Structural features of the coatings of the Ni-Al system obtained by air-plasma spraying

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Abstract. This article deals with the structural features of nickel aluminides coatings obtained by air-plasma spraying with the unit of annular injection of powder. The subsonic (plasma velocity is 1200 m/s) and supersonic (plasma velocity is 1900 m/s) regimes were used for coatings deposition. Ni₃Al powder (Ni is base; 13-15 wt. % Al) was applied to the pipes of low-carbon steel 20 (0.2 % C). The structure and phase composition of the coatings were investigated by optical microscopy, scanning electron microscopy, transmission electron microscopy, and X-ray phase analysis. It is established that the porosity of the coatings obtained at supersonic regimes is reduced by a factor of 2. Ni₅Al₃ and Ni₃Al₃ are shown to be the main phases of coatings. Ni₅Al₃ phase volume fraction of the coatings obtained at supersonic regimes is revealed to be lower which reduces the microhardness of these coatings. It is shown that Ni₃Al phase has subgrain structure and Ni₅Al₃ phase has lamellar structure.

1. Introduction

Plasma spraying is a widely used method of powder materials coatings deposition [1-5]. This technology is known to allow spraying of any materials (metals, ceramics, intermetallics) to any substrate [1, 2]. Plasma coatings are usually used for corrosion protection, for electrical insulation, for enhancing wear resistance and heat resistance etc. [2, 5, 6-9]. During the spraying, the powder particles are heated to molten or plasticized state, accelerated by the gas flow, and then deformed and crystallized after hitting the substrate surface thus forming laminated coating [1].

Currently the main method of powder injection into a plasma jet is cross-point injection through the powder supply tube [10-12]. This method of powder injection leads to raising the heterogeneity of temperature fields and plasma jet velocity which reduce the quality of the formed coatings. In this research the air-plasma spraying with the unit of annular injection of powder was used for the coatings formation. Previously we showed that this design of the plasmatorch allows obtaining high quality dense coatings from the materials of the system NiCrSiB [9] and B₄C-Ni [13]. The maximum porosity of the obtained coatings does not exceed 1…2 %. Unlike the listed materials, the porosity of the coatings of Ni₃Al powder obtained by this technology reached 6 % [8]. In addition, unmelted particles are presented at the obtained coatings. It is known that one of the ways to raise the density of ceramic and intermetallic coatings is the increase the sprayed particles velocity in the plasma jet [14,
This article presents results of structural investigations of Ni3Al coatings obtained by air-plasma spraying at subsonic and supersonic regimes.

2. Materials

Ni3Al powder 40…100 μm diameter was used as material for coating forming. The chemical composition of the powder was: Ni - base; 13…15 wt. % Al.

The air-plasma spraying was carried out at the Institute of Theoretical and Applied Mechanics SB RAS using the plasmatorch PNK-50 with the unit of the annular injection of powder. The cylindrical nozzle and the Laval's nozzle [16] were used to provide the subsonic (plasma velocity is 1200 m/s) and the supersonic (plasma velocity is 1900 m/s) regimes respectively. Pipes of steel 20 (0.2 % C) with 60 mm internal diameter and 3 mm wall thickness were used as the substrate. Previously, we determined the spraying optimal regimes for Ni3Al powder: the arc current was 200 A, the voltage was 223 V [8]. The air was used as a transporting, focusing and orifice gas, the blend of the air and the propan-butan was used as a protective gas. The spraying distance was 170 mm. To reduce the level of residual stresses after spraying, we carried out the annealing of steel pipes with coatings at temperature 300 °C for 5 hours.

The velocity and temperature measurement of Ni3Al particles during spraying at the subsonic regime was carried out using an optical measuring complex [1, 17]. It is established that the average values of the particles velocity at the spraying distance at various regimes were within the range of 200…230 m/s, and temperatures within the range of 2290…2410 K. The velocity and temperature measurement of Ni3Al particles in the supersonic regime were not carried out. However, authors in the paper [16] showed that at spraying of 20…63 μm diameter NiCrSiB powder on the same equipment the transition from the subsonic to the supersonic regime leads to increase of average velocity of particles from 300 to 500 m/s and to slight rise of their temperature.

We investigated the coatings structure using optical microscope Carl Zeiss Axio Observer Alm, scanning electron microscope Carl Zeiss EVO50 XVP and transmission electron microscope FEI Tecnai G2 20 TWIN. The transversal cross-sections were objects for structural investigations using methods of optical and scanning electronic microscopy. The samples were pressed into the polymer matrix and prepared by standard method including mechanical grinding and polishing. For transmission electron microscopy we cut 3 mm diameter workpieces from the coatings. The workpieces were mechanically thinned to the thickness of 90…100 μm. Then spherical holes were ground using abrasive paste and ion thinning. The phase composition of the coatings was studied using the X-ray diffractometer ARL XTRA in CuKα radiation. The coatings porosity was evaluated with the help Axio Vision Multiphase (Carl Zeiss) software. The coatings microhardness was estimated using microhardness tester Wolpert Group 402MVD at 100 N load.

3. Experimental details

Figure 1a and b shows the cross-sections of the compounds "coating-substrate" obtained at the subsonic and the supersonic regimes, respectively. Such defects as cracks or delaminating of coatings are not observed. The coatings material consists of particles melted in a plasma jet and plastically deformed particles. It can be noticed that unmelted (round) particles are also presented in the coatings obtained at subsonic regime (figure 1a, marked by circles). This type of particles are not observed in the coatings obtained at the supersonic regime. The porosity of the coatings obtained at the supersonic regime is 2 times lower (~ 2-3 %).

Figure 1c shows that two various phases (1 and 2) as well as regions with a mixed two-phase structure (3) are observed in the coatings obtained at the supersonic regime. Only mixed two-phase areas are presented in the coatings obtained at the subsonic regime [8]. Figure 1d shows a more detailed image of the two-phase area. There are dark gray grains with streaked structure. The plates direction in individual grains has different orientation. A light-gray phase is distributed on the grain boundaries.
Figure 1. Coatings structure: a – the subsonic regime; b-d – the supersonic regime. a-c – optical microscopy; d – scanning electron microscopy in back-scattered electrons. 1, 2 – areas with various phases; 3 – two-phase area.

X-ray diffraction analysis identified that Ni$_3$Al and Ni$_5$Al$_3$ are the main phases of plasma coatings (Figure 2). The volume fraction of Ni$_5$Al$_3$ phase in the coatings obtained at the subsonic regime is higher. It is also confirmed by microhardness measurements. The average microhardness for the coatings obtained at the subsonic regime is 630 HV, while only 430 HV for coatings obtained at the supersonic regime.

Figure 2. X-ray diffraction pattern of coatings: a – the subsonic regime; b – the supersonic regime.
The method of transmission electron microscopy was used for studying the features of the fine structure of nickel aluminides coatings. High speeds of mixing and cooling of the coating material lead to the formation of various phases. Electron diffraction patterns analysis indicates the presence of intermetallic phases Ni$_3$Al and Ni$_5$Al$_3$.

Figure 3a,b shows the image of the two-phase area of the coating. The grains with streaked structure (1 in Figure 3a) and the phase formed at the grains boundaries (2 in Figure 3a) are clearly visible. The dark-field image and the electron diffraction pattern confirm that the area 1 in Figure 3a is Ni$_3$Al phase (Figure 3b). Figure 3c shows the subgrain structure of the Ni$_3$Al phase. It can be seen that subgrains size does not exceed 500 nm. Figure 3d shows typical image of Ni$_5$Al$_3$ phase. This phase is represented by the packets of internally microtwinned plates that are equally oriented with every other plate. The plates thickness does not exceed 100 nm and their length is limited by the size of NiAl phase grains. It can be seen that the phase plates consist of thin plates that are twinned to each other in orientation.

![Figure 3. Bright field (a, c, d) and dark field (b) images of plasma coating structure. a, b – two-phase area of the coating; c – Ni$_3$Al phase; d – Ni$_5$Al$_3$ phase.](image-url)
4. Conclusions
1. The spraying of coatings from Ni$_3$Al powder at the supersonic regime allows to reduce porosity by a factor of 2 (up to 2-3 %).
2. X-ray diffraction analysis identified that Ni$_3$Al and Ni$_5$Al$_3$ are the main phases of plasma coatings. The volume fraction of Ni$_5$Al$_3$ phase in the coatings obtained at the supersonic regime is lower.
3. The structural investigation identified that the coatings formed at the supersonic regime consist of two various phases as well as two-phase areas. The coatings obtained at the subsonic regimes are characterized mainly by two-phase structure. The transmission electron microscopy showed that the Ni$_3$Al phase has subgrain structure, Ni$_5$Al$_3$ phase has lamellar structure.
4. The microhardness measurements established that the coatings obtained at the supersonic regime have lower hardness.

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