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Formation of the diffusion barrier at the interface of Cr20Ni80 alloy - Ni-Cr-Al coating

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Abstract. The effect of thermal influence conditions on the structure and chemical composition of the self-organizing diffusion barrier formed during high-temperature (1100 °C) long-term (up to 500 h) heating between the Cr20Ni80 alloy and the coating of the Ni-Cr-Al system is investigated. It is shown that the formation of a barrier, which is a Cr(Al) solid solution of variable composition, is due to the limited solubility of Cr in Ni aluminides. It is established that the growth of the thickness of the diffusion barrier is mainly due to the alloy Cr20Ni80, and the intensity of its growth and the content of chromium in it are determined by the temperature and time conditions of heating. With a diffusion barrier thickness of 55-60 μm, its further growth is stopped by blocking the diffusion flux of Ni from the alloy Cr20Ni80 into the coating.

1. Introduction

The most effective heat-resistant coatings are coatings based on nickel aluminides, high protective properties of which are provided by their ability to oxidize with a formation of an Al2O3 film. The durability of the coating is limited by the content of Al in its surface layer [1-5]. To stabilize the Al content, layered coatings with a diffusion barrier (DB) are required to prevent mass transfer between the coating and the substrate. We proposed a technology for obtaining such layered coatings of the Ni-Cr-Al system with a self-organizing DB. In previously published papers [6-11], it was shown that the phase transformations in the layered coatings of the Ni-Cr-Al system under high-temperature heating (up to 1100 °C) proceed in the following sequence: Ni2Al3 + CrAl7 → Ni2Al3 (Cr) + NiAl(Cr) → NiAl(Cr) → NiAl(Cr) + Ni3Al(Cr) → Ni3Al(Cr). An increase in the temperature and time of the thermal action leads to an equalization of the Al, Ni, and Cr content across the coating thickness due to the diffusion redistribution of the elements and to the formation of a secondary reaction zone with a high Cr content. This zone plays the role of DB, which prevents the penetration of Al atoms into the Cr20Ni80 alloy and provides in the studied time interval its content in the coating not less than 15 wt. %, sufficient to form on its surface an oxide film Al2O3.

In the present work, the effect of thermal influence conditions on the structure and chemical composition of the self-organizing DB, which is formed during high-temperature long-term heating, between the Cr20Ni80 alloy and the coating of the Ni-Cr-Al system is investigated.

2. Materials and methods

Metallographic studies, as well as the determination of the chemical composition and dimensions of the structural components of the DB, were performed on a dual-beam electron microscope Versa 3D.
Thermal treatment of composite samples «alloy Cr20Ni80 - coating of the Ni-Cr-Al system», obtained by the technology described in [6, 7], was carried out in the air atmosphere of the SNOL 8.2 / 1100 furnace at a temperature of 1100 °C with a yield of up to 500 h.

3. Results and Discussion

The formation of DB is associated in [12] with the phase equilibrium on the phase diagram. In the phase diagram of Ni-Cr-Al at 1100 °C, the α-Cr phase has common conodes with both β-NiAl (Cr) and γ-Ni (Cr,Al) (Figure 1). The diffusion path is shown in the diagram by a dashed line from the outer side to the inner one a → b → c → d → Ni-20Cr.

According to Fick's law, the resulting diffusion fluxes of aluminum from the coating $J_{Al}$:

$$J_{Al} = -D_{Al} \cdot \text{grad}(c),$$

where $D_{Al}$ is the diffusion coefficient of Al; $c$ is the concentration of Al; and alloying elements from the $J_M$ substrate (figure 2, a) ultimately lead to a decrease in the Al content in the coating below the critical value necessary to maintain its operability. DB prevents this process due to low values of $D_{Al}$ (figure 2, b).

The mechanism of formation and growth of DB is due to the limited solubility of Cr in Ni aluminides. Thus, for example, the solubility of Cr in NiAl at a temperature of 1100 °C does not exceed 5% by weight. The presence of a diffusion flux of elements from the substrate causes the Cr
atoms to accumulate at the «Cr20Ni80-coating» boundary, which leads to the formation of Cr-rich phases and the formation of a continuous interlayer.

It is established that in the investigated time range (up to 500 h) at 1100 °C in the first stage of DB formation an increase in the average Cr content to 87 wt.% occurs (Figure 3, a), and then, after the redistribution of elements in the coating, the diffusion of Al atoms in DB begins, which leads to a decrease in the average Cr content to 83 wt.%. The temperature and time conditions of heat treatment also affect the thickness of the DB (Figure 3, b). The growth in the thickness of the DB is mainly due to a decrease in the thickness of the alloy Cr20Ni80. After 100 hours of exposure at 1100 °C, the thickness of the DB is practically unchanged and is at the level of 55-58 μm.

Figure 3. Influence of the holding time at 1100 °C on the average weight content of Cr in DB (a) and the thickness of DB (b).

Analysis of the distribution of elements in the cross section of the DB after heat treatment at 1100 °C showed that the content of Ni in DB is reduced to 0% by 300 hours, and the Al content increases (figure 4). In this case, there is no interaction between the DB and the alloy Cr20Ni80. The phase composition of the DB after 300 hours of exposure is a solid solution Cr(Al) of variable composition (figure 5).

Figure 4. Maps of the distribution of elements in the DB after heat treatment 1100 °C.
4. Conclusions
The formation of a self-organizing diffusion barrier in the layered coatings of the Ni-Cr-Al system is due to the limited solubility of Cr in Ni aluminides. The presence of a diffusion flux of Ni and Cr from the alloy Cr20Ni80 into the layered coating causes the Cr atoms to accumulate at the «Cr20Ni80-coating» boundary, which leads to the formation of a continuous interlayer of a solid solution of variable concentrations of Ni and Al in Cr.

The growth of the diffusion barrier is mainly due to a change in the thickness of the alloy Cr20Ni80. The intensity of growth of the diffusion barrier and the Cr content in the latter are determined by the temperature-time heating conditions. With a diffusion barrier thickness of 55-60 μm, its further growth stops as a result of blocking the diffusion flux of Ni from the alloy Cr20Ni80 into the coating.

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Figure 5. Microstructures of DB after 1100 °C and holding for 100 (a) and 300 h (b).