Structure and phase composition of diffusion zones formed as a result of homogeneous and heterogeneous reactions at the boundary of the AD1-Cr15Ni60 composite

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Abstract. This paper presents the study results of the diffusion interaction processes at the interlayer boundary of explosion welded Cr15Ni60-AD1 bimetal during the occurrence of homogeneous (at the solid – solid interface) and heterogeneous (at the solid – melt interface) reactions. It was shown that the diffusion zone formed during homogeneous interaction has a layered finely dispersed structure, while in a heterogeneous one it is predominantly needle-shaped with large fragments of the structure. Diffusion zones are characterized by heterogeneity in chemical composition, while their phase composition is almost identical: CrAl₇, FeNiAl₉, (Fe,Ni,Cr)Al₉, (Fe,Ni,Cr)Al₅, NiAl₃, (Ni,Fe,Cr)Al. It has been established that the transition from the interaction at the solid – solid interface to the interaction at the solid – melt interface leads to a significant acceleration of diffusion processes.

1. Introduction
It is well known [1-5] that the heat resistance of nickel alloys can be increased by alloying their surface with aluminum. A dense Al₂O₃ oxide film is easily formed on the surface of nickel aluminides, which prevents oxidation of the base [6]. A new level of properties of nickel alloys can be achieved by creating layered intermetallic coatings of the Al-Ni-Cr system on their surface, in which each layer plays a certain functional load, which allows combining high thermal and heat resistance with adhesive characteristics [7-11]. The complex technological process for producing such coatings includes operations of explosion welding, pressure treatment and heat treatment in the conditions of solid-phase interaction or in the presence of a liquid phase. Semi-finished products for the production of layered Al-Ni-Cr coatings are explosion-welded layered composite materials of Cr20Ni80 - AD1 composition. From the point of view of the practical implementation of the complex technology, it is more rational to use instead of the Cr20Ni80 alloy its cheaper and more plastic analogue, the Cr15Ni60 alloy.

Since the phase and chemical composition of the layered coating, which determines its operability, is formed at the stage of diffusion annealing of the composite, the aim of this work was to study the processes of diffusion interaction at the interlayer boundary of explosion welded Cr15Ni60-AD1 bimetal as a result of homogeneous (at the solid – solid interface) and heterogeneous (at the solid – melt interface) reactions.

2. Materials and methods
The object of study is the Cr15Ni60 alloy - AD1 aluminum bimetal composition, obtained by explosion welding at the optimum mode, guaranteeing a minimum level of structural and chemical
microinhomogeneity in the heat-affected zone. Samples 10 × 2.5 × 10 mm in size were cut from the obtained Cr15H60 - AD1 blanks (the layers thicknesses of the Cr15Ni60 alloy and AD1 aluminum were 2 mm and 0.5 mm, respectively).

Heat treatment (HT) of the samples for the formation of diffusion interaction zones (DZ) at the Cr15Ni60 - AD1 boundary was carried out in the air atmosphere of the SNOL 8.2/1100 furnace at a temperature of 630 °C for 100 h (homogeneous interaction) and 800 °C for 3 h (heterogeneous interaction).

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 Bragg - Brentano geometry in radiation from a copper anode (λ = 1.5418 Å). The survey was conducted layer by layer in three sections located at different depths of the DZ. Phases were identified using the ICDD PDF-2 (2016) powder base.

3. Results and discussion

3.1. Homogeneous interaction

Investigations of the sample after heat treatment at 630 °C for 100 h (figure 1) showed that the DZ with a thickness of 230-250 μm formed as a result of homogeneous interaction has a complex finely dispersed structure characterized by inhomogeneous chemical composition.

Figure 1. SEM image of the DZ after HT at 630 °C for 100 h (a), distribution of chemical elements throughout its thickness (b) and diffraction patterns recorded at different depths of the DZ (c).
It should be noted that the detected structure is more characteristic of eutectic structures. An analysis of literature data [12-14] showed that if the eutectic temperature in the binary Al-Ni system is 644 °C, then the introduction of iron (Al-Ni-Fe system) leads to its decrease to 638 °C, and chromium (system Al-Ni-Cr) - up to 634 °C. In this regard, in the Al-Ni-Fe-Cr system, with the above-mentioned HT parameters, taking into account the temperature error of the furnace, it is quite likely to expect the formation of the DZ by the eutectic mechanism.

![Figure 2. SEM images of various DZ regions.](image_url)

More detailed metallographic studies showed that the first DZ region adjacent to the AD1 layer (figure 2, b) is a light matrix with a composition of ~ 85 at. % Al, ~ 11 at. % Ni, ~ 4 at. % Fe, inside of which dispersed dark rounded inclusions containing ~ 87.5 at. % Al, ~ 12.5 at. % Cr. In terms of composition, the indicated “light” regions most closely correspond to the FeNiAl₉ ternary intermetallic compound (phase τ₁) [15], and the “dark” regions correspond to the CrAl₇ compound (phase θ). In some sources [16], the θ phase is denoted as Cr₂Al₁₃ or Cr₇Al₄₅. The results of the X-ray phase analysis of this DZ area are shown in figure 1c.

In the second region of the DZ (figure 2, c), color differentiation of the structure is observed. The EDS analysis revealed the following. The darker areas correspond to the FeNiAl₉ intermetallic compound, and the light sections, consisting of ~ 82 at. % Al, ~ 8 at. % Ni, ~ 2.5 at. % Fe and ~ 7.5 at. % Cr, are the same compound in which, however, part of the iron and nickel atoms are replaced by chromium atoms. It is known that in the Al-Ni binary system the only compound that is a daltonide is formed - this is the π phase or the NiAl₃ compound (75 at.% Al, 25 at.% Ni). In [17] it is noted that up to 4 at. % Fe can be dissolved in it by substitution. On the other hand, the formation of the (Ni,Cr)Al₃ phase in the Al–Ni–Cr system is possible [18], in which part of the nickel atoms is replaced by chromium atoms. A certain shift of the reflections observed in the diffractogram (figure 1, c) relative to the tabular positions for the FeNiAl₉ phase suggests the formation of a compound of the type (Fe,Ni,Cr)Al₉.

At an equal distance from the AD1 and Cr₁₅Ni₆₀ layer, the third DZ region is located (figure 2, d), which is characterized by a finely dispersed structure. In addition to the previously discovered inclusions of the FeNiAl₉ and (Fe,Ni,Cr)Al₉ phases, light inclusions of ~ 77 at. % Al, ~ 23 at. % Ni corresponding to the NiAl₃ intermetallic compound. X-ray reflections of the latter are present on the diffractogram of this DZ region (figure 1c).

The fourth DZ region (figure 2, e) is identical in composition to the third one and is characterized by a finer-dispersed structure with an increased fraction of NiAl₃ inclusions.
The structure of the fifth DZ region (figure 2, f) contains a dark matrix without previously observed color differentiation; its composition is ~ 76 at. % Al, ~ 8.5 at. % Ni, ~ 5.5 at. % Fe and ~ 10 at. % Cr. Most likely, this composition corresponds to the FeNiAl₅ compound [15] with iron and chromium dissolved in it. This fact is reflected in the corresponding diffractogram (figure 1, c). We denote the detected phase as (Fe,Ni,Cr)Al₅. In the matrix phase, light inclusions of the NiAl intermetallic compound are evenly distributed.

A continuous layer adjoins the Cr15Ni60 alloy (figure 3), which, on average, contains ~ 50 at. % Al, ~ 30 at. % Ni, ~ 12 at. % Fe and ~ 8 at. % Cr and, together with the results of x-ray phase analysis (figure 1, c), most likely corresponds to the NiAl intermetallic compound (β-phase). It is known that the β-phase has a very wide region of homogeneity and, according to the data of [19], can dissolve iron in significant amounts and up to 8–12 at. % chromium. Denote the detected phase as (Ni,Fe,Cr)Al.

![Figure 3. SEM image of a continuous interlayer at the boundary of the DZ with Cr15Ni60 alloy (a) and distribution of elements over its cross section (b).](image)

### 3.2. Heterogeneous interaction

Investigations of the sample after HT at 800 °C for 3 h showed that the processes of heterogeneous interaction proceeded along the entire depth of the aluminum layer. The formed DZ with a thickness of ~ 500 μm has a predominantly needle structure with large fragments of the structure that are characteristic for the products of nonequilibrium crystallization. At the same time, there are no crystallization defects in the DZ, such as pores and cracks (figure 4).
Visually, the DZ formed in the process of heterogeneous interaction can be divided into two regions: a region with large fragments of the structure and a region with a finely dispersed structure adjacent to the Cr15Ni60 alloy.

Metallographic studies, X-ray phase and EDS analysis showed that in the first area of the DZ, in addition to areas of unreacted aluminum (the darkest in color), there are large inclusions of a dark gray color, corresponding in composition (~ 86.5 at.% Al, ~ 13 at.% Cr) to the CrAl\textsubscript{7} phase, which are in the gray matrix of various shades: darker sections of the composition ~ 81 at. % Al, ~ 14 at. % Ni, ~ 5 at. % Fe represent the FeNiAl\textsubscript{9} phase, and lighter with a composition of ~ 79 at. % Al, ~ 10 at. % Ni, ~ 6 at. % Fe and ~ 5 at. % Cr represent the (Fe,Ni,Cr)Al\textsubscript{9} phase. The latter, in contrast to the similar phase detected during homogeneous interaction, is characterized by almost equal iron and chromium contents.

Separate inclusions with composition ~ 76 at. % Al, ~ 24 at. % Ni concentrated at the boundary between the region of large fragments and the finely dispersed region, belong to the NiAl\textsubscript{3} intermetallic compound.

According to the results of the EDS analysis in the scanning mode along the line, the finely dispersed DZ region is most likely a mixture of phases (Fe,Ni,Cr)Al\textsubscript{9} and NiAl\textsubscript{3}. In the immediate vicinity of the Cr15Ni60 alloy there is a light interlayer with a thickness of ~ 3 μm corresponding to the composition of the previously detected phase (Ni,Fe,Cr)Al.

4. Conclusion
The diffusion zone formed on the interlayer boundary of the explosion welded Cr15Ni60-AD1 bimetal in a homogeneous interaction has a layered finely dispersed structure, and in a heterogeneous one, it is predominantly needle-shaped with large fragments of the structure.

Diffusion zones are characterized by heterogeneity in chemical composition, while their phase composition is almost identical: CrAl\textsubscript{7}, FeNiAl\textsubscript{9}, (Fe,Ni,Cr)Al\textsubscript{9}, (Fe,Ni,Cr)Al\textsubscript{5}, NiAl\textsubscript{3}, (Ni,Fe,Cr)Al. The structure of the diffusion zone formed by heterogeneous interaction contains fragments of unreacted aluminum. The transition from the interaction at the solid-solid interface to the interaction at the solid-melt interface leads to a significant acceleration of diffusion processes.

The obtained data can be used for practical purposes in assigning the optimal temperature and time conditions for the heat treatment of bimetallic semi-finished products of AD1 - Cr15Ni60 composition when creating layered coatings of the Al-Ni-Cr-Fe system.

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