The influence of the chemical composition of the Fe-Cr-Al system coatings on the oxide films phase composition

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Abstract. The phase composition of the oxide films on the surface of the Fe-Cr-Al system coatings is studied using glancing angle X-ray diffraction. It is shown that at 900 °C the formed oxide films consist of α-Al₂O₃ and (FeCr)₂O₃, to which FeAl₂O₄ oxide is added during long-term exposure. An increase in temperature to 1100 °C intensifies the growth of oxide films, and an increase in the aluminum content ensures a stable growth of α-Al₂O₃ and FeAl₂O₄ oxides. When the aluminum content in the coating is more than 10 at. % at large exposure times, metastable alumina δ-Al₂O₃ is formed, the formation of which is associated with a decrease in the concentration of chromium in thin surface layers.

1. Introduction
Improving the operational reliability of high-tech energy and chemical engineering products operating in extreme conditions at high temperatures in aggressive environments and under erosive influences is an urgent task. A critical characteristic of the materials used, limiting the service life of products, along with heat strength is their heat resistance and thermal stability. Volumetric alloying methods cannot achieve equally high values of these characteristics in one material, therefore, protective coatings are applied to the surface of the most loaded parts.

One of the most widely used currently are coatings based on the Fe–Cr–Al system. The heat resistance of this coatings in high temperature and corrosive environment is ensured due to the formation of the protective layers of Al and Cr oxides on their surface [1-5]. In [6], a sequence of technological operations was proposed to obtain on Cr15Al5 alloy surface a layered FeAl(Cr,Si) / Fe₃Al(Cr,Si) / Fe(Al,Cr,Si) coating, which provides stable oxide films formation. During operation, such coatings, due to available gradient concentrations, should cause a diffusion redistribution of chemical elements (Fe, Al, Cr and Si), which, ultimately, can lead to a decrease in the content of Al and Cr, and, consequently, a change in the phase composition of the protective oxide films.

The purpose of this work is to study the influence of the heat treatment parameters of the Fe-Cr-Al system coatings with various chemical compositions on the oxide films phase composition.

2. Methods
The different phase composition of the Fe-Cr-Al system coatings was ensured by hot-dip aluminizing of the Cr15Al5 alloy containing 10 at. % Al and 15 at. % Cr (hereinafter 10Al15Cr) in the silumin melt and subsequent heat treatment (HT) [6]. After HT at a temperature of 1100 °C for 20 h, the coating containing 40 at. % Al and 7 at. % Cr (hereinafter referred to as 40Al7Cr sample) was formed on the surface of the Cr15Al5 alloy. After 100 hours of exposure - 25 at. % Al and 11 at. % Cr (hereinafter referred to as 25Al11Cr sample) and after 500 hours of exposure - 18 at. % Al and 13 at. % Cr (hereinafter referred to as 18Al13Cr sample).
HT to study the influence of the temperature-time conditions on the phase composition of oxide films was carried out in a LOIP LF-7/13-G1 furnace in an air atmosphere at 900 and 1100 °C with holding for up to 20 h. Before each step of HT, the samples surface were subjected to mechanical cleaning with a metal brush and sandpaper with a grit of 1000 in order to remove oxide films. The microstructure of the samples was examined using an Olympus BX-61 microscope. Electron-optical studies and determination of the chemical composition were carried out using a Versa 3D Dual Beam scanning electron microscope. X-ray diffraction analysis was performed on a Bruker D8 ADVANCE ECO diffractometer in the radiation of a copper anode (\(\lambda = 1.5406 \text{ Å}\)) using a nickel K\(_\beta\) filter in the conventional symmetric Bragg–Brentano geometry and in the modified geometry by fixing incidence angle from 0.5° to 2° to provide glancing angle X-ray diffraction (GAXRD) technique [7]. The 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. The phase identification was carried out using the ICDD PDF-2 powder base (2016) and the Diffrac.EVA diffractometer software (version 4.2.1).

3. Results and discussion
A comparative analysis of the diffraction patterns of the experimental samples obtained using the conventional symmetric Bragg-Brentano geometry and the glancing angle XRD with an incidence angle of 2°, 1°, and 0.5° made it possible to establish the following (figure 1). On the conventional XRD pattern (BB), the reflections from the substrate are well distinguishable and have high intensity, while the reflections from the oxide films cannot be detected. Identification of the formed thin oxide films has been achieved by reducing the angle of incidence according to the GAXRD up to 2°. The decrease in the angle of incidence is accompanied by a decrease in the intensity of reflections from the substrate, and the intensity of reflections from oxide films remains almost unchanged. Since clearly distinguishable reflections corresponding to the oxide phases were observed in the GAXRD patterns with the angle of incidence of 2°, this scheme was used to determine the phase composition of the oxide films.

The diffraction patterns after HT at 900 °C from the surface of samples with different Al contents is shown on figures 2-5. On the surface of the 10Al15Cr sample (figure 2, a-b), after 1 h of exposure, a solid solution of Cr and Al in Fe is reliably identified. Reflections corresponding to corundum (\(\alpha\text{Al}_2\text{O}_3\)) and polycrystalline oxide (FeCr)\(_2\text{O}_3\), which has a trigonal structure similar to hematite (\(\alpha\text{Fe}_2\text{O}_3\)), are also observed. An increase in the exposure time to 20 h leads to an increase in the number of reflections corresponding to corundum, the disappearance of (FeCr)\(_2\text{O}_3\), and the appearance of hercynite FeAl\(_2\text{O}_4\). An increase in Al concentration on the surface to 18 at. % (18Al13Cr) (figure 3, a-b) leads to a decrease in the number of reflections corresponding to (FeCr)\(_2\text{O}_3\) after HT for 1 h, and the number of reflections from \(\alpha\text{Al}_2\text{O}_3\) increases. After 20 h, as in the 10Al15Cr sample, reflections corresponding to (FeCr)\(_2\text{O}_3\) disappear, hercynite reflections FeAl\(_2\text{O}_4\) appear, and the intensity of corundum reflections increases. Distinct reflections corresponding to the metastable alumina modification \(\delta\text{Al}_2\text{O}_3\) are also observed.
Figure 2. GAXRD patterns (2°) taken from the surface of the 10Al15Cr sample after HT at 900 °C, 1 h (a), 20 h (b), 1100 °C, 5 min (c), 20 h (d).

Figure 3. GAXRD patterns (2°) taken from the surface of the 18Al13Cr sample after HT at 900 °C, 1 h (a), 20 h (b), 1100 °C, 5 min (c).

For 25Al11Cr and 40Al7Cr samples (figures 4, 5), the oxidation behavior at 900 °C is completely analogous to those considered above. The intensity of reflections from αAl₂O₃ and Fe₆Al₄O₁₄ increases, and separate reflections of (FeCr)₂O₃ persist on long exposure times.

Figure 4. GAXRD patterns (2°) taken from the surface of the 25Al11Cr sample after HT at 900 °C, 1 h (a), 20 h (b), 1100 °C, 5 min (c).
40Al7Cr sample after HT at 900 °C, 1 h (a), 20 h (b), 1100 °C, 5 min (c), 20 h (d).

Heating at 1100 °C of the 10Al15Cr samples (figure 2, c-d) with short exposure times showed that in the initial stages, oxidation occurs only with the formation of corundum, and with an increase in the exposure time, reflections corresponding to $(\text{FeCr})_2\text{O}_3$ and $\text{FeAl}_2\text{O}_4$ appear. The heating of 18Al13Cr, 25Al11Cr, and 40Al7Cr samples showed similar results (figures 3-5). At short exposure times, corundum reflections first appear. As the HT time increases, $\text{FeAl}_2\text{O}_4$, $(\text{FeCr})_2\text{O}_3$ and $\delta\text{Al}_2\text{O}_3$ appear (figure 5, d).

The presence of the $\delta$ phase of Al oxide on all samples, except 10Al15Cr, is apparently associated with a decrease in the concentration of Cr in thin surface layers with long exposure times (figure 6), which ensures the accelerated transformation of metastable oxides into stable $\alpha\text{Al}_2\text{O}_3$ oxide (so-called the third element effect) [8-9].

**Figure 6.** SEM image of oxide layer (a) and distribution of chemical elements (b) in the 18Al13Cr sample.

**4. Conclusions**

The use of the glancing angle X-ray diffraction analysis with low incidence angle allows one to determine the phase composition of thin oxide films that form at high temperature on the surface of the Fe-Cr-Al system coatings by reducing the contribution of the substrate on the diffraction pattern.

At 900 °C on the surface of the coating containing 10 at. % Al, corundum ($\alpha\text{Al}_2\text{O}_3$) and polycrystalline oxide $(\text{FeCr})_2\text{O}_3$ are formed, which is replaced by hercynite $\text{FeAl}_2\text{O}_4$ at long exposure times. With an increase in Al concentration in the surface layer, metastable oxide $\delta\text{Al}_2\text{O}_3$ is additionally
formed. An increase in temperature to 1100 °C intensifies the oxidation process, while the oxidation behavior of the samples remains the same.

The presence of metastable modifications of Al oxide on the surface of the Fe–Cr–Al system coatings is associated with a decrease in the concentration of Cr in thin surface layers during long exposure times, where chromium ensures the accelerated transformation of metastable oxides into stable αAl2O3 oxide.

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