Aluminizing of the Cr15Al5 alloy surface by hot-dipping in the melt

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Abstract. The diffusion interaction at the interlayer boundary of the Cr15Al5 alloy during aluminizing by hot-dip in a molten bath of AK12M2 silumin is investigated. It is shown that subsequent heat treatment at 1000 °C leads to the formation on the surface of the Cr15Al5 alloy a coating of variable composition based on iron aluminides FeAl(Cr, Si) / Fe3Al(Cr, Si) / Fe(Al, Cr, Si). Grain growth in the Cr15Al5 alloy and a decrease in the density of carbide inclusions with their segregation along the grain boundaries ensures a decrease in its microhardness compared to as-received condition from 2.1 to 1.6 GPa.

1. Introduction
Heat-resistant precision alloys of the Fe-Cr-Al system (FeCrAl-alloys) are widely used as a material for electrical heating and resistive elements, structural components for accident tolerant fuel cladding, fast fission nuclear reactors, as first wall and blanket structures for fusion reactors, in household appliances [1-6]. The resistance of FeCrAl-alloys largely determined by the content of chromium and aluminum.

It is known that an increase in the aluminum content in FeCrAl-alloys leads to their embrittlement and complicates pressure treatment [7]. Therefore, an aluminum content in these alloys is limited to 5–5.8% [6, 8]. In [9], it was shown that an increase to 10 wt. % of the aluminum concentration in the Cr15Al5 alloy surface layer increases by an order of magnitude the onset time of the catastrophic oxidation stage compared with the initial state. Therefore, the search for methods for increasing the aluminum content in the FeCrAl-alloys composition after its formation to a ready product is relevant. One of such methods is hot-dip aluminizing followed by heat treatment. The search for optimal modes of aluminizing and subsequent heat treatment to obtain aluminum-rich intermetallic compounds in the surface layer of the Cr15Al5 alloy defined the objectives of the present study.

2. Materials and methods
Precision the Cr15Al5 alloy was used in this study because of the lowest chromium content. AK12M2 silumin was used as a bath melt because of the slower rate of melt oxidation in comparison with pure aluminum and its best casting properties.

Aluminizing was performed on rectangular samples of size 10x20x1.6 mm. Samples were previously ground on emery paper with 320 grit and degreased. For the qualitative process of aluminizing, polyester resin based flux and sodium tetraborate Na2B4O7 were used. The melt was heated to 740 °C, then the samples were dipped in it through a flux layer with an exposure time of 5 to 15 min.

Heat treatment (HT) was carried out in a SNOL 8.2/1100 furnace at a temperature of 800-1000 °C. Metallographic studies were performed on Olympus BX-61 modular metallographic microscope.
Electron-optical studies and the determination of the chemical composition were carried out on a Versa 3D Dual Beam scanning 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 (\( \lambda = 1.5406\AA \)) using a K\(_\beta\) nickel filter. Samples were examined for reflection, the intensity of the diffraction pattern was recorded using a linear-type SSD160 position-sensitive detector with 160 channels. Phases were identified using the ICDD PDF-2 (2016) powder base. Interpretation of the phase composition was performed using the software Diffrac.EVA (version 4.2.1). The measurement of microhardness was carried out on a PMT-3M with a load on the indenter of 100 g.

3. Results and discussion

According to the results of metallographic and X-ray diffraction analysis, it was found that the best results are obtained after dipping of the Cr15Al5 alloy in the silumin melt with an exposure of 10 min. A continuous coating is formed on its surface, the outer layer of which is (Al-Si) eutectic with inclusions of the Al\(_7\)Fe\(_2\)Si intermetallic (figure 1, a, b). The diffusion layer at the interface with the Cr15Al5 alloy consists of the Al\(_7\)Fe\(_2\)Si and Fe\(_2\)Al\(_5\) intermetallic layers that are not uniform in thickness (figure 2, a, b). In the last, there is a large number of Cr\(_3\)Si inclusions throughout the volume and the needle inclusions of the FeAl\(_2\) intermetallic along the border with the Cr15Al5 alloy.

![Figure 1](image1.png)

**Figure 1.** The structure (a) and the diffraction pattern taken from the surface of the coating (b) after dipping of the Cr15Al5 alloy in the silumin melt (740 °C for 10 min).

![Figure 2](image2.png)

**Figure 2.** SEM image (a) and the distribution of chemical elements in the diffusion zone (b) after dipping of the Cr15Al5 alloy in the silumin melt (740 °C for 10 min).
The subsequent heat treatment at 800 °C, 2 h of aluminized samples led to an almost complete transformation of the surface layer (figure 3, a). The obtained intermetallic coating had a complex phase composition and high hardness (6-8 GPa). An increase in the exposure time to 20 h led to the formation of a brittle layer in its composition, which is crumbling during the preparation of microspecimen (figure 3, b).

![Image](image1.png)

**Figure 3.** The structure of the coating after HT at 800 °C for 1 h (a) and 20 h (b).

To obtain less brittle aluminides on the surface of the Cr15Al5 alloy, it was decided to raise the annealing temperature to 1000 °C. The exposure for 5 h was not enough for the transformation of coating and a large number of discontinuities and chipping appeared on the sample surface (figure 4, a). An increase in the exposure time to 20 h ensured the formation of the defect-free surface of the sample (figure 4, b).

![Image](image2.png)

**Figure 4.** The structure of the sample with the coating after HT at 1000 °C for 5 h (a), 20 h (b), the distribution of chemical elements throughout the coating thickness (c) and the diffraction pattern taken from its surface (d).
Comparison of the data of energy dispersive (figure 4, c) and X-ray structural analysis (figure 4, d) allowed us to establish that the coating obtained on the surface of the Cr15Al5 alloy has a variable composition varying from surface to base in the following sequence: FeAl(Cr, Si) → Fe3Al(Cr, Si) → Fe(Al, Cr, Si).

Electrolytic etching of aluminized samples made it possible to reveal the structure of the Cr15Al5 alloy and ~ 260 um thick coating on its surface (figure 5). Due to the two-sided coating, the sample thickness increased by about 100 um. From the distribution of chemical elements (figure 4, c) it can be seen that the 1 mm thick core of the sample corresponds in composition to the Cr15Al5 alloy. However, HT led to a significant grain growth, segregation of carbide inclusions occurred with the formation of local carbide areas along the grain boundaries. Metallographic analysis made it possible to establish that the density of these inclusions in the plane of the microspeciment does not exceed 4%, which is 2.5 times less than the density of carbides in the Cr15Al5 alloy in the initial state (10%).

![Cr15Al5](image)

**Figure 5.** The structure of the Cr15Al5 alloy in the initial state (a) and with an aluminide coating formed on the surface (b) after electrolytic etching.

The microhardness of samples with an aluminide coating decreases linearly from the surface of the coating (~ 3.5 GPa) to the substrate (~ 1.6 GPa). Moreover, the microhardness of FeCrAl alloy significantly decreased in comparison with the initial state (~ 2.1 GPa), which can be explained by an increase in the grain size and decrease in the density of carbide inclusions.

4. Conclusion

To form an aluminide coating on the surface of the Cr15Al5 alloy, the composite obtained by dipping into the silumin melt must be heat treated at 1000 °C. The coating obtained has a variable phase composition: FeAl(Cr, Si) / Fe3Al(Cr, Si) / Fe(Al, Cr, Si) and its surface hardness is ~ 3.5 GPa.

Grain growth in the base material and a decrease in the density of carbide inclusions with their segregation along grain boundaries lead to a significant decrease in microhardness compared to the initial state (from 2.1 to 1.6 GPa).

Acknowledgments

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