CONTACT REACTION OF METALLIC TITANIUM WITH OXIDE REFRACTORY MATERIALS

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The formation of titanium coatings on the surface of oxide refractory materials during contact with metallic titanium occurs in the range 600-900°C [1, 2]. In this case there is an increase in the size of the polyhedral crystals of α-Ti, orientated chiefly in the plane of the substratum. X-ray analysis showed that the external layer of the coating consists of metallic titanium.

The present authors made thermodynamic calculations of the possible reactions, and studied the transverse sections of titanium coatings on the refractories.

The main reactions between oxides present in the composition of refractory materials, and metallic titanium can be considered to be the following:

$$SiO_2 + Ti \rightleftarrows TiO_2 + Si, \tag{1}$$
$$SiO_2 + 2Ti \rightleftarrows 2TiO + Si, \tag{1a}$$
$$2Fe_2O_3 + 3Ti \rightleftarrows 3TiO_2 + 4Fe, \tag{2}$$
$$Fe_2O_3 + 2Ti \rightleftarrows Ti_2O_3 + 2Fe, \tag{2a}$$
$$Fe_2O_3 + 3Ti \rightleftarrows 3TiO + 2Fe, \tag{2b}$$
$$Cr_2O_3 + 2Ti \rightleftarrows Ti_2O_3 + 2Cr, \tag{3}$$
$$Cr_2O_3 + 3Ti \rightleftarrows 3TiO + 2Cr, \tag{3a}$$
$$2Cr_2O_3 + 3Ti \rightleftarrows 3TiO_2 + 4Cr, \tag{3b}$$
$$2Al_2O_3 + 3Ti \rightleftarrows 3TiO_2 + 4Al, \tag{4}$$
$$Al_2O_3 + 2Ti \rightleftarrows Ti_2O_3 + 2Al, \tag{4a}$$
$$Al_2O_3 + 3Ti \rightleftarrows 3TiO + 2Al, \tag{4b}$$
$$ZrO_2 + Ti \rightleftarrows TiO_2 + Zr, \tag{5}$$
$$ZrO_2 + 2Ti \rightleftarrows 2TiO + Zr, \tag{5a}$$
$$TiO_2 + Ti \rightleftarrows 2TiO, \tag{6}$$
$$MgO + Ti \rightleftarrows TiO + Mg, \tag{7}$$
$$CaO + Ti \rightleftarrows TiO + Ca. \tag{8}$$

The change in free energy of reactions (1)-(8) with an increase in temperature is shown in Fig. 1.

Starting from the thermodynamic calculations in the range 298-1200°K the probability of contact reaction exists for the oxides SiO_2, Fe_2O_3, Cr_2O_3, and TiO_2; for the oxides Al_2O_3, ZrO_2, MgO, CaO, the probability of reaction with metallic titanium is low. Reactions are most possible with the formation of titanium monoxide, TiO.

Literature data has been published to confirm the results of thermodynamic calculations (for example, [3]); however, they refer usually to high temperatures, as a rule, above the melting point of titanium. It is stated [4] that at a temperature of about 1100°C titanium reacts with quartz according to the following reaction

$$7Ti + 3SiO_2 = 3TiSi + 2Ti_2O_3.$$

On the basis of the results of thermodynamic calculations we should expect the formation on the substratum–titanium boundary of a transition layer of titanium monoxide with the oxides SiO_2, Fe_2O_3, Cr_2O_3, and TiO_2.

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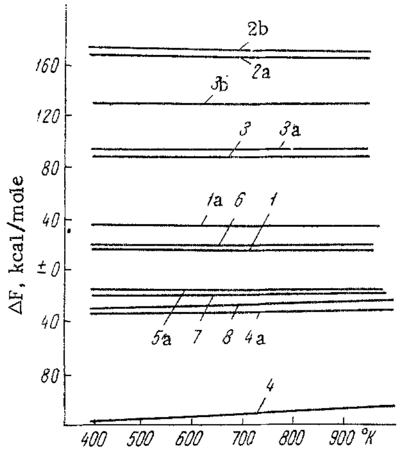

Fig. 1. Change in the free energy ΔF of the reactions (1)-(8) depending on the temperature.

Metallographic studies were carried out on the thin slides of titanium coatings formed on the surface of certain refractories.

The study of the cross section of the slides of titanium coatings obtained on alumina showed that at 500-900°C in most cases there is no noticeable transition layer between the metal and the ceramic, or it is very very slight. We observed penetration of titanium between the separate crystals of the oxide (Fig. 2).

On the specimens of zirconium dioxide and magnesium oxide (see Fig. 2) the reaction between the titanium coating and the material of the substratum is expressed in the penetration of titanium between the crystals of ZrO_2 and MgO, and the rupture of the edges of the crystals on the boundary of the coating and the ceramic. In some specimens of ZrO_2 we noted in places an orange color in the boundary layer of the coating. However, the transition layer is not always formed on the ZrO_2.

In the specimens of magnesia spinel (see Fig. 2) on the boundary with the titanium coating we noted an appreciable transition layer. It takes the form of bands of orange color in which darker and lighter spots can be seen. The band contains tongues of unreacted ceramic material of a gray color. On the boundary with this band the titanium coating is yellow in color, the density of which away from the transition layer is reduced.

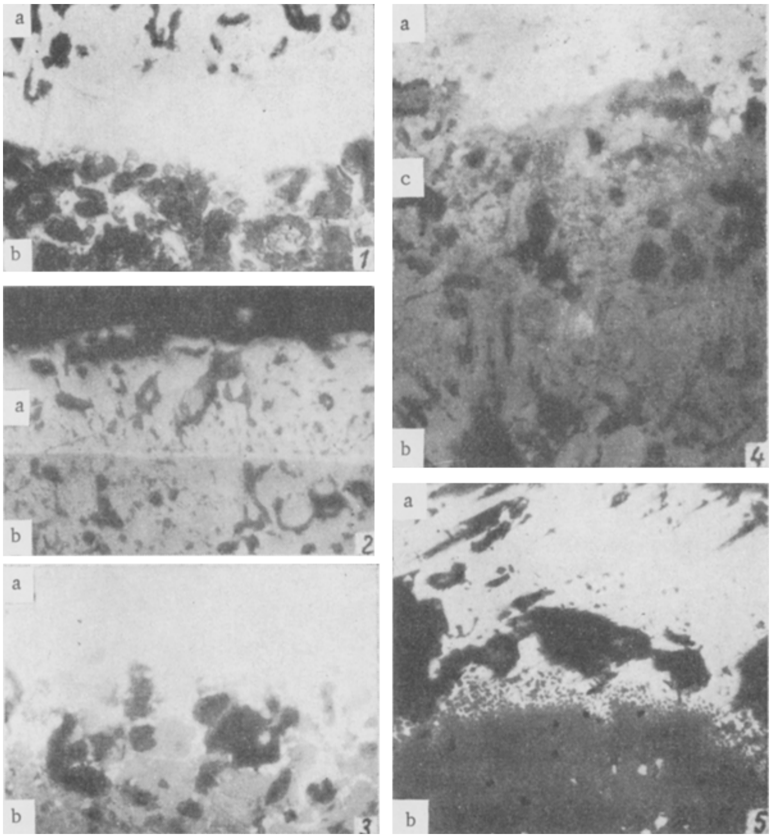

Fig. 2. Microstructure of the thin section of titanium coating on Al_2O_3 (1), ZrO_2 (2), MgO (3), $MgAl_2O_4$ (4), TiO_2 (5): a) coating; b) ceramic; c) transition layer; temperature: 2, 4) 950°C, remainder 850°C; soaking: 1-5 h, rest 3 h; × 115 (2); × 340 (1, 3-5). Reflected light.

On the boundary of TiO_2 with titanium coating mutual diffusion of the titanium and the ceramic is to be seen (see Fig. 2), and the penetration of the titanium in the ceramic is more intense. The titanium penetrates into the crystals, and also fills the space between the crystals and the cracks. The diffusion of ceramic into the titanium coating is noted in the form of dark colored points in a layer of titanium. There are pores in the titanium coating.

The most satisfactory explanation of the results of the experiments is given by the theory of diffusion welding, developed by a number of researchers, and most clearly formulated for cases of welding in vacuum [5].

Diffusion welding of materials is based on the capacity of physically pure surfaces to bond to these surfaces due to the presence of open atomic bonds. Diffusion processes occurring as a result of this increase the strength of the joint. Boundary diffusion occurs usually much more quickly than volume diffusion, increasing the reliability of the welded joint. An increase in the welding time increases the strength of the joint (bond) to a certain limit, after which because of the grain growth the strength of the bond is impaired.

It is established that the joint is actively made at temperatures of 60-80°C below the temperature of melting of the metal. In particular, positive results were obtained with the diffusion welding of titanium grade VT5-1 in vacuum at 800-850°C.

The formation of metallic coatings on refractories at high temperatures is stimulated, or accompanied, by chemical reaction between the metal of the coating and the material of the substratum. It is considered [6] that positive proof is the presence of a chemical bond between the coating and the substratum and the formation of a transition layer between the metal and the nonmetel.

Studies of the structure of titanium coatings in thin sections showed that the mutual diffusion of titanium and ceramic occurs on a front with the simultaneous formation of toothed wedges ensuring the strength of the bond between the substratum and the coating. Diffusion layers cannot be studied in detail but it is possible to note the possible signs of its formation, consisting in the development under the titanium coating of porous intermediate layers.

The formation of transition layers is of positive value, since owing to this the lattice parameters of the material of the substratum and the developing crystals of titanium tend to approximate to each other. This is confirmed by the formation of titanium coatings with identical crystalline structures on different materials and metals.

The study of the thin slides and previous tests [2] showed that noticeable transition layers of oxides of titanium are formed on refractories made from SiO_2, TiO_2, and spinel and in some cases on specimens of Al_2O_3, MgO, and ZrO_2. It should be borne in mind that the majority of the specimens, judging from observations under the microscope, contain glass phase which more actively reacts with metallic titanium than crystals.

The formations of crystals of titanium usually prevails over the diffusion processes, so the external surface of the coating consists of pure metallic titanium. Prolonged soaking at high temperatures may cause the breakdown of the crystals of titanium coating: diffusion starts to predominate over the separation of pure titanium. It is necessary also to mention that, as practice has shown with the production of coatings, when the thickness of the diffusion layer is increased (more than 3-5 μ) the strength of the bonding between the coating and the substratum is reduced.

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