Phase Composition and Structure of Multilayered Coatings of Ni–Al System

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Abstract. The nanostructured multilayer coating on the basis of the Ni–Al system is formed by magnetron sputtering. The structural-phase state of the coatings is studied by X-ray analysis. It is established that the coatings with different thickness of nanolayers has NiAl, Al_3Ni, Ni_2Al_3 phases and the solid solution of aluminium in nickel. There are different sets of these phases depending on the thickness of layers in the coatings.

Keywords: multilayered coatings, magnetron deposition, intermetallides, phase composition, microstructure

INTRODUCTION

The NiAl intermetallic compound is very promising due to its physical properties, such as low density, high melting point, oxidation resistance at elevated temperatures and high strength [1–3]. However its application in industry is limited because of brittleness at room temperature. The grain refinement down to the nanometer size improves its plasticity [4, 5]. Therefore, some attempts are made to obtain intermetallic compounds on the basis of Ni–Al with nanosized grains by ion-plasma spraying methods. In recent years, we observe an increase in the number of studies that are directly or indirectly related to producing new functional coatings on the basis of aluminum. One of the directions of this research concerns the development of nanoscale intermetallic systems [6].

The use of the coatings, consisting of nanoscale intermetallic compounds, is very promising. Such coatings extensively protect the bulk material due to their high hardness, high temperature resistance, and friction and wear resistance [7]. In the nanostructured states intermetallic compounds can significantly improve the mechanical properties of materials [8]. Thus, the formation of nanointermetallic in the coatings from metal materials can lead to a significant strengthening [9]. The purpose of this work is studying the structural-phase state of the multilayer coatings on the basis of the Ni–Al system produced by layering magnetron deposition of dissimilar materials with different thicknesses in the range from 9 to 135 nm.

EXPERIMENTAL

The deposition of coatings on the basis of Ni–Al was carried out using a vacuum system of the KVANT type [10]. The setup was equipped by magnetrons with nickel and aluminum targets and a vacuum-arc ion source with titanium cathode. The magnetrons were powered from sources operating in the stabilizing mode; the current frequency was 50 kHz. The sample was placed in a chamber on a rotating table. It was possible to place the sample

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in the following positions: in front of two magnetrons or in front of the ion source with a Ti target. The coatings were deposited on the titanium substrate at the temperature of 300°C in the vacuum chamber. Ion-beam treatment of the substrate surface by Ti ions was performed to improve adhesion between the substrate and the multilayer coating. The temperature was measured using the chromel-alumel thermocouple.

The structural-phase state of the multilayer coating was investigated by X-ray diffraction using the DRON-7 device in Co-K_α radiation. The crystalline lattice parameters were determined using the main diffraction maxima [11]. A fine structure of the multilayer coatings was investigated by transmission electron microscopy (TEM) on the JEM-2100 device. A foil was prepared by the "ross-section" method using the installation ION SLISER-EM-09100IS.

The layer thickness of the coating depended on the rotation rate of the object relative to the fixed magnetron and the discharge power. Three types of the samples with different thicknesses of coating layers were prepared for the experiment. For the first type of the coatings, the thickness of each layer of nickel or aluminum was about 9 nm. For the second type it was 35 nm, for the third type it was 140 nm. The total thickness of all coatings was about 9 μm (Table 1).

RESULTS

It is established that the coating is the phase of the Ni-Al equilibrium phase diagram in different structural modifications. There are some stable intermetallic compounds in the Ni-Al system having the melting point T_m = 854°C (Al_3Ni), 1133°C (Al_3Ni_2), 1638°C (NiAl), 1395°C ($AlNi_3$) [12]. Ni_2Al_3 and Ni_3Al compounds have a relatively narrow homogeneity region; NiAl has a wide homogeneity region, and the phase $NiAl_3$ corresponds to the formula composition. $NiAl_3$, Ni_2Al_3 and Ni_3Al phases are formed by the peritectic reactions. The phase composition of the multilayered coatings of all types and the crystalline lattice parameters of the basic phases are shown in Table 1.

It can be seen that the crystalline lattice parameters of the NiAl phase are a little different for the coatings of all types in comparison with a parameter of the bulk material lattice. It is shown in Table 1 and it is 2.88 Å.

The lower crystalline lattice parameter, compared with the table data, is explained by the substantial amount of aluminum involved in the $NiAl_3$ phase, which results in being NiAl depleted in aluminum. Excess aluminum combines with nickel and the solid solution of aluminum in nickel is formed. The crystalline lattice parameter slightly increases up to 3.523 Å. This fact is due to the difference in Al and Ni atomic radii. The atomic radius of Ni is greater than that of Ni (1.43 and 1.25 Å, respectively), which leads to the increase in the Ni lattice parameter. As it can be seen from Fig. 1, when the thickness of the deposited layers of nickel and aluminum increase, a number of phases and their relationship change. In the first type of the coating there is NiAl with maximum enthalpy of formation [12], a small amount of the $NiAl_3$ phase and the solid solution of aluminum in nickel. The $NiAl_3$ phase and the solid solution of aluminum and nickel are contained in a small amount up to 5%. The layers of nickel and aluminum in this type of the thin coatings are about 9 nm and they have equal thickness, i.e. their composition retains to form the Ni-l phase in the coating. The Ni_2Al_3 phase is added when the thickness of the layer is 35 nm (the coating of the second type). In the coating of the third type the quantity of the secondary phases substantially increases.

TABLE 1. The phase composition of the multilayered coatings on the basis of the Ni-Al system and their structural characteristics

Coating Type	The Thickness of the Coating Layer, nm	The Phases	The Lattice Parameter of NiAl, Å	The Lattice Parameter of the Solid Solution of Aluminum in Nickel, Å
I	9	NiAl, $NiAl_3$, α-Ti	2.867 ± 0.001	—
II	35	NiAl, $NiAl_3$, Ni_2Al_3, α-Ti the solid solution of aluminum in nickel	2.875 ± 0.001	3.525 ± 0.001
III	140	NiAl, $NiAl_3$, Ni_2Al_3, α-Ti, the solid solution of aluminum in nickel	2.873 ± 0.001	3.531 ± 0.001

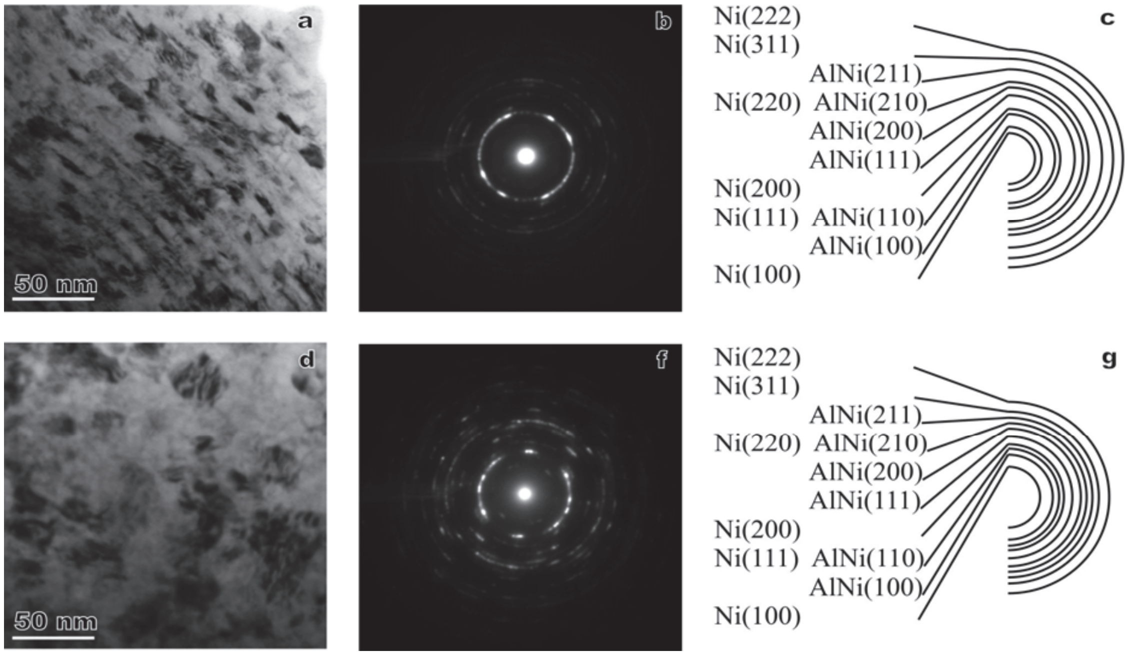

FIGURE 1. TEM images of the multilayered coatings on the basis of the Ni–Al system. TEM images of the area with contrast layers: the bright-field images (a), the microdiffraction patterns (b) and the scheme of their indexing (c). TEM images of the area with the formations passing through some layers: the bright-field images (d), the microdiffraction patterns (f) and the scheme of their indexing (g)

X-ray analysis confirms the investigation by TEM. Figure 1 shows a TEM image of the multilayer coating on the basis of the Ni–Al system with the coating thickness of 9 nm. Ni–Al and the solid solution of aluminium in nickel are identified by TEM (Fig. 1(c, g)). It should be noted that the multilayer coatings have characteristic areas: an area where there is a laminate contrast (1, a), the layers with separate areas where, apparently, SHS reaction occurs. Here it is possible to see the formations of areas throughout some layers (Fig. 1(d)).

The formation of the phases in the coatings is possible in the case of self-propagating high-temperature synthesis (SHS) at magnetron deposition. In our conditions, one of the varieties of SHS, namely, the solid-phase synthesis takes place. It occurs due to the interaction between nickel and aluminum in the interface area in thin films and starts at low temperatures. Several studies indicate that the initiation temperature of the solid-phase reactions in two-layer Al / Ni and the multilayers is in the range of 160°C–275°C [13]. The phase diagram of Al–Ni system shows five stable intermetallic compounds [2]. However, currently there is a definite answer to the question: what phase is the first form. In [13] it is shown, firstly, that the first phase, formed on the interfaces of the film condensates, is the phase which has the least temperature T_f of the structural phase transformation according to the equilibrium phase diagram. Secondly, the initiation temperature of T_0 of the solid solution reactions in thin films coincides with the temperature of the solid solution structural transformation of the first phase ($T_0 = T_f$).

The rule of the first phase, according to the author [14], should be fundamental to solid-phase synthesis, as it is a one-to-one correspondence between the initiation temperatures in two-layer film samples and the corresponding binary phase equilibrium diagram. However, the multilayer thin-film system is highly non-equilibrium, so it is not possible to give a definite answer.

Thus, the multilayer nanostructured coatings, having different phase composition, depend on the thickness of the coating formed by the magnetron sputtering method. NiAl with the superstructure B2 is the main phase of all types of coatings. There are the NiAl phases having the orthorhombic crystal lattice. There are also the phases having the hexagonal crystal lattice and the solid solution of aluminum in nickel in the coatings composition.

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