Investigation of fine metal films of the Ni-Al system by physical methods

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Abstract. The article describes the results of investigations of ultrathin Ni-Al films, obtained by the resistive method of thermal evaporation and having characteristic islands sizes of 700-1000 nm with a film thickness of about 500 nm. The work presents a method for producing a film using an installation for creating a high vacuum and subsequent film deposition. Investigations of the obtained film sample were carried out with the help of an optic microscope, a scanning probe microscope and a Fourier analyzer. Kinetic characteristics and relief of the film, characteristic islands sizes are established, the search for regularities in the island structure of films is carried out, and its electrical conductivity is determined.

1. Introduction

Currently, perspective researches on nanoscale objects carried out have made it possible to identify new fundamental properties of materials and their potential technological applications. Many investigations were devoted to studying physical and chemical properties of such materials, particularly, fundamental investigations were carried out using the number of heterogeneous catalysts, for example, the metal islands grown on thin films [1-4] or the surfaces of monocrystals [5, 6].

Thin metal films, metal nanostructures and nanoparticles are widely used in photonics, plasmonics, sensor technologies. Examples are optic fibers and waveguides with metal nanoparticles on the surface [7], chemical [8] and biological sensors [9], plasmon waveguides and nanocavities, nanoantennas [10] and optical nanotransistors [11], metamaterials [12], electromagnetic field concentrators [13], optical composites [14], LED [15], plasmonic photonic crystals and other nanoplasmonic devices.

A topical research object in various technology fields is alloys of the Ni – Al system. This alloy has properties such as high strength and heat transfer, is easy to process, has metal-like properties, and due to its low density and high strength, it can significantly reduce the weight of the product with strength characteristics similar to heavier materials.

These properties of the alloy made it possible to use NiAl in the aviation industry as elements of turbines of a gas turbine engine, in the space industry, in extreme conditions of mining and other fields of science and technology.

At present, an urgent task is to obtain binary and multilayer films of the Ni-Al system, to synthesize intermetallic compounds in them, and to study the structure of the films obtained. In the course of the research, it was found that thin intermetallic films obtained in a high vacuum have certain characteristics that are fundamentally different from the properties of macro-objects. Also, in such thin films, specific processes and phenomena are observed that are absent in macroobjects. By selecting the condensation
conditions and varying the components of thin films, it becomes possible to adapt them to the required parameters, which is of interest to developers in the field of microelectronics, nanoelectronics and in the development of various optical and chemical sensors. [16]

A thin film is a material belonging to two-dimensional nanostructured objects, which is a layer of a substance in contact with the gas phase on both sides and whose properties depend on the size in one of the directions (film or coating thickness). The dimensions of the films are comparable to the fundamental physical parameters, which have the dimension of length and are commensurate with the mean free path of an electron, the De Broglie wavelength, which is up to 100 nanometers in size.

The aim of this work was to obtain binary and multilayer films of the Ni-Al system, to synthesize intermetallic compounds, and to study the structure of the films by optical and probe microscopy, as well as by the eddy current method, and to determine the size of islands and the kinetics of the synthesis wave.

2. Material choices and design
In this work, the resistive method of thermal evaporation was used, in which an electric current is used to heat the evaporator, which in turn heats the evaporated material to the evaporation temperature, at which its atoms quickly evaporate from the melt. This method is based on the supply of energy to the evaporated substance by heat transfer from the heater.

The installation for applying thin films in vacuum has a system of nozzles connecting the main elements to create a high vacuum, that is, an NF backing vacuum pump (to create a preliminary vacuum of $10^{-1} – 10^{-2}$ Pa) and an ND diffusion pump (to create a high vacuum up to $10^{-5}$ Pa), with a working volume in which the deposition and synthesis of thin films occurs.

The working volume (RO) is a cylindrical glass dome that moves on hinges and can be folded upward to access evaporators, substrates, and other mechanisms for producing thin films. In the lowered state, the hood fits snugly against the vacuum rubber sealing O-ring.

The pumps are designed to create and maintain the required vacuum to obtain clean and high quality films. The unit uses a mechanical backing vacuum pump, which operates in the medium vacuum range and pumps out the unit elements for a preliminary vacuum of up to $10^{-2}$ Pa. The pumping process is based on the mechanical suction and expulsion of gases in the pump cylinder using a rotor with plates during their movement.

The study of the surface of the films was carried out with a NEOPHOD 32 optical microscope, and in particular, with its help, the structure of the surface of the films after the passage of the synthesis wave was studied.

Also, the study of the surface was carried out with a Solver NEXT probe microscope, the scanning element of which is specially prepared probes in the form of needles, the tip diameter of which is about ten nanometers. The working distance between the probe and the surface was 0.1 - 10 nanometers.

The processing of images of the surfaces of thin films obtained during the experiment was carried out using the Image Analysis program, in which it is possible to determine the size of islands, perform a Fourier analysis of the surface, an analysis of the surface roughness, and a fractal analysis of the surface of thin intermetallic films.
The radial growth rate of the island was calculated using (formula 3.1.2), turned out to be two orders of magnitude lower than the propagation velocity of the synthesis wave, and amounted to 0.028 mm/s, and the growth rate of the area of the nucleus (island) turned out to be an order of magnitude lower - 0.0034 mm²/s.

In table 1 the calculated front propagation velocity and the island growth rate are given, determined from the magnitude and time of moving objects in two consecutive frames.

**Table 1.** Velocity of front propagation and growth of Ni-Al film islands.

| Thin film system | r₁ - radius of the first island, μm | r₂ - radius of the first island, μm | Reaction front speed, mm/s | Radial growth rate of islands, mm/s | Island area growth rate, mm²/s |
|------------------|-----------------------------------|-----------------------------------|---------------------------|-----------------------------------|-------------------------------|
| Ni-Al            | 9.55                              | 27.95                             | 1.03                      | 0.028                             | 0.0034                        |

These results allow us to conclude that the synthesis wave is formed to a greater extent due to an increase in the number of islands, and not due to an increase in their area. The subsequent development of the islands indicates a sequence of other reactions leading to the final phase composition of the thin film. All changes can be traced by examining the surface microstructure as shown in (figure 1–4).
4. Surface examination with a scanning probe microscope

The structural features of the thin-film condensate of a binary Ni / Al film were investigated with a scanning probe microscope using the atomic force method (figure 5).

Figure 5. Structure of an intermetallic thin film of the Ni-Al system.

A comparison of the relief at different stages of the formation of an intermetallic film with protruding islands characteristic of metal films is shown in (figure 6–9).

Figure 6. Origin zone.
Figure 7. Growth zone.

Figure 8. Growth zone.

Figure 9. Coalescence zone.
For this film, an analysis of the surface graininess was carried out and the program identified 66 islands differing in size and shape, the dependence of the diameter on the number of which is shown in the histogram (figure 10), from which it follows that a larger number of islands have a diameter of 0.7 micrometers to 1.3 micrometers. The maximum peak falls within the range of dimensions 0.9 - 1 micrometer. The average diameter is 1.164 micrometers.

![Figure 10. Distribution of the diameter of the islands of the Ni-Al film.](image)

Also, for this film a Fourier analysis was performed (figure 11), which allows obtaining information on the structural properties of the surface. For the original 2D function this method allows calculating the discrete Fourier transformation, which is a function of two variables - spatial frequencies.

![Figure 11. Power spectral density function RadialPSD.](image)
The maxima of the radial distribution function indicate a combination of three periodicities (harmonics) in the structure of the islands of the intermetallic film. As follows from the radial distribution function, the spatial frequency at the first maximum is 0.468 μm⁻¹, which corresponds to a wavelength of 2.136 μm. In the second maximum, the frequency is 0.643 μm⁻¹, which corresponds to a wavelength of 1.553 μm. And in the third maximum, the frequency is 0.994 μm⁻¹ with a wavelength of 1.005 μm. The packing periodicities of the islands show that islands of different sizes are distributed with corresponding periodicities, and this indicates the self-organization of the island structure during the formation of an intermetallic film.

The final stage of the study was to determine the electrical conductivity of the film under study. For this purpose, the previously developed software and hardware complex IETP-4 was used. The measurement was carried out with the help of the eddy-current method of control using a surface-mounted superminiature eddy-current transducer [17]. After testing the operation of the system with different amplitudes of the exciting signal and at different frequencies, an amplitude of 1.1 V and a frequency of 3 MHz were chosen as the working ones. To eliminate random measurement errors caused, in particular, by the noise of the amplifying system, the obtained data were averaged according to the standard technique.

In figure 12 the initial data are presented: the measured values of the voltage on the measuring winding of the VTP (eddy current transducer), in the absence and in the presence of an Al film. Area 1 (N = 150-600) corresponds to the signal in the absence of the control object – VTP (eddy current transducer) uncompensation. Area 2 (N = 620 - 1190) corresponds to the signal in the presence of a film. In Fig. 13 is a diagram of an algorithm for calculating the electrical conductivity of a film from the difference between the signal from the film and the signal from the substrate.

![Figure 12](image-url)  
**Figure 12.** Determination of the average signal amplitude, <A1, 3> - signal swing without film, <A2> - in the presence of film.
Figure 13. Determination of the average signal amplitude, \(<A1>\) - signal swing without film, \(<A2>\) - in the presence of film.

In Area 1, the averaged signal amplitude was 14.53 mV, in Area 2 - 5.41 mV. The difference between the amplitude in Area 1 and the amplitude in Area 2 (\(\Delta U\)) is 9.12 mV.

The electrical conductivity (\(\sigma\), MSm / m) is determined according to the experimentally obtained equation \(f(x) = 0.0809x - 0.3696\), according to the graph constructed from samples of films with known electrical conductivity, where point 1 corresponds to a film sample with electrical conductivity of 0.1 MSm / m and a signal amplitude difference of 16.8 mV, point 2 corresponds to a film sample with an electrical conductivity of 1.23 MS / m and a signal amplitude difference of 19.6 mV. Based on the results of approximating the data obtained by measuring samples with a known specific electrical conductivity, it was possible to establish the specific electrical conductivity of the film - about 0.14 MSm / m.

5. Conclusion
1. In the course of research, it was found that the synthesis wave has a complex structure, consists of reaction islands and three zones formed as a result of multiple nucleation of reaction centers, creating the apparent effect of a continuous synthesis wave.

2. The kinetic parameters of the synthesis wave and islands were determined, as well as their sizes. It was found that the speed of the synthesis wave was 1.03 mm / s, and the radial growth rate of the island was 0.028 mm / s. The size distribution of the islands indicates that the average diameter of the islands in the taken area unit was 1.164 micrometers.

3. The Fourier analysis carried out indicates the presence of periodicities in the island structure of the intermetallic film.

4. It is revealed that the island structure is a complex periodic three-mode structure with the periodicity parameters of 2.136 µm, 1.553 µm, and 1.005 µm, respectively.

5. The value of the electrical conductivity of the film is established - about 0.14 MSm / m.

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