

The Fine Structure of Coatings on the Basis Ni–Al Formed by the Magnetron Method

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Abstract. Phase composition, fine structure and surface morphology of intermetallic coatings are investigated by X-ray analysis and TEM. It is shown that Ni₃Al is the main phase of the intermetallic coating for all the investigated samples. There is a Ni–Al phase in the samples of the first type. Three types of grains, differing in size, are discovered in the structure of nanocrystalline coatings: dislocation free, dislocation, and fragmented. The internal stresses, obtained by TEM and X-ray analysis, have close values.

Keywords: phase composition, microstructure, intermetallide, grain size, magnetron deposition, ion implantation

INTRODUCTION

Intermetallic compounds Ni₃Al and Ni–Al have a number of unique properties and they are the objects of numerous investigations [1, 2]. The interest to the intermetallic compound of nickel with aluminium and, in particular, to the intermetallide of Ni₃Al as a constructional material is determined by the anomalous temperature dependence of its mechanical properties. It means that in the certain temperature interval when the temperature increases, mechanical properties do not decrease, and on the contrary, they increase. In pure metals, the resistance to deformation always decreases when the temperature increases. The Ni–Al system, apart from solid solutions, has four equilibrium phases: NiAl₃ (ϵ -phase), Ni₂Al₃ (δ -phase), NiAl (β -phase), Ni₃Al (γ' -phase) and a non-equilibrium phase of Ni₅Al₃ [3]. Ni–Al (superstructure B2) and Ni₃Al (superstructure L1₂) are the most promising for use as a coating [4].

Magnetron deposition is the most widespread and reliable deposition of the coating on the basis of Ni–Al alloys. High-energy ion beams represent the effective modification way of the structural-phase condition and mechanical properties of the surface layer. It allows producing the coatings with higher mechanical properties. In [5] we closely investigated the effect of ionic-beam processing, substrate temperatures on the structural-phase state, nanohardness and wear resistance of the intermetallic coatings produced by magnetron deposition.

It is known [6] that in some cases alloying by the third element allows improving the material properties essentially. In the present work, we continue to study the technological parameter effect on the structural-phase state of the nanocrystalline intermetallide of Ni₃Al. Besides, the effect of the third element such as boron on the structure and mechanical properties of the intermetallic coatings are studied.

The effect of aluminum and boron ion implantation on the phase composition and a fine structure of the coating on the basis of the Ni–Al system, obtained by the magnetron deposition method, are investigated in this work.

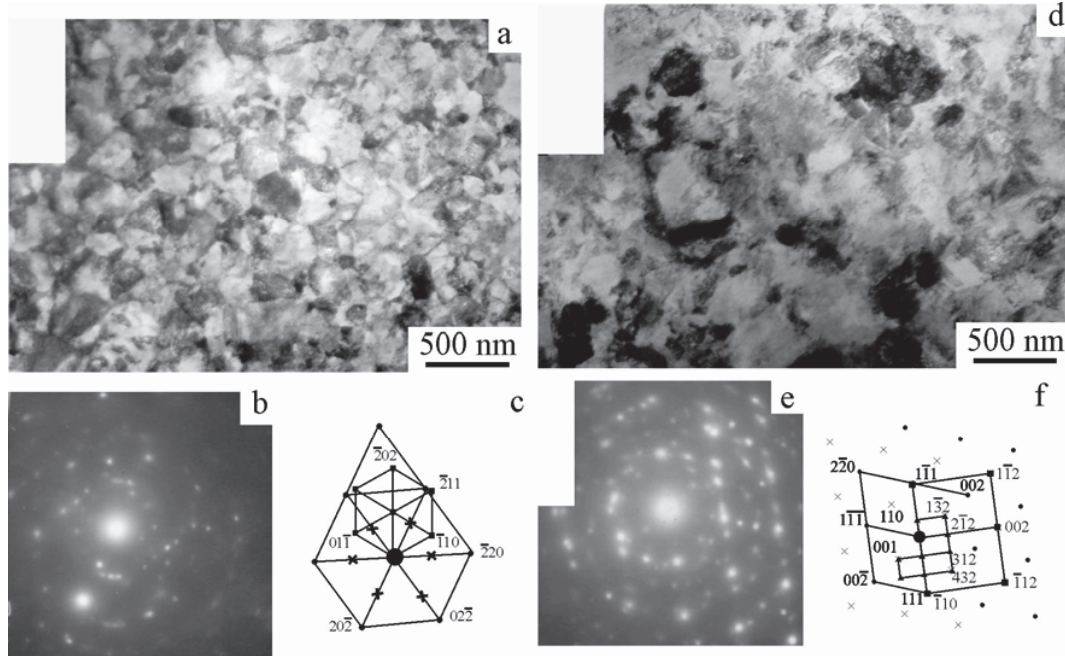


FIGURE 1. TEM image of the Ni_3Al coatings, the first and second type: (a, d) the bright-field images; (b and e) the microdiffraction patterns; (c and f) the schemes of indexing. Dots denote Ni_3Al (111); crosses, superstructural reflections of Ni_3Al ; squares, Ni-Al (111); triangles, AlB_{12} (420)

EXPERIMENTAL

Ni_3Al coatings were deposited by the KVANT magnetron sputtering system combined with an arc evaporator with aluminium cathode [7]. Ion implantation was accomplished using a DIANA-type device.

The phase composition and crystalline structure parameters of the intermetallic coatings were examined by X-ray. Internal stresses were the result of the analysis of X-ray line-broadening profiles and could be determined from the local changes in the lattice parameters. The stresses value was estimated as $\Delta d_{\max}/d$, where d was the lattice plane spacing. For cubical syngony $\Delta d/d = \Delta a/a$, $\sigma \cong (\Delta d/d)E$, where E was the elasticity modulus, $\Delta d/d$ and $\Delta a/a$ depended on the direction at the anisotropic E [8]. Meanwhile the direction was not taken into account in our case. Electron microscopy studies were carried out using the EM-125 electron microscope. Quantitative characteristics of the intermetallic coatings (dislocation density, curvature-torsion amplitude of the crystal lattice, and microstress) were obtained following the procedure described in detail in [9].

Two sets of the samples were prepared for study at different technological parameters: set 1, obtained by magnetron deposition with a substrate heated up to 600 K using a spiral, and set 2, obtained in the same manner with a subsequent aluminum and boron implantation.

TABLE 1. Structure characteristic of the coating on the basis of Ni–Al

The Type of Samples	The Phases	The Grain Size, nm	The Volume Fraction of Phases	The Internal Stresses (TEM) σ , MPa	The Internal Stresses (X-ray) σ , MPa	The Average Dislocation Density $1/\text{cm}^2$
I	Ni_3Al	150 ± 7	0.98	420 ± 20	400 ± 20	4.3×10^{10}
	NiAl	50 ± 3	0.2	–	–	–
II	Ni_3Al	210 ± 10	0.97	370 ± 15	400 ± 20	3.2×10^{10}
	NiAl	75 ± 4	1.5	–	–	–
	AlB_{12}	160 ± 30	1.5	–	–	–

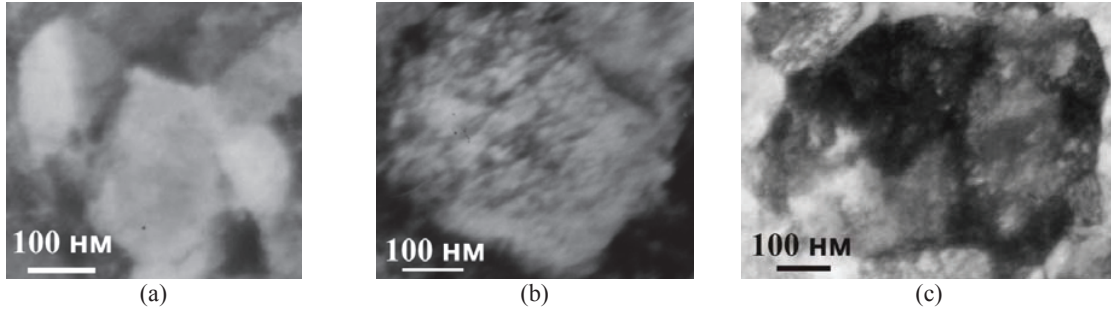


FIGURE 2. TEM images of the grains with different types: (a) dislocation free grains; (b) dislocation grains; (c) fragmented grains

RESULTS AND DISCUSSION

Figure 1 shows TEM images of the coatings, the first and second types. As it can be seen, there are two phases in the coatings: the basic Ni_3Al phase with L1_2 superstructure and the NiAl phase with B2 superstructure. The Ni_3Al phase consists of rather large particles (150 nm). The NiAl particles are round; they are localized in the grain joints and along the grain boundaries.

The average size of the particles of this phase is 50 nm. The quantitative data on the corresponding phase composition are given in Table 1. In the second type of the coatings, implanted by Al and B ions, the average grain size is slightly higher—about 210 nm for Ni_3Al grains and 75 nm for NiAl grains. The lamellar inclusions of the AlB_{12} phase are located along the boundaries of the Ni_3Al phase. It is found by TEM that the Ni_3Al phase consists of three types of grains: dislocation free grains (DFGs), dislocation grains (DGs), and fragmented grains (FGs) differing in size (Fig. 2). The smallest grains are dislocation-free, the largest ones are fragmented. The examples of TEM images of the grain size are shown in Fig. 2.

Figure 3 shows the grain size distributions in the coating of the first and the second types. It can be seen that the existence interval of all the grain types significantly expands in the coatings of the second type. In the coatings of the first type, the existence area of dislocation-free grains is in the range of 40–180 nm, while in the coatings of the second type they are from 40 to 280 nm. The most probable value of the grain size in the coating of the first type is 60 nm, for the coating of the second type it is 120 nm.

Koneva was the first who discovered such regularity for the pure monocrystalline metallic samples of Cu, Ni, and CuAlO [10]. That regularity was observed for the first time in the ordered nanocrystalline alloys studied in this work.

We measure the scalar density of the dislocations in Ni_3Al grains both as the material average $\langle\rho\rangle$, and as the average value of the grains of different types.

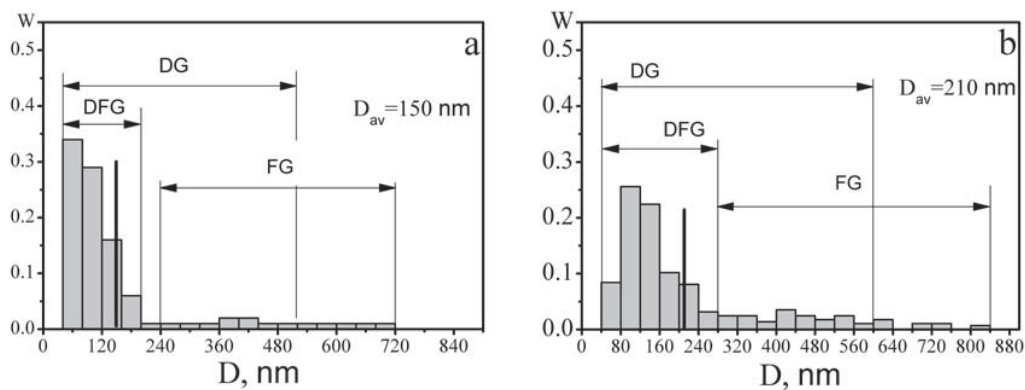


FIGURE 3. The grain size distributions of Ni_3Al in the samples of the first type I (a) and the second type II (b)

The resulting data are also given in Table 1. As it can be seen from the Table 1, the sample of the first type has virtually the same scalar density of dislocations in the grains with DG and FG substructures. The boron and aluminum implantation lowers the value of the scalar density of dislocations, both for the whole material and inside the grains of different types. In addition, it should be noted that the dislocation grains has the largest density of dislocations.

It means that partial etching of the material occurs in the process of implantation. It is known that the accumulation of high scalar density of dislocations, organized in the substructure of the material (chaotic, reticulated, cellular, fragmented), produces shear stress, i.e., the field of stress produced by the dislocation structure.

The value of shear stress is determined using the method described in [10, 11]. Using the value of ρ , internal stress fields σ in the material of the coatings are measured. Also, the internal stresses are determined using the line-broadening profiles by the X-ray method. They are 400 nm for all types of the samples. The corresponding data are listed in Table 1. It can be seen that the internal stresses, determined by X-ray and TEM, are close.

CONCLUSION

Using the X-ray and TEM analyses it is established that there are intermetallic Ni₃Al and NiAl in the coatings of the first type and Ni₃Al, NiAl and AlB₁₂ in the coatings of the second type.

Three types of grains differing in size are discovered in the structure of the nanocrystalline coatings: dislocation free, dislocation, and fragmented. The internal stresses, obtained by the TEM and X-ray analyses, have close values.

ACKNOWLEDGEMENTS

The work was supported within the scope of the basic scientific research of state academies of sciences for 2013–2020, performed within the scope of the state task “Science NRTPU”

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