Self-propagating high-temperature synthesis of heat-resistant electrically conductive coatings based on Ni-Al and Ti-Al-C compounds

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Abstract. Coatings based on aluminium nickelides and Ti$_2$AlC, Ti$_3$AlC$_2$ MAX-phases are obtained by the method of self-propagating high-temperature synthesis. The processes occurring in the powder mixture of nickel and aluminium, as well as in the titanium-aluminium-carbon mixture are studied. The effect of the thickness of the coating on the maximum temperature and velocity of combustion wave is found. The coating consists of small crystals NiAl, Ni$_3$Al or Ti$_2$AlC, Ti$_3$AlC$_2$, fused together. The coating has high electrical conductivity and can be used as heat-resistant protective coatings or electric heaters.

1. Introduction

Compounds formed in the Ni-Al and Ti-Al-C systems have high heat resistance, oxidation resistance, hardness and electrical conductivity [1, 2]. Coatings of these materials are used as heat-resistant protective layers [3]. Traditionally, such coatings are produced by the method of air-plasma spraying [4]. The method requires the use of a large amount of energy to create a plasma and to provide a high temperature for melting the coating components. In this paper, we have proposed a method for obtaining a coating, which consists in applying a mixture of powders of the initial components to the substrate. Heating a portion of the powder layer leads to an exothermic synthesis reaction of compounds with increasing temperature. Further, the reaction spreads over the surface in the form of a combustion wave. Thus, the energy costs are insignificant and are only needed to initiate the process.

This process is the essence of obtaining materials by the method of self-propagating high-temperature synthesis (SHS). The method is often used to obtain materials in the system Ni-Al and Ti-Al-C, pressed from powders in the form of a cylinder or other three-dimensional shapes [5-9]. For samples in the form of a powder mixture layer, the research of processes in the combustion wave, the laws of change in velocity, and other process parameters was practically not carried out. Separate studies on this subject are known [10, 11]. Therefore, such studies are relevant. In this work, the coatings from aluminium nickelide and MAX phases Ti$_2$AlC, Ti$_3$AlC$_2$ are intended for use as heat-resistant protective coatings and high-temperature film electric heaters. Typically, such heaters are obtained either by sputtering refractory materials using magnetron sputtering methods or similar methods [12].

A method is also known in which a mixture of metal powder or a metal alloy is applied onto a substrate and heated in an electric furnace in an inert atmosphere to a temperature of about 1300 K. The particles of glass melt and bind the metal particles [13]. Thus, a conductive coating is obtained. The methods described above have such disadvantages as the complexity of the equipment used, high energy
costs. The method proposed by us is simple, requires little energy, allows 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 effect of the layer thickness on the temperature and speed of propagation of the combustion wave, the structure and electrical conductivity of the coating. The paper is structured as follows: section 2 describes the experimental technique. The section 3 presents experimental data and characteristics of the obtained coatings. Section 4 presents the conclusions drawn from the research results.

2. Procedure
To obtain a coating based on aluminium nickelides, a mixture of powders of nickel UT1 and aluminium grade ASD-4 was prepared in a ratio of 31.5 wt. % Al and 68.5 wt. % Ni. And to obtain coatings based on the MAX phases of Ti₂AlC, Ti₃AlC₂, powders of titanium PTX with a particle size of less than 40 μm, aluminium (ASD-4), carbon black (PM-15) were used in a ratio of 70 wt. % Ti, 20 wt. % Al and 10 wt. % carbon black. The powders were previously annealed in vacuum at 200 °C. A mixture of powders in the form of a suspension in isopropyl alcohol was applied onto a ceramic plate VK-1 through a stencil with a thickness of 0.3 to 2 mm and a width of 20 mm. The coating was dried in air at room temperature for 24 hours. Previously, thermocouples of the ТСА or WRe 5/20 brand were fixed on the ceramic plate at a distance of 10 ± 35 mm from each other. To record thermograms, thermocouples were connected to an ADC and a personal computer. The propagation velocity \( \omega \) was determined from the delay of the signal from two thermocouples (figure 1). The speed of propagation of the front calculated by the formula: \( \omega = \Delta t / \Delta h \). Here, \( \omega \) is the speed of propagation of the front, \( \Delta t \) is the delay of the signal from two thermocouples and \( \Delta h \) is a distance from each other. The initiation of the reaction was carried out using an electric helix 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 \( 1 \times 10^{-2}-1 \times 10^7 \) Ω.

![Figure 1. Experimental setup.](image)

In separate experiments, the temperature of the combustion wave was measured by spectral pyrometry [14]. To determine the temperature, radiation from the site \( (5 \times 10^{-3} \text{ m}) \) of the reaction wave through the optical fiber introduced into the reaction chamber was recorded by a spectrometer (HR 4000, Ocean Optics) \( (200 \div 1100 \text{ nm}, \text{ frequency } 220 \text{ Hz, duration of signal accumulation in a single spectrum } - 4.5 \cdot 10^{-3} \text{ s}) \). The obtained spectra were plotted in the Wien coordinate plane: \( x = \lambda^{-1}, y = \ln (\lambda^2 I) \) (here, \( \lambda \) is the wavelength, \( I \) is the spectral intensity of the radiation). data in the wavelength range of 500 \( 

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580 nm, meaning the fulfillment of the similarity condition, allowed by angle Pull straight find the temperature corresponding to each spectrum. The equation was a direct least squares method. Temperature detection error caused by the linearity of the standard deviation of the experimental points does not exceed 1%.

3. Discussion

The experimental results show that after initiating the reaction, a burning wave with a front about 5 mm wide runs through the sample. The burning wave profile is shown in figure 2a. The temperature in the wave of combustion is much lower than that of cylindrical samples of similar composition. This is due to the large heat sink for flat specimens. On the profile of the combustion wave for samples of the Ni-Al system, a bend is observed at a temperature of about 920 K. This temperature corresponds to the melting point of aluminium (930 K). This suggests that the process proceeds through a liquid-phase mechanism. The wave propagation velocity (5 ÷ 10 mm/s) is close to the velocity of the combustion wave front of cylindrical samples of similar composition.

![Figure 2. Combustion wave profile (a) and the emission spectrum from the combustion wave (for Ni-Al) (b) 1 – Ti-Al-C system, 2 – Ni-Al.](image)

For samples of composition 2Ti-Al-C, the temperature of the combustion wave front is higher than for samples of Ni-Al. This is also consistent with the data obtained for cylindrical samples. The emission spectrum from the combustion wave, shown in figure 2b, is close in shape to the spectrum of the thermal radiation of a heated body; the characteristic emission bands of the ions of the components of the initial mixture are not observed. The brightness temperature calculated from the emission spectra at 200 ÷ 300 K above the temperature measured by a thermocouple. This may be due to the effect of radiation from the oxidation products of the powders, since the experiment was conducted in air.

Figure 3 shows the micrograph of the sample area after the passage of a combustion wave. The arc-shaped zones of material penetration are visible. These zones characterize the front of the burning wave and it is not flat, but curved. The reason for this phenomenon may be the fact that at the edge of the strip the heat sink is much larger and the local speed is less. With a larger magnification, it can be seen that the sample consists of small droplets of material, fused together.

![Figure 3. Photos of the surface of the sample Ni-Al after SHS at different magnifications.](image)
With a coating thickness of less than 0.2 mm, the front does not spread, and with a thickness of more than 1.5 mm, the ceramic substrate is destroyed due to thermal shock. With an increase in the thickness of the coating as NiAl, the speed of the combustion wave front and the maximum temperature increase (figure 4a). This is due to the fact that the amount of heat released in the combustion wave increases. Heat losses are proportional to the sample area and, when its diameter changes, increase to a lesser degree than heat generation. Consequently, the energy of the system increases and, as a result, the temperature and speed of propagation of the front. In layered systems, the sample thickness is analogous to the diameter for cylindrical samples and the observed patterns are similar.

![Figure 4.](image)

**Figure 4.** The front propagation velocity (curve 1) and the maximum temperature (curve 2) of Ni-Al (a) and Ti-Al-C (b) coatings of various thickness.

![Figure 5.](image)

**Figure 5.** Sample diffractograms: I – NiAl, II – Ti2AlC (a). Phases are designated: 1 – NiAl, 2 – Ni3Al, 3 – Ti2AlC2, 4 – Ti3AlC2, 5 – TiC.

From figure 4b it can be seen that a similar regularity is observed for the Ti-Al-C system, however, with a large layer thickness, the maximum front temperature decreases, and the velocity tends to a constant value. This is due to the deterioration of heat transfer along the layer due to loosening of the powder layer under the action of gases adsorbed on the powder [11].

The Ni-Al coating contains NiAl and Ni3Al phases (figure 5). The predominant phase is NiAl. Nevertheless, the presence of the Ni3Al phase indicates a significant lack of response in the combustion wave. This is due to the fact that the temperature in the combustion wave is much lower than for samples in the form of a cylinder. Increasing the thickness of the coating increases the concentration of the target phase NiAl. This is due to the increase in temperature in the combustion wave and the intensification of
Figure 6a shows the microstructure of the Ni-Al coating. It can be seen that the coating consists of droplets of the material, fused together and the phases NiAl and Ni\textsubscript{3}Al are distributed in each other. The coating based on the Ti-Al-C system consists of the phases Ti\textsubscript{2}AlC, Ti\textsubscript{3}AlC\textsubscript{2}, TiC. With an increase in the thickness of the powder mixture, the content of Ti\textsubscript{2}AlC relative to Ti\textsubscript{3}AlC\textsubscript{2} increases. The high content of titanium carbide indicates a significant failure in the system. Figure 6a shows a micrograph of the Ti\textsubscript{2}AlC coating site. It can be seen that the coating consists of small rounded particles, often hollow, fused together. With a larger magnification, it can be seen that the particles consist mainly of needle-like crystals of MAX phases. Ni-Al coating consists of rounded solid particles fused with each other. At high magnification, it can be seen that the particles consist of two phases NiAl and Ni\textsubscript{3}Al distributed in each other.

![Figure 6](image_url)

**Figure 6.** Microstructure of the coating Ni-Al (a) and Ti\textsubscript{2}AlC (b).

The electrical resistance of the coating based on Ni-Al and Ti-Al-C systems is 2 ÷ 8×10\textsuperscript{-2} Ω. 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 particles fused 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.

### 4. Conclusions

1. The effect of the thickness of the powder layer and the mixture ratio on the front propagation velocity and the maximum temperature of the reaction wave is studied during SHS of powder layered mixtures of Ni-Al and Ti-Al-C.
2. The coating consists of round fused particles based on heat-resistant phases NiAl, Ni\textsubscript{3}Al or Ti\textsubscript{2}AlC, Ti\textsubscript{3}AlC\textsubscript{2}
3. The optimum thickness of the coating is 0.2 ÷ 1.2 mm.
4. The Ni-Al and Ti-Al-C based coating possesses an electrical resistance in the range of 2 ÷ 8×10\textsuperscript{-2} Ω and can be used as film heaters.

### Appendices

**MAX phases** - chemical compounds with a crystal lattice of the MAX type. Where M is an element from the group of transition metals (Ti, Zr, etc. A - elements Al, Si, etc., X - 'elements C, B, etc.
SHS – self-propagating high-temperature synthesis.

ADC – analog to digital converter.

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