Nanosized Intermetallic Compounds are the Main Factor of Low- and High-Temperature Properties Increase of Metallic Materials

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Abstract — Fundamental and technological aspects of nanosized intermetallic compounds utilization as implanted layers and deposited films are discussed in a present paper. The discussion of theoretical and experimental results obtained at present time and the predicted high properties of nanosized intermetallic compounds are shown.

1. Introduction

At present nanotechnological methods are in progress. Pounding the polycrystalline grains and decreasing the dimension ratio of metallic and ceramic materials increase their yield point and deformation resistance. Another method of increasing durability is to use materials with strong inter atomic bonds instead of ordinary metals and alloys. Intermetallic compounds [1, 2] are of that kind. It is the only materials with metallic bonds which deformation resistance increases with temperature. Characteristics of intermetallic compounds with nanosize are not sufficiently known. The nano-intermetallic coatings and surface layers are very perspective. They protect the materials because of their great hardness, friction and deterioration resistance, and high temperature durability. In a nano structural state, even at low and middle temperatures, intermetallic compounds have good plasticity, which allows to improve the mechanical properties of materials. Thus, surface layers containing the nano-intermetallic compounds provide strong strengthening. Creation of inter metallic structures in a nano-crystalline state in the subsurface layer can be made by the high intensity metal ion beams acting on the material surface. A high intensity ion implantation provides a great dose rate of implanted ions, and heating a target to a needed temperature. It leads to creation of modified layers of micron thickness, which consist mainly of intermetallic phases [3, 4].

2. Experimental

The formation of intermetallic phases in the nickel and titanium surface layers was carried out using high intensity implantation of aluminum and titanium ions [3, 4]. The high intensity ion implantation was carried out using the "Raduga-5" [5] source based on continuous-discharge vacuum arc plasma generation at an accelerating voltage of 20 kV. The implantation regimes were differed in the accelerated voltage, distance from a source, temperature of a target and, correspondingly, the dose of irradiated ions (see Table).

Table. Maine characteristics and implantation regimes of nickel and titanium samples

Target	Implanted ions	Implantation regimes			Characteristics of implanted layers		
		Temperature K	Time of treatment, min	Dose of irradiation, 10^{18} ion/sm^2	Thickness of ion-alloyed layers, nm	Average size of formed phases, nm	Regions of intermetallic phases and solid solution (SS) localization with respect to the depth
Ni	Ti	850	120	0.3	600	35	Ni$_3$Ti (100–300 nm) NiTi (100–500 nm) Ti$_2$Ni (100–500 nm) SS of Ti in Ni (to 600 nm)
		1000	120	2.9	1600	40	Ni$_3$Ti (200–700 nm) NiTi (200–800 nm) Ti$_2$Ni (300–500 nm) SS of Ti in Ni (to 1000 nm)
Ni	Al	450	20	0.4	280	65	β-NiAl (10–50 nm) γ'-Ni$_3$Al (to ~90 nm) γ-SS (to ~280 nm)
		500	20	2.0	350	24	β-NiAl (to ~70 nm) γ'-Ni$_3$Al (to ~150 nm) γ-SS (to ~350 nm)
		1600	20	10	1000	38	β-NiAl (to ~50 nm) γ'-Ni$_3$Al (to ~120 nm) γ-SS (to ~1000 nm)
Ti	Al	1173	12	0.22	400	20	γ-TiAl (50–160 nm) α_2-Ti$_3$Al (50–220 nm) α-SS (50–400 nm)
		1173	35	0.62	1600	32	γ-TiAl (80–450 nm) α_2-Ti$_3$Al (80–520 nm) α-SS (80–1600 nm)
		1173	60	1.1	2000	52	γ-TiAl (170–700 nm) α_2-Ti$_3$Al (170–900 nm) α-SS (170–2000 nm)
		1173	125	2.2	2600	70	γ-TiAl (400–1250 nm) α_2-Ti$_3$Al (400–1600 nm) α-SS (400–2600 nm)

The concentration profiles of elements across the nickel surface layers of the implanted materials were

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determined using the Auger electron spectrometry (AES) and the Rutherford back scattering (RBS) method. The phase composition and structural state were investigated by X-ray diffraction (XRD) method and transmission electron microscopy (TEM). The microhardness tester "Nano Hardness Tester NHT-S-AX-000X" of the Swiss firm "CSEM" equipment with a Vickers nanoindentor was used for the investigation of the mechanical properties.

3. Results and discussion

We have proved that a high intensity ion implantation allows to implant the alloying atoms at the depth greater than the ion pass in metallic matrixes. In accordance with EAS and RBS data, a maximum thickness of an ion alloyed layers was 1000 nm for Ni-Al, 1600 nm for Ni-Ti, and 2600 nm for Ti-Al systems (see Table). A maximum concentration of alloying elements was 60−70 at. %.

We have shown that the ion implantation of nickel and titanum samples at high intensity regimes leads to formation in the surface layers nano crystalline phases of intermetallic compounds with the grain average size 20−70 nm, distributed uniformly through the depth. At that, solid solutions of alternating depth composition including nanocrystalline intermetallic phases are also produced. Fig. 1 shows TEM pictures of the surface titanium layers implanted by aluminum.
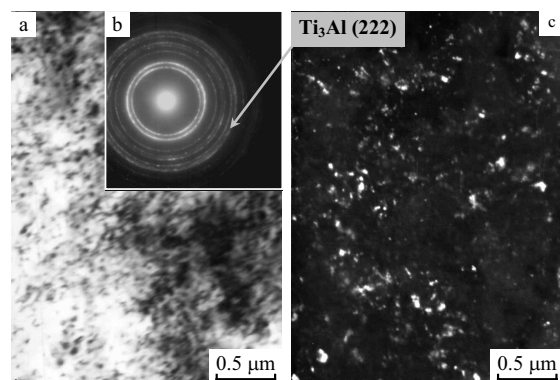

Fig. 1. TEM images of the titanium surface layer implanted with aluminum ions at dose $2.2 \cdot 10^{17}$ ion/cm^2: bright-field image (a); microdiffraction pattern (b); dark-field image (c)

We have established some correlations of creating ion alloyed nickel and titanium layers while high intensity implantation. In all regimes, we have observed creation of nanosized intermetallic phases with composition: NiAl and Ni$_3$Al for Ni-Al system, TiAl and Ti$_3$Al for Ti-Al system, and TiNi and Ni$_3$Ti for Ni-Ti system (see Table) [3]. Besides the intermetallic compounds submerged in a solid solution, in Ni-Ti and Ti-Al systems, the oxide and carbide phases are produced (see Table).

Investigation of the ion alloyed titanium layers implanted by aluminum has shown formation of a surface layer (coating). The coating represents an oxide − carbide layer (OCL) including Al, O, and C atoms. This layer has great adhesion and can improve the physical chemical characteristics of implanted samples.

A dependence found between the irradiation parameters, ion alloyed layer thickness, and the average size of intermetallic phases is very important for practical application. The layer thickness and the average size depend on the ion flux intensity, ion energy, temperature, the treatment time, and others. For example, increasing a treatment time and dose while irradiating titanium targets by aluminum ions leads to a linear increase of the implanted layer (including OCL) thickness and grain average size. For the nickel and titanium samples, a nano grain structure of intermetallic phases and solid solutions of implanted metal in metallic matrixes is typical.
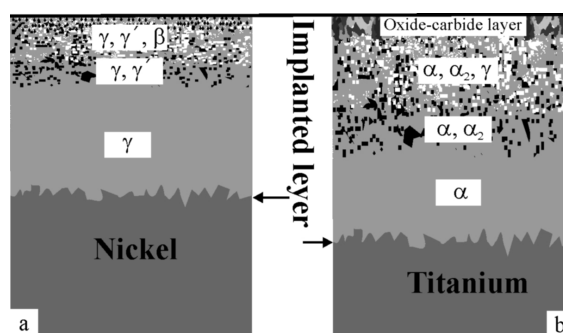

Fig. 2. Schematics of localization of the formed phases with respect to the depth of the ion-alloyed nickel (a) and titanium layers (b). Ni-phases: γ-solid solution of Al into Ni; γ'-Ni$_3$Al; β-NiAl. Ti-phases: α_2-Ti$_3$Al; γ-TiAl; α-solid solution Al into Ti

Fig. 2 shows the disposition of phases formed in Ni and Ti targets while ion implantation. In ion alloyed nickel layer implanted by aluminum there are three zones (beginning from the irradiated surface into the sample depth). The first zone includes three phases: γ'-Ni$_3$Al, β-NiAl, and γ-solid solution of Al in Ni; the second zone contains two phases: γ'-Ni$_3$Al and γ-solid solution; in the third zone there is only γ-solid solution [3].

Unlike nickel samples, in titanium samples there are two regions smoothly transforming in each other with depth. The first region is an oxide-carbide layer; the second one consists of nano intermetallic phases and nano metric Al solid solution in Ti. The second region can also be subdivided in three zones: three-phase (α_2-Ti$_3$Al, γ-TiAl, and α-solid solution); two-phase (α_2-Ti$_3$Al and α-solid solution), and single-phase (α-solid solution) zone (Fig.2) [4].

In applications, it is very important creating ion alloyed layers including several regions of a different phase composition. The region with Ni$_3$Al and NiAl, Ti$_3$Al and TiAl, NiTi and Ni$_3$Ti, and solid solution are near the surface. At that, because of formation the

mixture of intermetallic phases, a very stabile material, with good anticorrosion and antioxidation features is produced. Increasing the three-phase region thickness improves the material mechanical characteristics.

Tests on the implanted samples mechanical characteristics have shown that for all modified samples, microhardness at a depth of two microns is greater than that one of initial materials. For example, for titanium samples (Fig. 3) implanted by $2.2 \cdot 10^{18}$ ion/cm^2, the 1.5–3.0 factor microhardness increasing in the surface layers with thickness about 1.0 micron is observed. Studying the tribological characteristics has shown that with growing temperature (up to 500 K), the wear of alloyed materials does not change, the nonimplanted materials wear being 2–3 times greater.

Strengthening of fine-grain materials is based on a well-known Hall-Patch ratio [6], which describes hardening of grain-border type:

$$\sigma = \sigma_0 + kd^{-1/2}, \qquad (1)$$

σ is a fluidity tension (resistance of a deformed material with an average grain d); σ_0 is a deformation resistance when there is no grain border; k is a Hall-Patch coefficient.
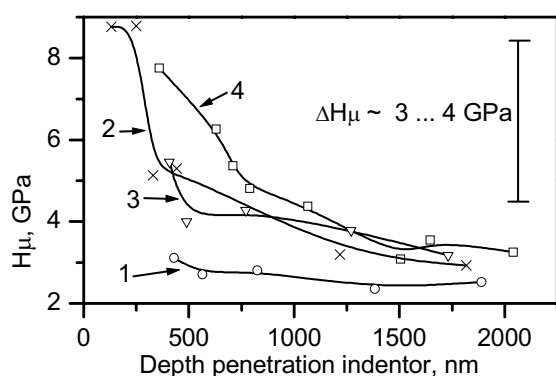

Fig. 3. Mechanical properties of the unimplanted (1) and titanium implanted at dose: $6.2 \cdot 10^{17}$ ion/cm^2 (2); $1.1 \cdot 10^{18}$ ion/cm^2 (3); $2.2 \cdot 10^{18}$ ion/cm^2 (4)

It follows from equation (1) that the deformation resistance increases with decreasing grain size. A deformation resistance rate depends on the Hall-Patch coefficient In our experiments, the size of intermetallic particles and solid solution grains is about several tens nano meters and is not greater than 100 nm (see Table). A grain border strengthening increases greatly for ordered alloys and intermetallic compounds in comparison with pure metals. Indeed, for pure nickel, the Hall-Patch coefficient is 0.30 MPa·m$^{1/2}$ [6]. For non-ordered alloys Ni$_3$Fe and Ni$_3$Mn, the coefficient reaches 0.80 MPa·m$^{1/2}$. If in these alloys there is a long range ordering, the Hall-Patch coefficient increases up to 0.95–1.00 MPa·m$^{1/2}$. In accordance with literature

data, the coefficient (k) for Ni$_3$Al is in the range 0.67–1.47 MPa·m$^{1/2}$, its average value being 1.00 MPa·m$^{1/2}$. Thus, for 50–100 nm grains, additional strengthening of nanograins layers formed by Ni$_3$Al and solid solution Ni-Al is 3.0–4.0 GPa. There are analogues characteristics for materials including nano intermetallic phases of Ti$_3$Al. An additional strengthening leads to a greater assurance factor and durability of surface layers. Fig. 3 (on the right) shows the strengthening in accordance the Hall-Patch equation, while pounding grains up to 50–100 nm. Fig. 3 (on the left) confirms it.

4. Conclusion

We have studied physical chemical characteristics of the nickel and titanium samples, implanted either by aluminum or by titanium ions. The ion alloyed layer thickness and the average grain size of intermetallic phase and solid solution (in this layer) depend on an ion treatment time and irradiation dose. Localizations of implanted phases have been found and similarities in structures of ion alloyed surface layers of nickel and titanium samples have been observed. The regions with intermetallic phases of NiAl and Ni$_3$Al, TiAl and TiAl, Ni$_3$Ti and NiTi, and a solid solution are closest to the surface. An extremely stabile material with great surface hardness at middle and high temperature and great corrosion and oxidation resistance is produced. The experimental data on increasing micro hardness of materials with nano-intermetallic phases coincide with theoretical evaluation.

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