Microstructure and mechanical properties of Ni-Al intermetallic thin coatings produced by magnetron sputtering

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Abstract. In the present study the thin NiAl intermetallic foils formed on different types of substrates by magnetron sputtering technique were investigated. To provide the deposition of intermetallic NiAl compound in one step without additional heat treatment the composite targets assembled from parts of Al and Al plates were used. The structure of formed thin NiAl coatings was studied using scanning electron microscopy and X-ray diffraction analysis. Mechanical properties were assessed by nanohardness measurements and wear testing of deposited coatings. During sputtering the distance from the target to the substrates varied from 60 to 100 mm to estimate the effect of this parameter on structure and properties of the coatings. The results revealed that thin coatings sputtered at the closer distance from the target to the substrates had the higher hardness about 11 GPa and exhibited the high level of wear properties.

1. Introduction
In the present time, intermetallics are known as effective materials for protective coatings of metals and alloys used in aircraft and rocket building, microelectronics, chemical and petroleum industries. Among all intermetallic compounds nickel aluminides are of particular interest, especially Ni₃Al and NiAl, whose main advantages are a relatively high melting point (1385–1638 °C), a relatively low density (5–7.5 g/cm³), a high elastic modulus (190–290 GPa), resistance to creep. The NiAl phase is characterized by high wear resistance and resistance to oxidation (including elevated temperatures), which makes it attractive for use as protective heat-resistant and wear-resistant coatings. Today, nickel aluminides are actively used as coatings for gas turbine engines based on nickel superalloys and stainless steel products, as sublayers for magnetic recording devices, surface catalysts, and thermistor thin films in microelectronics. Nevertheless, the problem of the brittleness of intermetallic materials still remains the topical. Besides, it is necessary to solve the problems of improving the coating to the substrate, increasing the resistance to oxidation and tribotechnical properties.

Magnetron sputtering is the technique which allows depositing coatings formation with high density of micro- or nanocrystalline structures, provides the complete absence of the capillary phase,

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possibility of cladding the coatings on the thermosensitive materials at low temperatures, high deposition rate, and high mechanical and functional properties of formed coatings.

There are two approaches to form intermetallic coatings by magnetron sputtering technique. The first is the simultaneous deposition of two or more metallic targets in a chamber with two magnetrons. The second is the preliminary manufacturing of a multicomponent target corresponding to the desired composition. In the case with simultaneous deposition from two or more targets, it is problematic to vary the number of knocked out atoms, so it is difficult to deposit the material of a given composition. In addition, devices with several magnetrons are quite expensive. When manufacturing multicomponent targets, as a rule, hot isostatic pressing or spark plasma sintering are used. These technologies are quite and time-consuming processes, which causes additional material costs. The feature of the proposed approach is the use of composite targets, which is assembled from alternating blocks of two materials. The number and width of Ni and Al parts in the composite target is chosen based on the composition of the coating to be obtained. Such approach will allow quickly and efficiently deposit thin layers with a given composition, and allows rationally use the capabilities of simple sputtering device equipped with the only one magnetron.

Thin coatings and thin foils were obtained and studied on the basis of various combinations of materials: Ni-Al, Ni-Al-X (where X = N, Cu, W, Ti, etc.) [1-5], Ti-Al, Ti-Al-X (X = C, Cu, Ni, Co, Fe, Cr, Nb) [6-8], Fe-Al, Ni-Ti, AlNiAl2O3, Al-Au [9], Al-Zr [10]. The main methods for studying thin intermetallic coatings are scanning and transmission electron microscopy and X-ray phase analysis. Due to the small thickness of the coatings, the strength properties are mainly evaluated by the method of nanoindentation. Magnetron sputtering of nickel and aluminum with subsequent heat treatment showed that fining of the structure to nanometer sizes reduces the temperature of intermetallic formation to below the melting point of aluminum (190–250 °C) [1, 2, 11]. At the moment, a lot of scientists are trying to increase the adhesion of intermetallic coatings based on nickel and aluminum to the substrate, to eliminate the delamination during thermal cycling, to avoid the diffusion of coating materials in the substrate during heating, to eliminate increase of tribotechnical properties. Such problems can be partly solved by doping other elements, by fining the nanostructure, by varying the modes of magnetron sputtering and using different heat treatment modes [2, 7, 12–15].

The author found the only publication [15], in which target consisting of concentric parts (inside part - a circle of nickel, outside part - a ring of aluminum) were used. Nevertheless, structural features of nanostructure and phase analysis weren’t presented enough in details. Thus, the purpose of the present study is to evaluate the structure and mechanical properties of intermetallic coatings sputtered from composite targets assembled from Ni and Al parts on metallic and non-metallic materials in various sputtering conditions.

2. Materials and methods

The target consisted of alternating bars (strips) of cp-nickel and cp-aluminum cut from plates on wire electrical discharge machine Sodik AG400L. Diameter of the target was 75 mm, the width of side Ni and Al plates was 17.5 mm, the width of central was 10 mm, the thickness of the target was 4 mm. Cp-titanium, steel (0.2 wt. % C), Al2O3 (doped with spinel MgAl2O4) and silicon monocrystallic plates were used as substrates. Magnetron sputtering experiments were carried out on magnetron sputtering device PVD-DESK-PRO. The base pressure of vacuum system was reduced to 5·Е-5 prior to sputtering. During the deposition process in the atmosphere of high purity Ar (99.999%) a pressure was maintained at 5 – 5.4 ·Е-3 hPa. The applied DC power was 600 W. In the study the varied parameters were the distance between table and magnetron, and magnetron power (table 1).

The micro- and nanostructure of deposited coatings on the top of the surface and in the cross section were investigated on scanning electron microscope (SEM) Carl Zeiss EVO 50 XVP, with the scale ×1000…×300000 and accelerating voltage 3–10 keV. X-ray analysis were carried out in 0–0 diffractometer ARL X’TRA using Cu Kα1 + α2 radiation with the scanning step 20 = 0.05° and dwell time 3…10 pps. Nanohardness measurements and scratch tests were conducted on scanning nanohardness tester Naniscan-3D equipped with atomic force microscope in Institute of Laser Physics
(Novosibirsk). The hardness of the material was determined by penetration depth of Berkovich diamond pyramid with the loading increased from 0.1 to 50 mN). The loading during scratch tests were varying in the same range. The coatings were scratched in two different ways: face forward and edge forward orientation of the indentor. Scratch tests provide information about maximum loading at which plastic deformation of the material and delamination of the coating begins. The tribological properties were estimated on by wear test Naniscan-3D using Berkovich indentor at the loading 20 mN, the number of cycles was 500.

### Table 1. Parameters of magnetron sputtering experiment.

| Material of the substrate | Distance from the target to the substrate (h), mm | Duration of sputtering, min | Power, W |
|---------------------------|-----------------------------------------------|-----------------------------|----------|
| Al2O3, Si                 | 100                                           | 30                          | 600      |
| Al2O3, Si                 | 85                                            | 30                          | 600      |
| Al2O3, Si                 | 60                                            | 30                          | 600      |
| Al2O3, Si                 | 100                                           | 2                           | 600      |
| Ti                        | 60                                            | 30                          | 600      |
| Steel                     | 60                                            | 30                          | 600      |

3. Results and discussion

3.1. Structure of deposited coatings

SEM investigations of fracture surface in the cross section of the samples showed that the coatings has columnar nanostructure, which is typical for materials obtained by magnetron sputtering technique (figure 1). The intermetallic layer near the substrate is the smallest and has equiaxial shape. Further increase in the film thickness leads to the formation of a columnar structure that is explained by the Volmer-Weber film growth mechanism, where at the initial stage equiaxed nanoscale crystallization centers nucleate, and then they increase and form the columnar structure. The appearance of fracture surface indicates the brittle fracture of intermetallic layers. The coating thickness increases with decrease of the distance from the target to the substrate and reaches 1.8 μm, 3.2 μm and 5μm at 100, 85 and 60 mm, respectively. The morphology of the deposited surface at different height of sputtering significantly changes. On figure 2 the top surface of coatings deposited on Si substrates are presented. At the distance 100 mm the velocity of sputtered depositing atoms is low, thus, the crystals grow slowly and nothing disturb their formation and growing of clusters at the top layer. When the substrate is situated closer to the target and to the source of Ar atoms (h = 60 mm) the top surface is densifying by just accelerated atoms from the target, besides, concentration of Ar atoms is greater at this distance, therefore, some atoms can deform the surface when randomly interacting with it.

3.2. X-Ray analysis

The samples deposited during 30 minutes were used for X-ray analysis because of thickness of the obtained surface. Phase identification revealed the presence of the only intermetallic phase NiAl, peaks of initial metallic components presenting in the target weren’t found (figure 3). Thus, the suggestions can be made, that the reaction with formation of intermetallic phases goes after the deposition on the atoms due to the heating of the substrate.

Reflections of NiAl (111) planes show great intensity on X-Ray diffraction patterns that indicates strong crystallographic texture that isn’t typical for this phase. Formation of textured crystal structure in the coatings can be possibly connected to the columnar atom-to-atom mechanism of its growing. As it was described before, grains forming on the substrate at the first stage of the film growing are
mostly equiaxial. At the distance 100 mm growing rate of the coatings isn’t very high, thus, equiaxial grains takes most part of the coating. That is why the relative intensity correlates with powder diffraction pattern of the NiAl phase. With increase of growing rate of the coatings at closer distance (h = 85 and 60 mm) columnar oriented crystal growing becomes predominant, and at the distance h=60 mm in deposited coatings almost all crystallographic planes except (111) degenerate, which is represented in the diffraction pattern — there is only one, but extremely intense, reflection of (111) phase (figure 3 a).

![Figure 1](image1.png)

**Figure 1.** Microstructure of thin intermetallic NiAl coatings in the cross section sputtered at the distance from the target to substrate (from left to right): 100 mm, 85 mm, 60 mm.

![Figure 2](image2.png)

**Figure 2.** Microstructure of the top surface of thin intermetallic NiAl coatings sputtered at the distance 100 mm (a) and 60 mm (b).

Crystallographic texture in this case depends on growing rate of planes with different crystallographic orientation. Besides, the structure of substrates can also influence on the orientation of as deposited crystals. The phase composition of coatings sputtered on different substrates (steel, titanium, alumina and silicon) is the same, the X-ray diffraction revealed only NiAl phase in deposited coatings (figure 3 b). Nevertheless, X-ray reflexes of intermetallic coatings on metallic substrates show more uniform distribution of its intensity. The intensity of (111) planes in the coatings sputtered on metallic substrates is relatively low, besides, the reflexes of planes (110) and (211) appears which wasn’t found in X-ray diffraction patterns of coatings sputtered on silicon and alumina plates. This can be explained by different roughness and surface morphology of the substrates, the quality of preparation of substrates and the physical properties of the substrate materials.

3.3. Nanohardness measurements

The nanohardness of intermetallic coatings reaches the highest values ~10 GPa in the samples sputtered at the distance 100 mm. Measurement results showed that nanohardness value slightly grows with when the distance from the target to the substrates becomes less. According to SEM results, such behavior can be connected to aforementioned differences in structure of surfaces.
It also should be noted that nanohardness of NiAl coatings deposited at the distance 60 mm on metallic substrates reaches 12 GPa and higher, when coatings sputtered on non-metallic (Al2O3 and silicon) substrates exhibited the level of nanohardness about 10 GPa. Basing on X-ray diffraction investigations, such behavior of nanohardness level can be connected to anisotropy of mechanical properties in thin layers with difference crystallographic orientation.

3.4. Scratch and wear tests

Samples with the thin layers sputtered during 2 min at the distance 100 mm and power 700 W were used to estimate the adhesion behavior of intermetallic coatings by scratch tests. Adhesion behavior was estimated on samples sputtered during 2 min, because in this case the maximum loading is enough to penetrate the entire thickness of the coatings. To carry out wear tests, the samples sputtered during 30 min were chosen, because their greater thickness will allow much number of cycles.

AFM image of the scratched sample presented on figure 4 a. Profile 1 on figure 4 b corresponds to edge-forward movement of the pyramidal indenter (reproduces micro-cutting of material); profile 2 – face-forward movement (represents plastic extrusion).

As it can be seen from the measurement results, the indenter penetration depth into the samples during scratching reaches 0.25–0.30 μm. The coating thickness on these samples, measured on interferometer, reaches 0.22 μm. Thus, the conclusion can be made that in the process of testing the indenter penetrates the entire depth of the coating, and also enters into the substrate material. Images of sample profiles show that there are no peeling and chips along the entire length of the scratches both on metallic and silicon substrates that can be the evidence of good adhesion of intermetallic coatings to the substrate material.

The results of wear tests showed that substrates didn’t broke or delaminated after 500 cycles of wearing by Berkovich indentor at the loading 20 mN. The coatings sputtered at the distance 60 mm exhibited the best wear results, depth of wear crater after 500 cycles was ~500 nm. The samples deposited at 85 and 100 nm showed more intensive wearing; the depth of the tracks after 500 cycles was ~600 nm. The obtained results correlate with microhardness measurements and also can be an effect of slight densifying of the intermetallic layer at the close distance to the target. The nanohardness and wear properties of obtained coatings are comparable and even exceed the level of NiAl coatings obtained at similar conditions [15].
Figure 4. AFM image of the tracks after the scratching tests (a), profile measured by the black line on AFM image (b).

4. Conclusions
As a result of the carried out investigations the following conclusions can be drown. Magnetron sputtering of Ni and Al of the composite target assembled from the parts of elemental blocks of pure initial metals allows deposition of intermetallic thin coatings containing only NiAl intermetallic phase. Magnetron sputtering promotes the growth of columnar grains with (111) plane preferable orientation. The morphology of the surface and grain size depends on the distance between the target and the substrate; in particular, moving the substrate closer to the target leads the densification of the depositing surface and increase of the depositing rate. This fact influences on nanohardness level, which grows from 10 to 11 GPa with the reduction of the distance from target to the substrates, and affects the wear characteristics, which increase by 20%.

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