Structure and phase composition transformation in Cr20Ni80 + Ni2Al3 + CrAl7 layered coating under thermal effect

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Abstract. The thermal stability of the Cr20Ni80 / (Ni2Al3 + CrAl7) layered coating on M1 copper substrate was studied. It is found, that the sequence of phase transformations in layered coating during the heat treatment in temperature range of 700-1000 °C is Ni2Al3 + CrAl7 → Ni2Al3(Cr) + NiAl(Cr) → NiAl(Cr). It is shown, that an increase in temperature and duration of thermal effect leads to the alignment of Al, Ni and Cr content over the coating thickness due to the diffusion redistribution of elements and to the formation of a secondary reaction zone with a high chromium content.

1. Introduction
One of the effective methods of protecting copper parts and components of metallurgical equipment from oxidation is the formation of protective coatings on their surface based on nickel aluminides [1, 2].

In [3-10], the technological process for producing layered coatings of the Al-Cr-Ni system is described. The implementation of this allows to obtain on the protected base the “Cr20Ni80 alloy - nickel aluminate” coating, high protective properties of which arise from the existence of dense oxide Al2O3 films on the nickel aluminate surface [11-13]. The technology of producing Cr20Ni80/(Ni2Al3 + CrAl7) layered coating involves applying of Cr20Ni80 alloy and AD1 aluminum on the base by explosion welding and following heat treatment (HT) of the layered composite, ensuring the formation between Cr20Ni80 and AD1 of the solid phase diffusion zone of the intermetallic composition (CrAl7, NiAl3 and Ni2Al3). During the cooling under the action of thermal stresses [14, 15] the layer AD1 spontaneously detaches, revealing the surface of the coating.

The objective of this work is to study the thermal stability of the Cr20Ni80/(Ni2Al3 + CrAl7) layered coating on M1 copper substrate.

2. Materials and methods
Experimental samples for the study were obtained by applying of alloy Cr20Ni80 (0.5 mm) and aluminum AD1 (0.7 mm) on 10 mm thick M1 copper substrate using explosion welding and their HT conditions of 600 °C, 50 hours.

HT of samples coated with Cr20Ni80/(Ni2Al3 + CrAl7) was carried out in a SNOL 8.2 / 1100 furnace at a temperature of 700–1000 °C with exposure times of 10–50 hours. The upper limit of the temperature range was determined by the copper melting point. The lower limit is a significant slowdown of diffusion processes at lower temperatures.
Electron-optical studies and the determination of the chemical composition were carried out on a Versa 3D Dual Beam scanning double-beam electron microscope. X-ray diffraction analysis was performed on a Bruker D8 ADVANCE ECO diffractometer in the Bragg-Brentano geometry under normal conditions in the copper anode radiation ($\lambda = 1.5418\text{Å}$) using a nickel K$_\beta$ filter. Samples were examined for reflection, the intensity of the diffraction pattern was recorded using a linear-type position-sensitive detector SSD160 with a number of channels 160. Phases were identified using the ICDD PDF-2 (2016) powder base. Interpretation of the phase composition was performed using the software for the diffractometer Diffrac.EVA (version 4.2.1).

3. Results and discussion
Analysis of the SEM images and the elemental composition of the coating after heat treatment at 700 °C at 10 hours exposure showed the formation of secondary reaction zone with an increased Cr concentration (Ni - 42.57 wt.% , Cr - 52.53 wt.%) with a thickness about 6 microns (figure 1) at the Cr20Ni80-coating (Ni$_2$Al$_3$ + CrAl$_7$) boundary.

![Figure 1. SEM image of the structure (a) and diffraction pattern (b) of the coating after HT 700 °C, 10 h.](image)

Heat treatment at 800 °C, 10 hours leads to a partial dissolution of the CrAl$_7$ intermetallic compound and the formation of a multilayer structure. The first layer is Ni$_2$Al$_3$ with CrAl$_7$ inclusions.
(layer 1, figure 2); the second (layer 1’, figure 2) is a Cr solid solution based on Ni$_2$Al$_3$. It is followed by a solid solution of Cr based on NiAl (layer 2, figure 2) and secondary reaction zone (layer 3, figure 2), consisting of a mixture of solid solutions of Cr (Al, Ni) (dark inclusions) and Ni (Cr).

**Figure 2.** SEM image of the structure of the coating after TO 800 °C, 10 hours.

The elemental composition of the layers is given in table 1. An increase in the exposure time leads to the complete dissolution of CrAl$_3$, the saturation of the Ni coating layers, and the Ni$_2$Al$_3$ → NiAl phase transition in layer 1. At 50 hours, the layers 1 and 2 (figure 3) have the same phase composition NiAl(Cr) and differ only in concentrations of Ni (64 and 73 wt.%, respectively). In secondary reaction zone there is an increase in the Cr content and an increase in the size of Cr (Al, Ni) inclusions (area 3, figure 3, table 1).

**Table 1.** The results of X-ray spectral analysis of the coating after HT 800 °C.

| Element | Element content, wt. % (see figures 2, 3) |
|---------|------------------------------------------|
|         | Layer 1 | Layer 1' | Layer 2 | Dark inclusions in area 3 |
|---------|---------|----------|---------|--------------------------|
| Ni      | 56,36   | 60,20    | 69,40   | 32,85                    |
| Cr      | 5,04    | 4,23     | 5,10    | 64,72                    |
| Al      | 38,6    | 35,57    | 25,58   | 2,43                     |
|         | 10 hours|          |         |                          |
| Ni      | 64,42   |          | 72,86   | 14,14                    |
| Cr      | 5,43    |          | 5,61    | 85,16                    |
| Al      | 30,16   |          | 21,53   | 0,70                     |
|         | 50 hours|          |         |                          |
An increase in heat treatment temperature up to 900 °C intensifies diffusion processes, the concentration of Ni in the coating increases. The coating now is a three-layer system (figure 4): layers 1 and 2 — NiAl (Cr) with a Ni concentration of 68.02 and 74.75 wt.% at 50 hours. In the secondary reaction zone the growth of Cr (Al, Ni) inclusions occurs more intensively than at 800 °C, and the Cr content increases from 85.16 to 88.3 wt.% (table 2).

Table 2. The results of X-ray spectral analysis of the coating after HT 900 °C, 50 hours.

| Element | Element content, wt. % (see figure 4) |
|---------|-------------------------------------|
|         | Layer 1  | Layer 2  | Dark inclusions in area 3 |
| Ni      | 68,02    | 74,75    | 8,28                     |
| Cr      | 5,20     | 4,23     | 88,3                     |
| Al      | 26,78    | 21,02    | 3,42                     |

At 1000 °C after 50 hours of exposure, only two layers exist in the coating structure: NiAl (Cr) and the secondary reaction zone, which consists only of solid solutions based on Cr with an average content ~ 95 wt. % (figure 5, table 3).
Figure 5. SEM image of the structure of the coating after HT 1000 °C, 50 hours.

Table 3. The results of X-ray spectral analysis of the coating after HT 1000 °C, 50 hours.

| Element | Element content, wt. % (see figure 5) |
|---------|--------------------------------------|
|         | Layer 1 | Point 2 | Point 3 |
| Ni      | 75,26   | 5,87    | 2,68    |
| Cr      | 5,13    | 76,11   | 95,34   |
| Al      | 19,61   | 18,02   | 1,98    |

4. Conclusions
1. Phase transformations in Cr20Ni80/(Ni2Al3 + CrAl7) layered coatings during heat treatment in the temperature range 700–1000 °C proceed in the following sequence Ni2Al3+CrAl7 → Ni2Al3(Cr) + NiAl(Cr) → NiAl(Cr). Increasing the temperature and time of thermal exposure leads to the alignment of the content of Al, Ni and Cr through the thickness of the coating due to the diffusion redistribution of elements and to the formation of a secondary reaction zone with a high content of chromium.

2. The formation of the secondary reaction zone arises from the limited solubility of Cr in Ni aluminides. The diffusion flux of Ni and Cr from alloy Cr20Ni80 in the coating formed after the initial (600 °C, 50 h) heat treatment forces the Cr atoms to accumulate at the Cr20Ni80-coating boundary, which leads to the formation of a solid interlayer of a variable concentration of Ni and Al in Cr.

Acknowledgments
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