical properties of Ti–Sn–O alloys showed that the optimal amount as an alloying addition is 0.35% (1 at.%).

This work concerns the effect of 0.35% O on the scale resistance of binary titanium alloys with tin under the same conditions in which the scale resistance was determined for binary Ti–Sn alloys, i.e., at 700-1000°C in air.

We investigated Ti–Sn–O alloys with 0, 2.5, 5, 7.5, and 10% Sn and 0.35% O. Alloys weighing 0.5 kg were prepared by melting with a nonconsumable electrode in an atmosphere of purified argon. To obtain a homogeneous composition the ingots were remelted three times. The original materials were iodide titanium, ChDA tin, a Ti–Sn alloy with 45.4% Sn, and a Ti–O alloy with 20.5% O. The alloys were forged at 1000° and annealed at 800°.

Ground cylindrical samples with a diameter of 5 mm and height of 20 mm were oxidized to constant weight at 1100°. They were heated in muffle furnaces without forced circulation of air. The alloys were oxidized at 700, 800, and 1000° for 1-20 h.

Figure 1 shows the variation of weight gain with time for Ti–Sn–O alloys oxidized at 700, 800, and 1000°. The weight increase Δp (the ratio of the absolute weight increase, mg, to the total surface of the

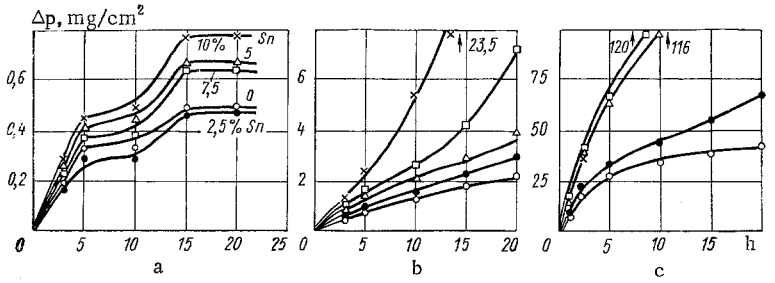

Fig. 1. Weight increase vs oxidizing time for Ti–Sn alloys with 0.35% O at different oxidizing temperatures. a) 700°C; b) 800°C; c) 1000°C.

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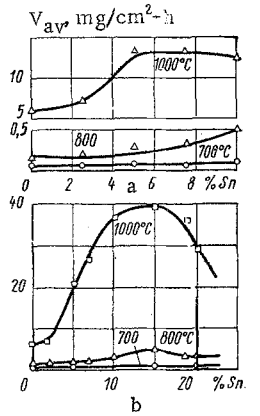

Fig. 2. Average oxidation rates at different temperatures vs tin content of Ti–Sn + 0.35% O alloys (a) and Ti–Sn alloys (b) (according to data from [2]).

sample, cm^2) is plotted along the x axis. The samples were weighed on analytical balances with an accuracy of 0.0002 g before and after oxidation.

The results indicate that the scale resistance of the alloys decreases with increasing concentrations of tin at all temperatures tested. However, the rate of decrease of the scale resistance is substantially lower for the ternary alloys than for binary alloys of titanium with tin. Comparison of the oxidation curves of binary Ti–Sn alloys [2] with the results from the present investigation indicate that the addition of 0.35% O to titanium alloys with 5-7% Sn lowers the susceptibility to oxidation by a factor of 3-5.5 at 800° and a factor of 1.5 at 1000° in tests for 20 h.

From the variation of the weight gain with time we calculated the average oxidation rate of Ti–Sn alloys with 0.35% O at the three temperatures indicated after the initial oxidation period, defined as the linear portion of the curve. Figure 2a shows the variation of the average oxidation rate with the tin content of the alloys. Figure 2b shows the average oxidation rate of binary Ti–Sn alloys as a function of tin content, which was calculated in the same manner from data in [2]. The comparison indicates that the presence of 0.35% O in solid solutions of Ti–Sn increases the resistance of the alloys to oxidation.

The outward appearance of the samples after oxidizing for 20 h at these temperatures showed that all alloys are coated with a thin silvery film after oxidation at 700°. The largest weight increase of samples with 10% Sn at this temperature was 0.7 mg/cm^2 (Fig. 1).

After oxidation at 800° the samples were coated with a dense white layer of tightly adherent scale. At the metal–scale interface beneath this layer there was a black layer that increased in thickness with increasing concentrations of tin in the alloy.

With oxidation at 1000° there were no qualitative changes in the oxide films, although the upper layer became very loose and was easily peeled from the substrate.

The samples were sectioned for phase analysis of the scale after different oxidizing treatments of the ternary alloys. The scale was analyzed in the URS-50-IM diffractometer, using Cu radiation and a nickel filter, at a speed of 2 deg/min. It was found that the outer layer of thick white scale consists only of TiO_2, while the scale next to the metal consists of TiO and metallic tin with TiO_2.

Figure 3 shows the x-ray patterns for the metal–scale interface in a sample of Ti + 10%Sn + 0.35% O oxidized at 1000° for 20 h. The data calculated from the x-ray patterns are given in Table 1.

The data obtained indicate that the layer of scale at the metal–oxide interface consists mainly of TiO and metallic tin. It should be noted that the density of this layer increases with the tin content of the alloy.

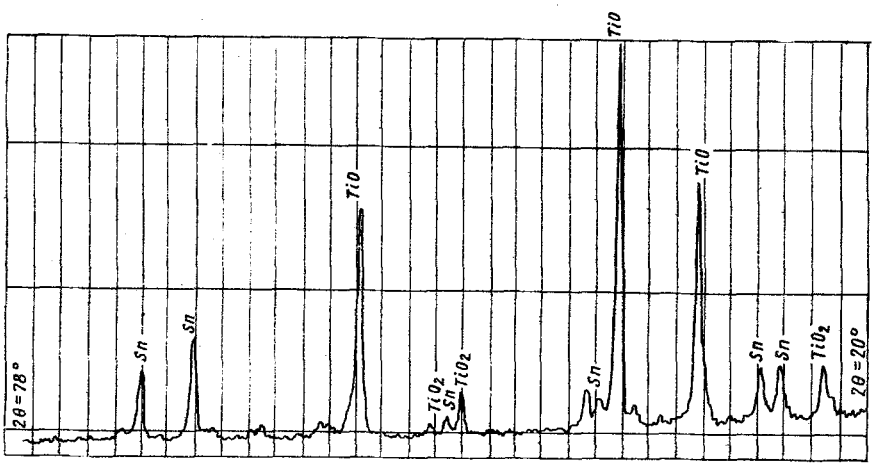

Fig. 3. Diffraction pattern of Ti + 10% Sn + 0.35% O oxidized at 1000°C for 20 h.

TABLE 1

2θ	θ	d Å	TiO	TiO_2	Sn
27°15′	13°40′	3,25	—	3,23	—
30°20′	15°10′	2,95	—	—	2,91
31°50′	15°50′	2,80	—	—	2,79
36°30′	18°15′	2,45	2,41	—	—
42°30′	21°15′	2,12	2,08	—	—
43°45′	21°50′	2,06	—	—	2,05
44°45′	22°20′	2,02	—	—	2,01
54°00′	27°00′	1,70	—	1,68	—
55°00′	27°30′	1,66	—	—	1,65
56°30′	28°15′	1,63	—	1,62	—
61°45′	30°50′	1,50	1,472	—	1,48
74°30′	37°15′	1,27	—	—	1,298
78°00′	39°00′	1,22	—	—	1,20

Thus, the intensity of reflections of metallic tin from the alloy with 10% Sn is higher than from the alloy with 5% Sn oxidizing at the same temperature.

The results of the investigation confirmed our assumptions concerning the oxidation mechanism of pure titanium and its alloys with tin. It was shown in [4-6] that with oxidation of titanium in air even at temperatures below 1000° there is not only diffusion of oxygen into the metal but also diffusion of titanium ions through the scale, which is confirmed by the presence of growth texture in the outer layer of scale. At temperatures above 1000° the diffusion of titanium ions increases; at 1100-1200° it becomes the determining stage of oxidation [7].

According to [1], two-way diffusion also occurs during oxidation of binary Ti–Sn alloys, as was confirmed by structural indications. The presence of metallic tin at the metal–scale interface led these authors to conclude that tin, diffusing into the upper layer from the solid solution leaves vacancies and facilitates the diffusion of titanium. For this reason the alloying of titanium with tin induces a considerable reduction of the scale resistance at 700-1000° [1].

Our data on ternary Ti–Sn–O alloys, as compared with Ti–Sn alloys, indicate that the oxidation mechanism of the alloys is identical, but the oxidation rate is lower when oxygen is added to the binary Ti–Sn alloys. Evidently this is explained by the strong interatomic bonds between the binary and ternary α solid solutions. Alloying of titanium with tin lowers the strength of interatomic bonds [8, 9]. The addition of oxygen to binary Ti–Sn alloys increases the modulus of elasticity and reduces the mean-square displacement of atoms, which indicates an increase in the strength of interatomic bonds in the lattice of the ternary α solid solution.

Thus, the presence of oxygen in binary Ti–Sn alloys prevents diffusion of titanium to the scale during oxidation and lowers the oxidation rate of the alloys due to the higher strength of interatomic bonds in the lattice of the solid solution.

CONCLUSIONS

1. The scale resistance of Ti–Sn–O alloys at 700-1000° with up to 10% Sn and with 0.35% O indicates that the presence of oxygen in Ti–Sn alloys lowers the oxidation rate at all temperatures tested. However, the oxidation rate still tends to increase with the tin content of the alloy.

2. The oxidation mechanism of binary Ti–Sn and ternary Ti–Sn–O alloys at these temperatures is the same. An increase in the strength of interatomic bonds due to solution of oxygen in binary solid solutions of Ti–Sn slows down the diffusion of titanium during oxidation and explains the increase in the scale resistance of Ti–Sn–O α solid solutions.

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