JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **7** No 2, 02034(6pp) (2015)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **7** № 2, 02034(6cc) (2015)

Formation of Multi-coatings on Nickel: Structure, Phase formation, Physical and Chemical Properties

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(Received 02 April 2015; revised manuscript received 20 April 2015; published online 10 June 2015)

Methods of aluminum-silicon and titanium-aluminum coatings of nickel in a mixture of metal powders, aluminum oxide Al_2O_3 and ammonium chloride NH_4Cl were proposed. Phase and chemical composition, structure, microhardness of multicomponent diffusion coatings involving aluminum and silicon, titanium and aluminum on nickel were established. It is shown that diffusion coatings consist of the compound zone and transition zone, which is a solid solution of saturating elements in nickel.

Keywords: Diffusion coatings, Aluminum-silicon, Titanium aluminum-silicon, Titanium-aluminum, Solid solution, Microhardness, oxides, Intermetallides.

PACS numbers: 61.46. – w, 62.20.Qp, 62.20. – x, 68.55.Nq

1. INTRODUCTION

A trend of increased use of nickel and nickel alloys in various industries has been observed during the last decade. Competitiveness of nickel alloys is determined by a successful combination of their properties, namely, high strength-to-mass ratio, heat resistance and high corrosion resistance in many environments. High cost, low surface hardness and wear resistance are the main disadvantages of nickel alloys. Elimination of these disadvantages can be achieved by deposition of protective coatings.

There are known ways of deposition of the diffusion and condensed coatings to protect parts made of nickel from gas and sulfide corrosion [1-3]. Low corrosion resistance because of the limited composition, low adhesion to the substrate, low thermal resistance and endurance limit [1-3] are the disadvantages of the known diffusion coatings.

In the works, the investigation results of the coatings obtained by single- and two-stage circulating chromium-aluminum [2, 3] are presented, and the physical and chemical conditions of the surface modification of steels by vanadium, carbon and nitrogen [4] are studied. The authors of [5] have studied the influence of different ways of modification (volume – by boron and zirconium; surface – by cobalt aluminate; combined (with simultaneous use of the volume and surface)) on the structure and properties of nickel alloys. It is established that these coatings correspond to modern requirements and can be an alternative of the diffusion saturation in powders.

We can note that the proposed innovative methods of metallization, namely, titanium-aluminum and aluminum-silicon, can make a worthy competition to the specified technologically complex processes.

2. EXPERIMENTAL TECHNIQUE

Carbonyl nickel was selected as the material of the work base in order to solve the problems stated in this work. Deposition of two-component coatings of different composition was realized in the work. Chemical-thermal treatment (CTT) was carried out in a closed reaction space (in a container with a consumable seal) in a powder mixture in the shaft-furnace SShOL 1.1.6/12.

In this work, three processes were studied, namely, aluminum-silicon, titanium-aluminum and titanium-aluminum with pre-deposition of the titanium nitride TiN layer. In implementing the last process, titanium nitride TiN layer was deposited on the samples by the physical deposition method from the gas phase, on the plant VU1B with titanium cathode (Table 1). As a result, thickness of the nitride layer was equal to 0.5-1.0 μm.

Composition of the saturating mixture and optimal modes of the corresponding processes are experimentally determined (see Table 1).

Samples with coatings were studied by the methods of physical materials science, such as X-ray structural, micro X-ray spectrum, metallographic, and durometric analysis. X-ray structural study was performed on the diffractometer Rigaku in copper monochromatic $Cu_{K\alpha}$-radiation with the wavelength of $\lambda = 0.1541841$ nm. The chemical composition of the coatings was determined on the scanning electron microscope CamScan 4D with the system of the energy-dispersive X-ray spectrum microanalyzer INCA-200 Energy. Determination of the microhardness and thickness of the obtained layers was performed on the plant PMT-3 by indentation of a diamond tetrahedral pyramid with the vertex angle of 136° under the load of 0.2-1.0 N not less than in 10-15 fields of view. Thickness of the area with an increased content of saturating elements was taken as the protective coating thickness. Clearly defined phase boundaries give the possibility to determine the thickness of separate layers using PMT-3. The obtained results are confirmed by the X-ray structural, micro X-ray spectrum and durometric analysis. Thickness of the transition zone was estimated as the thickness of the layer, whose microhardness differs from the microhardness of the master structure of the work alloy. Microstructural investigations were performed on the microscope NEOPHOT-21 in the magnification range of 50-1000 times in light and dark fields. Nital (3-5 % solution of HNO_3 in ethyl alcohol) and Murakami reagent (10 g of $K_3(FeCN)_6$, 10 g of NaOH,

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100 ml of H_2O) were used to detect the microstructure [6]. The latter allows to differentiate phases which are not detected by usual etching methods.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Based on the results of the X-ray structural analysis of the initial nickel sample, its lattice spacing before CTT was equal to $a = 0.3526$ nm. It may be noted that lattice spacing of raw nickel slightly differs from that in [7], where $a = 0.3524$ nm. This difference can be explained by the presence in nickel for CTT of a small amount of iron. According to the micro X-ray spectrum analysis, this content is equal to 0.04 wt. %.

The analysis showed that aluminum-silicon of nickel leads to the formation of multilayer structures based on the compounds of nickel and aluminum. The sequence of arrangement of layers in a protective coating is the following: an Al_2O_3 oxide layer is formed directly on the surface, then layers of NiAl compound, a layer of two compounds NiAl and Ni_3Al, an, a Ni_3Al layer of an insignificant thickness adjoins directly to the base.

The central layer of two compounds NiAl and Ni_3Al is formed, most probably, during cooling after CTT completion at the temperature of 1000 °C. According to the state diagram of Ni-Al [7], solubility of nickel in compound NiAl decreases from 80 wt. % at 1000 °C to 76.5 wt. % at 550 °C. In this case, intermetallic alloy Ni_3Al is isolated from NiAl compound. It is assumed [8] that ordering of the NiAl structure with the formation of the ordered structure of CsCl type takes place at this temperature.

There are the laws of change in lattice spacing of the NiAl phase in the homogeneity range [8]. This phase has the lattice of the CsCl type with Ni atoms located in the center of the unit cube and Al atoms in the cube corners. Lattice spacing of $Ni_{0.5}Al_{0.5}$ compound is equal to $a = 0.2887$ nm. With the content of Ni not less than 50 wt. %, lattice spacing decreases. An expected increase in the lattice spacing does not occur with substitution aluminum for nickel. The latter is because positions of nickel are not replaced by aluminum. With the content of Ni more than 50 wt. %, nickel replaces the vacant positions of aluminum. Lattice spacing, in this case, decreases because atomic sizes of nickel are less than the atomic sizes of aluminum.

Titanium-aluminum of nickel by the ways 2 and 3 leads to the formation of a multilayer coating based on Ti and Al. In the composition and structure these coatings can be divided into two zones (Table 2), such as the external one – zone of compounds, to the composition of which oxides (Al_2O_3, Ni_2Ti_4O) and intermetallic alloys (Ni_2AlTi, NiTi, Ni_3Al) enter, and the transition zone. It is clear that a layer of titanium nitride TiN is present in the coating obtained by the way 3. Thickness of the TiN layer after sequent CTT – titanium-aluminum – has not almost change and is equal to 0.5-1.0 μm. This fact confirms the stability of existence on nickel of the TiN compound at high temperatures, and 1050 °C is the temperature of titanium-aluminum.

The investigation results of the phase and chemical compositions, structure and some properties of the coatings obtained in this work are represented in Table 2 and Fig. 1-Fig. 4.

As a result of titanium-aluminum on the outside of the protective coating, Al_2O_3 layer is revealed (Table 2), which directly adjoins a layer of the Ni_2Ti_4O compound. Further the NiTi layer is located. We should note that two last layers are well revealed by the microstructural analysis. Their total thickness does not depend on the method of titanium-aluminum (way 2 or 3) and is equal to 4.0-7.0 μm.

By the X-ray structural analysis we have shown the presence in the zone of compounds of isolated nickel sublayers with the lattice spacing significantly larger than the lattice spacing of the initial nickel and nickel of the transition zone (Table 2, Fig. 3, Fig. 5). Areas of these sublayers of the thickness from 5 μm to 15 μm are light-colored and elongated parallel to the diffusion front of a grain, located between the layers of $AlNi_2Ti$ and Ni_3Al compounds, sometimes on the boundary between the zone of compounds and transition zone.

By the micro X-ray spectrum analysis it is established that content of aluminum in Ni sublayers is much less than in $AlNi_2Ti$, Ni_3Al layers and larger than in a solid solution (s.s.) of the transition zone. Existence in the Ni_3Al layer of two zones with different content of Ni [9] is the well-known feature of the aluminide coating obtained on nickel from the mixture of ferroaluminum and aluminum chloride. But we should note here that in the analysis of the state diagram of Ni-Al such layering is not discovered [9] indicating that the arrangement of layers revealed in this work is only possible at titanium-aluminum of Ni. Lattice spacing of the transition-zone nickel decreases from the boundary of the zone of compounds to the base that is confirmed by the distribution of chemical elements in the coating (Table 2, Fig. 4, Fig. 6). Microstructure of titanium-aluminum layers on Ni, which is determined when imaging in backscattered electrons (BSE), gave the possibility to reveal the structure of the zone of compounds, whose isolated layers (grey and light-grey areas with developed boundaries on the images) did not have pores and cracks (Fig. 3, Fig. 5, Fig. 7).

Structure of the transition zone of a diffusion titanium-aluminum layer is revealed in the work by etching of the transverse sections by Murakami reagent. Grains are dark grey colored with twins, with a light boundary and base of the thickness of 5.0-7.5 μm. Thickness of the transition zone is larger than the penetration depth of titanium and aluminum into nickel (Fig. 7). It is established that this region of the transition zone is doped with oxygen, whose content in thickness is equal to 0.7-0.8 wt. %; at that the maximum content of oxygen is observed in its central areas. Analysis of the state diagram of Ni-O implies a slight solubility of oxygen in nickel at room temperatures. At the same time, it is known [8] that at 600 °C concentration of oxygen in nickel is equal to 0.02 wt. % and slightly increases with temperature decrease. We should note that thickness of the zones of compounds obtained by the ways 2 and 3 is almost identical. Transition zone in the coating with titanium nitride is two times thinner than at usual titanium-aluminum (the way 2).

The latter is conditioned by the influence of the TiN layer on the diffusion of saturating elements of titanium, aluminum as well as oxygen into the base, and diffusion of nickel into the coating.

Table 1 – Rational composition of the initial reagents and technological parameters of the chemical-thermal treatment of nickel

No	Process	Composition of the saturating mixture, wt. %	Process temperature, °C	Process duration, hours
1	Aluminum-silicon	Al – 45, Si – 15, Al_2O_3 – 35, NH_4Cl – 5	1000	4
2	Titanium-aluminum	Ti – 45, Al – 15, Al_2O_3 – 35, NH_4Cl – 5	1050	4
3	TiN (PVD)* + Titanium-aluminum	Ti – 45, Al – 15, Al_2O_3 – 35, NH_4Cl – 5	1050	4

*- pre-deposited by the PVD method titanium nitride TiN layer of the thickness of 0.5-1.0 μm

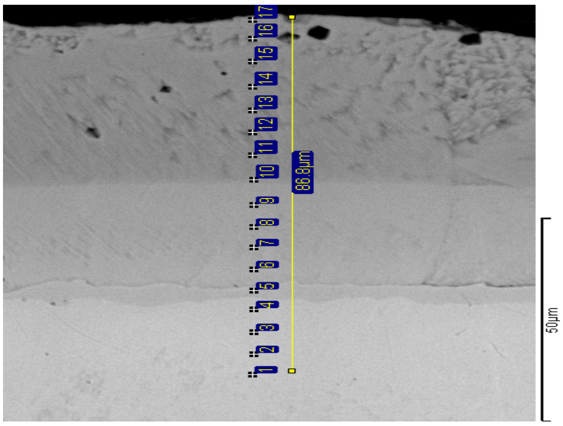
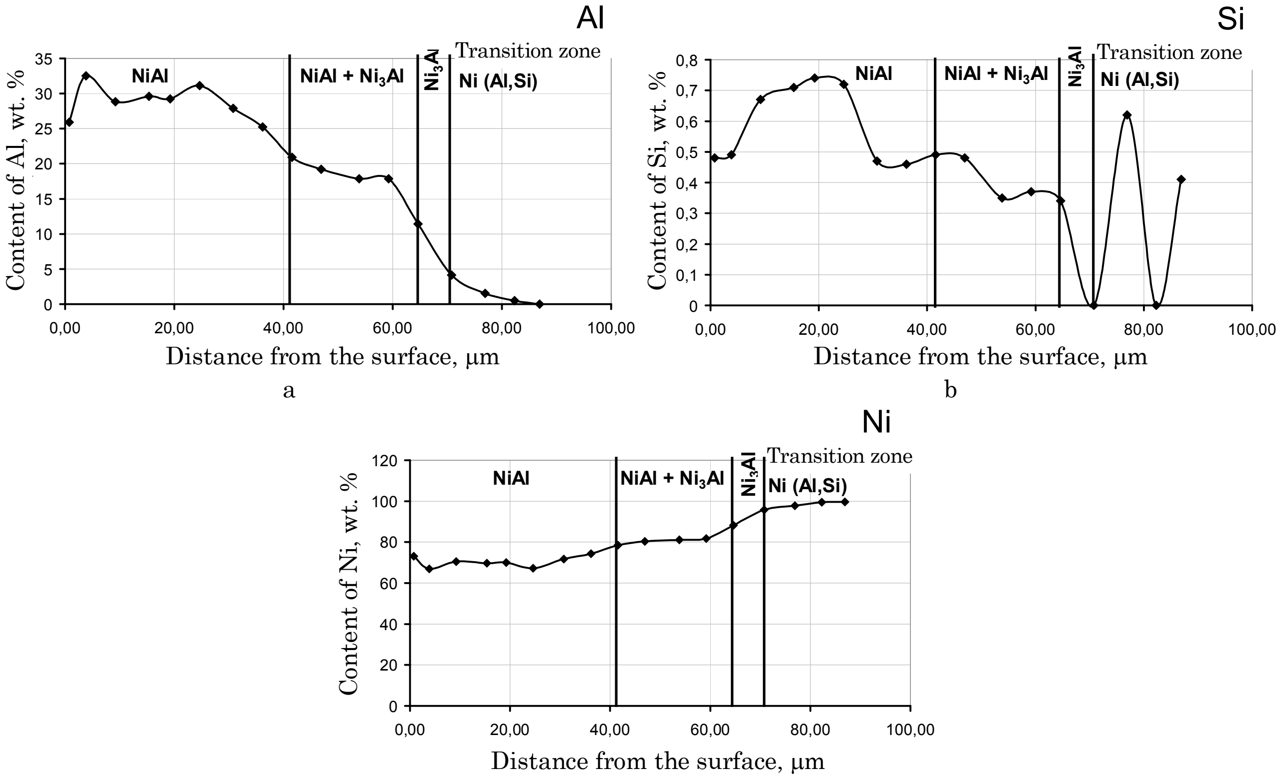


Fig. 1 – Microstructure of the aluminum-silicon coating on Ni: T = 1000 °C, τ = 4 hours



a

b

c

Fig. 2 – Distribution of Al (a), Si (b) and Ni (c) in thickness of the protective coating after aluminum-silicon of Ni: T = 1000 °C, τ = 4 hours

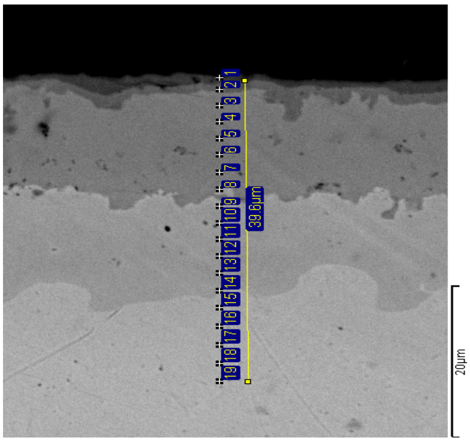
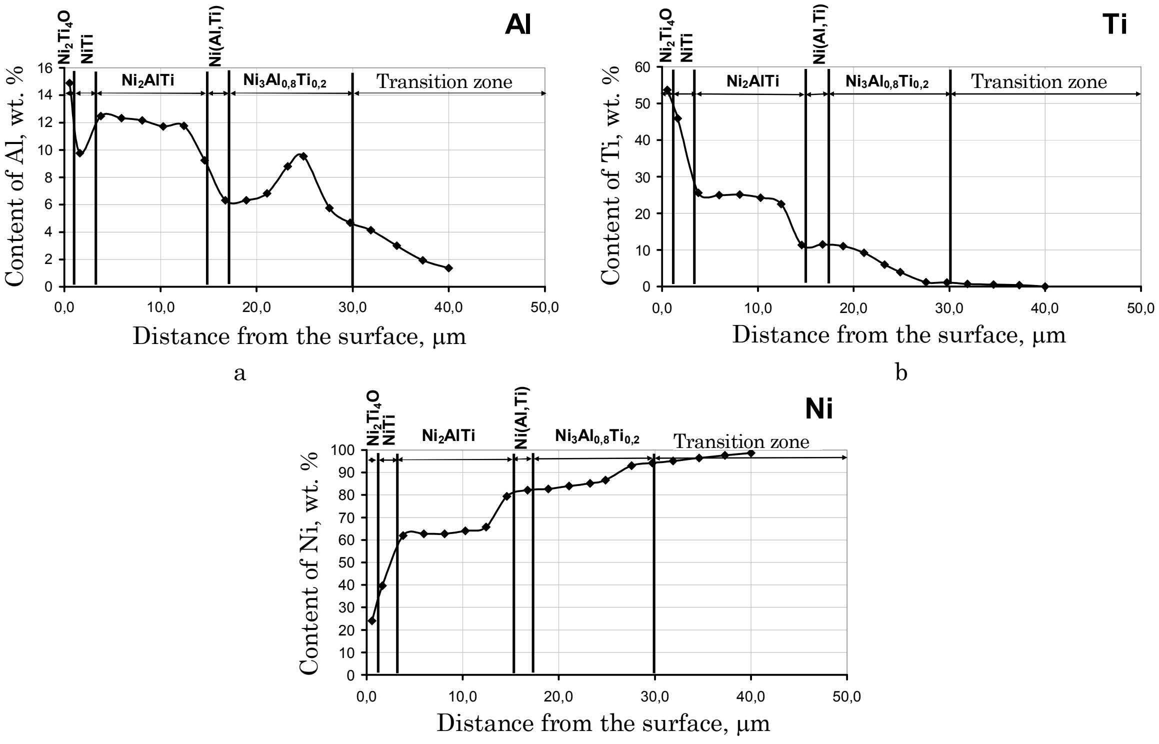


Fig. 3 – Microstructure of the titanium-aluminum coating on Ni: $T = 1050$ °C, $\tau = 4$ hours



a

b

c

Fig 4 – Distribution of Al (a), Ti (b) and Ni (c) in thickness of the protective coating after titanium-aluminum of Ni: $T = 1050$ °C, $\tau = 4$ hours

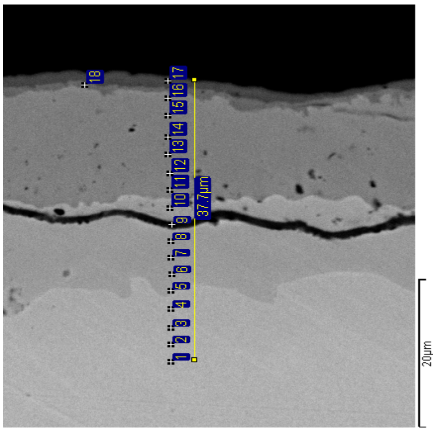
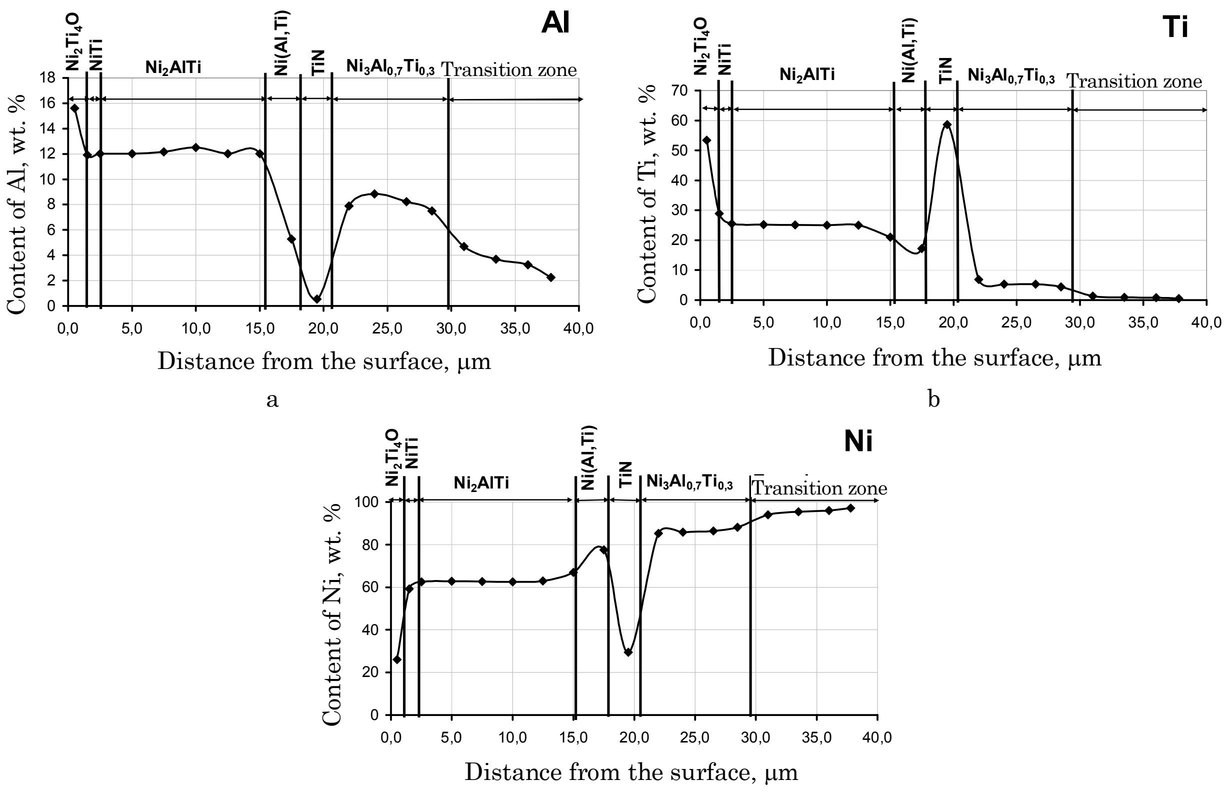


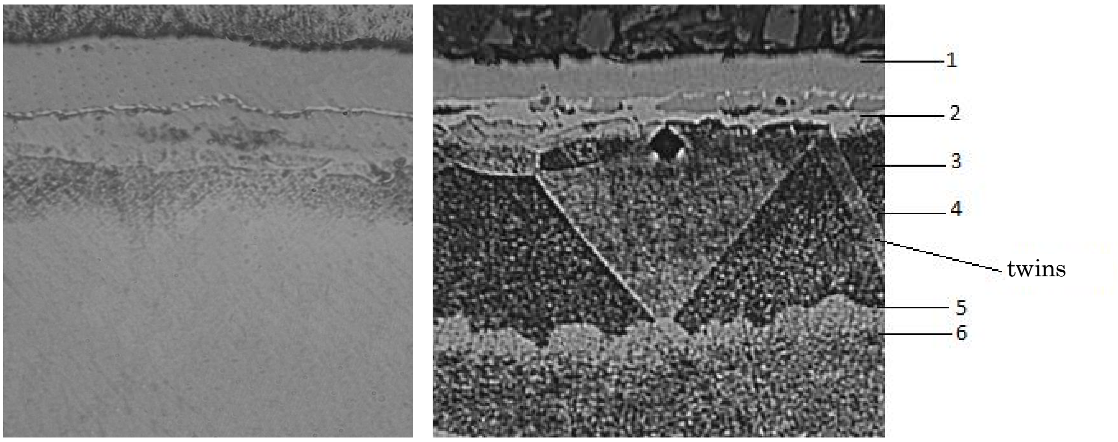
Fig. 5 – Microstructure of the titanium-aluminum coating on Ni with pre-deposited TiN layer (PVD) when imaging in backscattered electrons, $T = 1050$ °C, $\tau = 4$ hours



a b

c

Fig. 6 – Distribution of Al (a), Ti (b) and Ni (c) in thickness of the protective coating after titanium-aluminum of Ni with pre-deposited TiN layer (PVD), $T = 1050$ °C, $\tau = 4$ hours



a b

Fig. 7 – Microstructure of the titanium-aluminum Ni: without etching (a); after etching by Muramaki reagent (b): 1-2 – zone of intermetallic alloys (NiTi, Ni_2AlTi, Ni(Al,Ti), $Ni_3Al_{0,8}Ti_{0,2}$); 2-3 – zone of Ni(Al,Ti) solid solution; 3-4 – zone of Ni(Al) solid solution; 4-5 – zone of Ni(O) solid solution; 5-6 – boundary with the base of the thickness of 5.0-7.5 μm. Images are obtained by the optical microscopy method, x 150

It was shown by the micro X-ray spectrum analysis that a light boundary limiting a layer of solid solution of oxygen in nickel almost does not contain iron, whose concentration in the base is on the level of 0.04 wt. %. It is established that during titanium-aluminum, iron of the base diffused to the surface, where its concentration in the zone of compounds reached 0.06-0.10 wt. %. Grains of nickel of the base are grey-, light-grey colored with typical twins.

Extreme behavior of the distribution of oxygen in the transition zone is confirmed by the distribution of microhardness. Maximum microhardness is revealed for the layer of the transition zone with the maximum content of oxygen and is equal to 1.5 GPa. Such microhardness is, probably, conditioned by the presence in the structure of nickel of dispersed inclusions of NiO oxide. Maximum microhardness in the zone of compounds is revealed for the TiNi layers – 8.0-9.1 GPa and for TiN – 22.6 GPa.

Table 2 – Phase composition and properties of two-component coatings on Ni

No	Type of treatment	Zones of the coating	Phase composition*	Lattice spacing, nm	Layer thickness, μm	Microhardness, GPa
1	Aluminum-silicon**	Zone of compounds	NiAl	0.2869	41.0-45.0	4.3-3.0
			NiAl + Ni_3Al	–	25.0-27.0	3.6-2.4
			Ni_3Al	0.4323	5.0-6.0	3.0-2.0
		Transition zone	Ni(Al,Si)	0.3539	10.0-15.0	1.6-1.5
			Ni(Si)	0.3530	5.0-7.0	1.5-0.9
			Ni(O)	0.3526	20.0	0.9-0.8
2	Titanium-aluminum**	Zone of compounds	Ni_2Ti_4O	1.1841	2.0-2.5	5.1
			NiTi	0.3060	2.0-4.5	9.1
			Ni_2AlTi	1.1385	12.0-15.0	4.8-4.9
			Ni(Al,Ti)	0.3591	2.0-8.5	1.8
			$Ni_3Al_{0.8}Ti_{0.2}$	0.3577	10-18	4.2
		Transition zone	Ni(Al,Ti)	0.3581	15.5	1.8
			Ni(Al)	0.3541	20.0	0.8-1.5
			Ni(O)	0.3531	44.5	0.8-1.4
3	TiN (PVD)*** + titanium-aluminum	Zone of compounds	Ni_2Ti_4O	1.1836	1.5-2.0	4.8
			NiTi	0.3062	2.5-5.0	8.9
			Ni_2AlTi	1.1379	14.0-15.0	4.7-4.8
			Ni(Al,Ti)	0.3588	8.0-12.5	1.9
			TiN	–	0.5-1.0	22.6
			$Ni_3Al_{0.7}Ti_{0.3}$	0.3577	4.0-11.5	4.0-4.2
		Transition zone	Ni(Al,Ti)	0.3570	11.0-12.5	1.8
			Ni(Al)	0.3540	10.0-12.0	1.4-1.8
			Ni(O)	0.3530	15.0-19.5	1.0-1.5

*– Al_2O_3 compound is revealed on the surface of the samples treated by method 2 and 3; $a = 0.4762$ nm and $c = 0.5145$ nm

**– Ni is the phase composition of the base with the lattice spacing $a = 0.3526$ nm and microhardness 0.8 GPa

***– titanium nitride TiN layer pre-deposited by the PVD method, of the thickness of 0.5-1.0 μm

4. CONCLUSIONS

The innovative CTT methods of nickel are proposed in the work. The structure, phase composition and microhardness of two-component protective coatings, which are formed as a result of aluminum-silicon and titanium-aluminum of nickel in the mixture of powders of metals, aluminum oxide Al_2O_3 and ammonia chloride NH_4Cl, are studied. The barrier function of the layer based on titanium nitride TiN is analyzed for work in extreme conditions. Phase and chemical compositions, structure, microhardness of the obtained coatings are established.

It is shown that diffusion coatings are composed of the zone of compounds and transition zone, which is a solid solution of saturating elements in Ni. NiAl, Ni_3Al are included into zone of compounds during aluminum-silicon, and Ni_2Ti_4O, Ni_2AlTi, TiNi, $Ni_3(Al_xTi_{1-x})$ with microhardness of 3.0-12.5 GPa – at titanium-aluminum.

Multicomponent coatings based on Ti, Al, and Si on nickel and its alloys can be promising in composition, structure, and properties when operating under the action of high temperatures, corrosive media, and severe conditions of wear.

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