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Abstract

Full Text

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THIN OXIDE FILMS ON TITANIUM, ZIRCONIUM, MOLYBDENUM, AND TITANIUM ALLOYS

(Presented by Academician A. N. Frumkin, April 28, 1960)

A large number of works (1–3) have been devoted to the question of the oxidation of titanium, zirconium, and molybdenum at temperatures above 300°. But very little information is available on the oxidation of these metals in the temperature range 20–300°. The aim of the present investigation was also to study the kinetics of oxidation of Ti, Zr, Mo, a Ti alloy with 10% Mo, and a Ti alloy with 3% Al and 5% Cr, specifically in the temperature range 50–400°.

In the investigations the previously described (1,4,5) optical polarization method was used for measuring the thicknesses of thin invisible films forming on metals; it is based on the study of the character of the ellipticity of light reflected from the surface under investigation. The initial surface was taken to be the surface of the metal specimen after polishing and thorough degreasing (in a Soxhlet apparatus). Thus the subsequent oxidation at specified elevated temperatures led to the thickening of the already existing "natural" oxide film on the surface of the metal, which was not taken into account in the calculation of the thickness measurements. Oxidation was carried out in a tube furnace in a stream of oxygen. The duration of the oxidation process for each temperature was 6 hr. Measurements of film growth were made every 60 min; for this purpose the specimens were removed from the furnace and rapidly cooled. After the measurement was completed, the specimens were again placed in the furnace. The entire oxidation cycle for the whole temperature range (50–400°) was carried out on the same specimen.

Fig. 1. Change in film thickness as a function of temperature and oxidation time: 3 –Ti alloy with 10% Mo, 4 –Ti alloy with 5% Cr and 3% Al, 5 –Ti

Figures 1 and 2 give the results of measurements (the mean of several determinations) of the growth of the oxide film on the metals and alloys studied as a

Fig. 2. Change in film thickness as a function of oxidation temperature and time: 1 –Zr, 2 –Mo

Figure 2: Fig. 2. Change in film thickness as a function of oxidation temperature and time: 1 –Zr, 2 –Mo

Fig. 3. Change in oxidation rate with temperature: 1 –Al, 2 –Cr, 3 –Ti, 4 –Zr, 5 –Mo, 6 –Ti alloy with 5% Cr and 3% Al, 7 –Ti alloy with 10% Mo

Figure 3: Fig. 3. Change in oxidation rate with temperature: 1 –Al, 2 –Cr, 3 –Ti, 4 –Zr, 5 –Mo, 6 –Ti alloy with 5% Cr and 3% Al, 7 –Ti alloy with 10% Mo

function of time. Table 1 summarizes the values of the oxide-film thickness after a 6-hour oxidation cycle of the specimens studied.

The data obtained show that oxidation becomes noticeable at 50° for Zr, at 100° for Ti and the alloy Ti + 10% Mo, and at 150° it is also noticeable for Mo and the alloy Ti + 5% Cr + 3% Al. On examining the curves presented, it can be seen that at the initial temperatures of the investigation, for all the metals and alloys studied, the oxidation rate, rapid at first, practically falls to zero and oxidation ceases when the forma-

···the forming layer of the reaction product reaches a certain limiting thickness. In this case, the change in the thickness of the oxide film with time can be expressed mathematically by a logarithmic equation:

$$L = k \lg(k_1 t + k_2). \qquad (1)$$

Plotting the thickness of the oxide layer as a function of the logarithm of time gives a straight line.

Fig. 2. Change in film thickness as a function of oxidation temperature and time: **1** –Zr, **2** –Mo

Fig. 3. Change in oxidation rate with temperature: **1** –Al, **2** –Cr, **3** –Ti, **4** –Zr, **5** –Mo, **6** –Ti alloy with 5% Cr and 3% Al, **7** –Ti alloy with 10% Mo

Upon transition to higher temperatures, when the slope of the film-thickness/time curves begins to change, the oxidation rate obeys a parabolic dependence

$$L^2 = k_3 t. \qquad (2)$$

The stability of the surface oxides decreases as the temperature rises, and the oxidation rate is determined by the rate of diffusion of ions in the crystal lattice of the oxide. In this case a linear dependence is obtained if the film thickness is plotted against the square root of time. In both equations (1) and (2), L denotes the thickness of the oxide film, and t is time.

Table 1 shows the temperature ranges within which, for each metal and alloy studied, one of the above laws of the oxide growth rate was established.

After certain temperatures, different for different metals, have been reached, the oxidation rate increases rapidly (Fig. 3). For Zr and Mo, rapid film growth is observed after 200°; for the Ti + 10% Mo alloy, for Ti, and for the Ti + 5% Cr + 3% Al alloy—after 350°.* Noteworthy is the— the fact that within the range 200–400°, despite the sharp increase in the oxidation rate of Mo, the oxidation rate of the Ti alloy with 10% Mo is lower than that of Ti.

The composition of the oxide film on titanium, obtained in an atmosphere of oxygen or air at temperatures not exceeding 800°, is TiO_2 with the rutile structure ([6], [11], [12]). At oxidation temperatures above

Table 1

Metal, alloy	at 50°	at 100°	at 150°	at 200°	at 250°	at 300°	at 350°	at 400°	Composition of the oxide films at room temperature	Activation energy of the oxidation process, kcal/mol
Titanium (iodide)	no change	logarithmic	logarithmic	parabolic	parabolic	parabolic	parabolic	parabolic	TiO_2 (rutile) ([6])	250–300°10 000

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* The chromium and aluminum oxidation curves shown in Fig. 3 are taken for comparison from the data of T. N. Krylova ([9]).

Metal, alloy	at 50°	at 100°	at 150°	at 200°	at 250°	at 300°	at 350°	at 400°	Composition of the oxide films at room temperature	Activation energy of the oxidation process, kcal/mol
Zirconium (iodide)	logarithmic	logarithmic	logarithmic	parabolic	parabolic	parabolic	parabolic	parabolic	ZrO_2, cubic lattice up to 250°C with transition to monoclinic as the temperature is increased (⁷)	200–250°21 200

Metal, alloy	at 50°	at 100°	at 150°	at 200°	at 250°	at 300°	at 350°	at 400°	Composition of the oxide films at room temperature	Activation energy of the oxidation process, kcal/mol
Molybdenum (technical)	no change	no change	parabolic	parabolic	parabolic	parabolic	parabolic	parabolic	MoO_3 up to 300°; above 300° — MoO_3 and MoO_2 (8)	150–300°20 000
Titanium + 10% molybdenum	no change	logarithmic	logarithmic	parabolic	parabolic	parabolic	parabolic	parabolic	apparently, a solid solution of TiO_2 and x MoO_3	200–350°12 000
Titanium + 3% aluminum + 5% chromium	no change	no change	logarithmic	logarithmic	logarithmic	logarithmic	parabolic	parabolic	apparently, a solid solution of TiO_2, x Cr_2O_3 and y Al_2O_3	

800° the formation of layered films is observed, consisting of a TiO layer adjacent to the metal–oxide boundary, a middle layer of Ti_2O_3, and an outer TiO_2 layer at the oxide–gas boundary. The composition of the oxide film on zirconium when it is oxidized in oxygen at temperatures not exceeding 250-300° is ZrO_2 with a cubic structure; at 250° and above a textured monoclinic modification arises ([7]). The increase in the oxidation rate observed at 250-300° is associated with the growth of the monoclinic modification of ZrO_2. At temperatures up to 300° the film on molybdenum is MoO_3. In the temperature interval 300-700°, along with MoO_3, MoO_2 also appears, apparently as a product of the dissociation of MoO_3 according to the reaction:

$$2MoO_3 \to 2MoO_2 + O_2,$$

with subsequent preferential oxidation of molybdenum only to MoO_2. This phenomenon explains the minimum on curve 2 in Fig. 2, which occurs during oxidation of molybdenum at 350°.

On chromium and aluminum, the films formed in air at various temperatures consist only of the oxides Cr_2O_3 and Al_2O_3, respectively ([8], [10]).

Plotting $\lg k$ as a function of $1/T$ gives a straight line. From the slope of the straight line obtained for each metal and alloy studied, the values of the activation energy of the oxidation process were calculated (see Table 1). The reported activation-energy values show that the process of interaction of Zr and Mo with oxygen proceeds by one and the same mechanism; the latter differs somewhat from the mechanism of the process of interaction of Ti and its alloy with Mo (10%), whose behavior is also similar to one another. This can possibly be explained by the fact that, apparently, on the Ti alloy with 10% Mo a mixed oxide is formed, representing a solid solution of TiO_2 and $xMoO_3$. The formation of a mixed oxide may be favorable to some extent, since its relatively high heat of formation will cause a decrease in the vapor pressure of MoO_3. In addition, if the oxide is mixed, then Mo^{6+} ions will replace Ti^{4+} ions in the TiO_2 lattice, and replacement of an ion in the lattice by an ion of higher valence and of the same radius (ionic radii: $Ti^{4+} = 0.64$ Å; $Mo^{6+} = 0.68$ Å) should lead to a decrease in the number of vacant oxygen-ion sites, owing to the appearance of an additional number of free electrons, since titanium dioxide is a semiconductor with electronic conductivity. Thus, in this case the addition of molybdenum to titanium will not impair its heat resistance but, on the contrary, may even improve it somewhat, as we observe. As for the Ti alloy with 5% Cr and 3% Al, its significantly higher resistance to oxidation, compared with titanium, can possibly be explained by the formation of a mixed oxide $(TiO_2, Al_2O_3, Cr_2O_3)$ of the spinel type. And, as is known, lattices of this type possess high resistance to oxidation.

Fig. 4. Change in film thickness with titanium oxidation temperature: **1** –in air saturated with water vapor; **2** –in dry air.

Fig. 4. Change in film thickness with titanium oxidation temperature: 1 —in air saturated with water vapor; 2 —in dry air

Figure 4: Fig. 4. Change in film thickness with titanium oxidation temperature: 1 —in air saturated with water vapor; 2 —in dry air

Figure 4 shows the oxidation curves of titanium in the interval 50—250° in dry air and in air saturated with water vapor. From Fig. 4 it is seen that the thickness of the film formed on titanium at temperatures up to 200° in dry air is twice as great as in humid air. At 250°, when the bond with water becomes weak, the film thickness reaches one and the same value both in dry and in humid air. The hydrated film, apparently, is more compact and contains fewer defects than the film formed in dry air.

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