Coating in the Ni-Al system using the SHS method

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Abstract. Using the method of self-propagating high-temperature synthesis, coatings based on aluminum nickelides were obtained. The processes occurring in the layers of a powder mixture of nickel and aluminum are studied. The influence of the coating thickness and the degree of dilution of the powder mixture with aluminum oxide on the maximum temperature of the combustion wave and the rate of its propagation is established. The coating consists of small crystals of NiAl, Ni3Al, fused together. The coating has good electrical conductivity and can be used as electric heaters.

1. Introduction
Intermetallics formed in the Ni-Al system have high thermal stability, resistance to oxidation, hardness and electrical conductivity [1,2]. Coatings from these materials are used as heat-resistant protective layers [3]. Traditionally, such coatings are produced by the method of air-plasma spraying, the advantages of which include the possibility of coating on parts of any geometry and dimensions and low cost of the process [4]. The disadvantages are high porosity of coatings [4].

In this paper, we proposed a method for obtaining a coating, which consists in applying a mixture of nickel and aluminum powders to a substrate. Heating the portion of the powder layer leads to the appearance of an exothermic reaction of aluminum nickelides synthesis with increasing temperature. Later the reaction spreads over the surface in the form of a combustion wave. This process is the essence of obtaining materials by self-propagating high-temperature synthesis (SHS). Self-propagating high-temperature synthesis is a simple and reliable method of obtaining products made of aluminum nickelides. SHS processes in the Ni-Al system have been studied in sufficient detail [5]. However, such studies were carried out for samples pressed from powders in the form of a cylinder. For samples in the form of a layer of a powder mixture, studies of processes in the combustion wave, the regularities of the change in velocity, and other parameters of the process have not been practically carried out. Therefore, such studies are relevant. In this work, aluminum nickelide coatings are designed for use in high-temperature film electric heaters. Typically, such heaters are obtained either by spraying refractory materials using magnetron sputtering methods or by analogous methods [6]. A method is also known in which a mixture of metal powder or metal alloy with alkali glass powder is applied to a substrate and heated in an electric furnace under an inert atmosphere to a temperature of about 1000 °C. Glass particles melt and bind metal particles [7]. Thus, an electrically conductive coating is obtained. The methods described above have such drawbacks as the complexity of the equipment used, high energy costs. The method we propose is simple. Energy in this method is required only to initiate the process. For this, a
laser, an electric discharge, or the like can be used. The method makes it possible to obtain coatings on products of any shape, with the most complex geometry of the pattern.

The aim of the work is to study the influence of the layer thickness and the degree of dilution of the initial mixture with an inert diluent on the temperature and speed of propagation of the combustion wave, the structure and electrical conductivity of the coating.

2. Procedure

Powders of nickel UT1 and aluminum of ASD-4 grade were mixed in a ratio of 31.5% by weight. % Al and 68.5 wt. % Ni to obtain an intermetallic compound NiAl. The powders were annealed in a vacuum at 200 °C. Alumina powder (XC) was used as an inert substance. Thermocouples of TXA mark were fixed on a ceramic plate at a distance of 35 mm from each other. A mixture of powders in the form of a suspension in isopropyl alcohol was applied to a plate of ceramic VK-1 through a stencil with a thickness of 0.3 to 2 mm, a width of 20 mm. The coating was air dried at room temperature for 24 hours. To register thermograms, thermocouples were connected to the ADC and a personal computer. The propagation velocity was determined by delaying the signal from two thermocouples (figure 1).

![Figure 1. The equipment for experiments.](image)

Initiation of the reaction was carried out with an electric spiral heated by an electric current from an autotransformer. The phase composition of the synthesis products was determined on a portable desktop X-ray instrument RIKOR, (radiation CoKα) provided by Tomsk Common Use Center SB RAS. Microstructural studies were conducted using an optical microscope (Axiovert 200M, KarlZeiss). The electrical resistance of the coatings was measured with an ohmmeter F-410 measuring range 1×10⁻²-1×10⁻⁷ Ω.

3. Discussion

The experimental results show that after the initiation of the reaction, a combustion wave with a width of the order of 5 mm runs through the sample. The profile of the combustion wave is shown in fig. 2a. The temperature in the combustion wave is significantly lower than for cylindrical samples of similar composition. This is explained by the large heat dissipation of flat samples. On the profile of the combustion wave, an inflection is observed at a temperature of about 600 °C. This temperature corresponds to the melting point of aluminum (620 °C). This allows us to say that the process proceeds through a liquid-phase mechanism. This mechanism is confirmed by the fact that the propagation velocity of the wave (about 10 mm/sec) has a large value and is close to the velocity of the combustion wave front for cylindrical samples of similar composition. In figure 2b is a photomicrograph of the sample section after the combustion wave passes. The figure shows the arc-shaped zones of penetration of the material. These zones characterize the front of the combustion wave. It can be seen that the front...
is not flat, but curved. The reason for this phenomenon may be that at the edge of the band the heat sink is much larger and the local speed is less.

**Figure 2.** Profile of the combustion wave a), a photomicrograph of the coating area after the SHS b).

In figure 3a shows the dependence of the maximum temperature of the combustion wave and its propagation velocity on the coating thickness. It is seen that, with increasing thickness of the coating, the velocity of the combustion wave front and the maximum temperature increase. An analogous dependence is also observed for cylindrical samples with an increase in their diameter. This is due to the fact that the amount of heat released in the combustion wave increases. The heat losses are proportional to the area of the sample and, with a change in its diameter, increase to a lesser extent than heat release. Consequently, the energy of the system increases and, as a consequence, the temperature and velocity of propagation of the front. In layer systems, the thickness of the sample is an analog of the diameter for cylindrical samples and the observed regularities are similar.

**Figure 3.** The front propagation velocity (curve 1) and the maximum temperature (curve 2) of coatings of different thicknesses (a) and when the mixture is diluted with aluminum oxide (b)

In figure 3b the dependence of the maximum temperature of the combustion wave and its propagation velocity on the degree of dilution of the powder mixture with an inert substance (Al$_2$O$_3$) is presented. It can be seen from the figure that an increase in the content of aluminum oxide reduces the maximum temperature of the combustion wave and the rate of its propagation. This is due to the fact that aluminum oxide is not involved in the chemical reaction and is an inert substance. But the heating consumes part of the energy released in the chemical reactions that occur in the combustion wave. This regularity agrees with the theoretical concepts of the course of processes of a combustion wave.

X-ray phase analysis showed that the coating contains the NiAl and Ni$_3$Al phases (figure 4a). The predominant phase is NiAl. Nevertheless, the presence of the Ni$_3$Al phase indicates a significant underreaction in the combustion wave. This is due to the fact that the temperature in the combustion wave is much smaller than for the samples in the form of a cylinder. In addition, after the coating is
separated from the substrate, a thin layer of metallic aluminum remains on it. Therefore, the aluminum phase is not detected on the diffractogram. Increasing the coating thickness increases the concentration of the target NiAl phase. This is due to the fact that as the thickness of the powder layer increases, the temperature in the combustion wave increases. This leads to an intensification of processes and an increase in the degree of conversion. In figure 4b is a photomicrograph of the coating section. It can be seen that the coating consists of small crystals fused together. The coating is dense, homogeneous, open pores are absent.

![Diffraction pattern](image)

**Figure 4.** Diffraction pattern a) and microstructure of the coating. Phases: 1 - NiAl, 2 - Ni$_3$Al.

The electrical resistance of the coating is $2.8 \times 10^{-2}$ Ohm. This coincides with the resistance value for cylindrical samples obtained by the SHS method. This is due to the fact that the coating consists of many small crystals that have direct contact with each other. It should be noted that the electrical resistance decreases with increasing coating thickness, which indicates that the resistivity of the coating material remains constant.

Thus, in the course of the work, the influence of the coating thickness and the degree of dilution of the powder mixture with an inert substance on the maximum temperature of the combustion wave and its propagation velocity is shown. It is shown that the coating consists of small crystals of NiAl, Ni$_3$Al, fused together. The coating has good electrical conductivity and can be used as electric heaters.

4. Conclusion

1. The principal possibility of SHS-processes in thin layers of a mixture of powders based on nickel and aluminum is shown.
2. The effect of the thickness of the powder layer and the degree of dilution of the mixture on the propagation velocity of the front and the maximum temperature of the reaction wave are studied.
3. It is shown that the coating consists of small crystals of NiAl, Ni$_3$Al, fused together.
4. The coating has good electrical conductivity and can be used as electric heaters.

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