Structure and properties of nitrides on the surface of collagen

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Abstract. A study of the structure and composition of titanium and hafnium nitride coatings, deposited by condensation from plasma phase, on the leather by methods of scanning electron microscopy and x-ray fluorescence analysis. Nanostructured nitride coatings don't degrade the properties of the leather and also inhibits the growth of pathogenic microflora and slow the migration of chromium ions.

Nanostructured, superhard nitride coatings are condensed from the plasma phase by magnetron sputtering and cathodic arc deposition. Some condensates, for example, hafnium inhibit the growth of the pathogenic microflora, and may be used in medicine [1].

Of particular interest are hafnium nitride coatings on a natural collagenic substrate. They could be used to produce orthopedic products.

Collagen is the main structural protein. It is polymer with NH_2 and COOH active groups. Collagen forms the fiber by aggregation of microfibrils. Porous nanostructure of the dermis is the foundation of natural leather materials which tanning with aldehyde, titanium, zirconium, and chrome compounds.

Research material is the chrome leather for artificial limbs and parts of musical instruments according to national standards. The leather contains to 16 % chemically combined and adsorbed moisture. Reduction of moisture content to 10% or less and heating to 100 °C or more leads to changes in structure of collagen. And the leather loses their shape and all properties permanently. The leather is used in the production of artificial limbs, orthopedic insoles, stump sockets and others. These products must meet the requirements of national standards. Leather material is in the contact with the human skin directly. Therefore it must meet the medical, technical and sanitary-chemical requirements, including durability, elasticity, hypoallergenic, no toxicity. The chrome leather is not fully responsible this requirements, because it contains chromium. Because of secretion of the sweat glands, chrome migrates to human skin and causes allergic reactions. Collagen is ideal place for the development of pathogenic microflora such as bacterial and microfungal infections. Antiseptics don't solve problems of toxicity and allergic reactions.

The new nanostructured coatings are known to inhibit the growth of pathogenic microflora. They are based on hafnium nitrides and condensed from the plasma phase in nitrogen atmosphere.

Cathodic arc deposition is widely used in all over the world to synthesize extremely hard film to protect the surface of cutting tools and extend their life significantly. A wide variety of coatings can be created by this technology including TiN, HfN, aluminium, chromium, etc.

Properties of collagen materials are fundamentally different from the properties of metals. Primarily, they have a low thermostability (up to 100 °C), high moisture content in the structure and dielectric properties. That limits the use of vacuum technology for modification of the leather and allows the use of only the elements of this technology. Before condensation the leather is kept at a

pressure of 0.01 Pa. It's necessary to prevent loss of vacuum. Then the synthesis and condensation are carried out at higher pressure of nitrogen. Arc evaporator was turned on periodically to create a low temperature condensing mode. The coating was formed on the obverse and underside of the leather by rotation in front of evaporator.

Defective samples were determined by organoleptic method. The consumer characteristics, surface topography, composition of the condensates at the macro and micro level were measured on the rest of samples. The end result of working off of the technology was to evaluate the properties in accordance with national standard requirements.

The surface topography of nitride coating on the leather with maximal condensation time is shown in figure 1. It is fundamentally different from the relief of coatings on metals. Relief of coating on the leather resembles a mountain landscape in microsizes with elements having a nominal diameter of 1-3 μm. Projections of balls with a diameter of 0.3-3 μm are dropping phase. They are formed by arc evaporation cathode metal. Large drops with diameter of 2-4 μm spontaneously fall from the surface to the bottom of the vacuum chamber. But small ones (200-300 nm in diameter) stick to the surface. Then they are overgrown nitride phase.

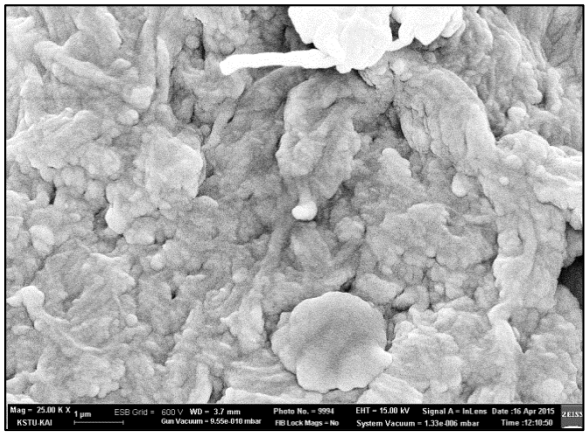

Figure 1. SEM image of the surface topography of nitride coating on the leather.

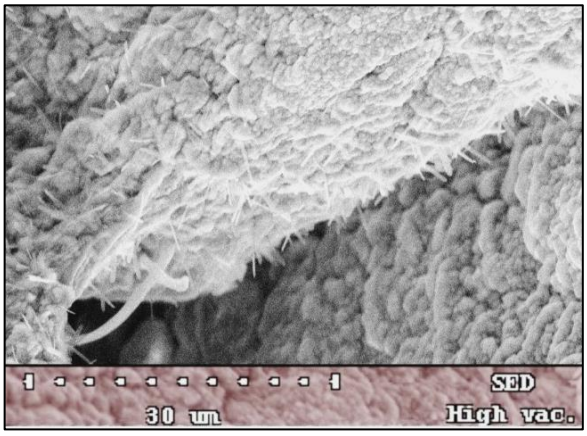

Figure 2. SEM image of nanowhiskers.

The reason of this hillocky relief of coating was revealed by changing the condensation regime. Figure 2 shows the nanowhiskers with length of 5-6 μm and diameter of 40-80 nm. When there is no shaking of rotation, they grow with abnormal speed. And then they fall randomly to the surface and adhere to it due to the Van der Waals forces. Further, they are also overgrown nitride phase and form the characteristic relief.

Crystals grow fragmentary and form scales (dendrites) under condition of limited time of condensation. They are not connected with each other. They are fixed only at the elastic collagen substrate and can move relative to each other (figure 3). Such coatings don't crack and don't hinder the permeability and elastic properties of the leather.

The scales are ordered and range in size from 0.1 to 1.0 μm. They cause diffraction of the incident light. It gives the surface a golden color. Also the iridescent color pattern can appear. It has the characteristic metallic luster. And it appears when sizes of the scales are changed monotonically.

The scaly structure of the coating on the leather was visualized by scanning electron microscopy at workstation Auriga CrossBeam using secondary electrons (figure 4) with the energy dispersive spectrometer INCA. It allowed to more accurately examining the structure and composition of the individual fragments.

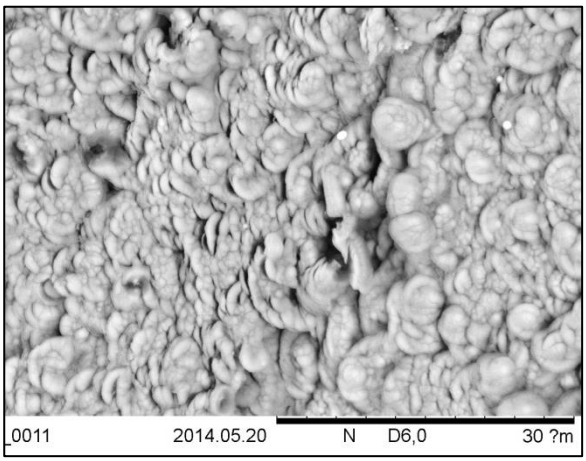

Figure 3. SEM image of the scaly structure of nitride coating on the leather.

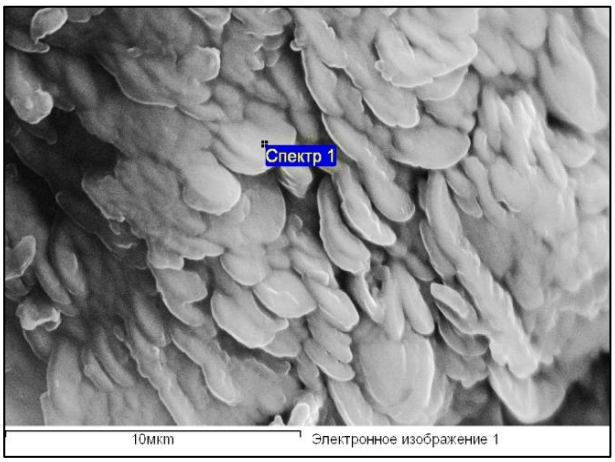

Figure 4. SEM image of the scaly structure of nitride coating on the leather.

The distribution of elements on the electron energy spectrum is shown in figure 5. Composition of outer layer of scaly coating at depths of several atomic layers showed the presence of hafnium oxide and titanium in a ratio of 1:4.

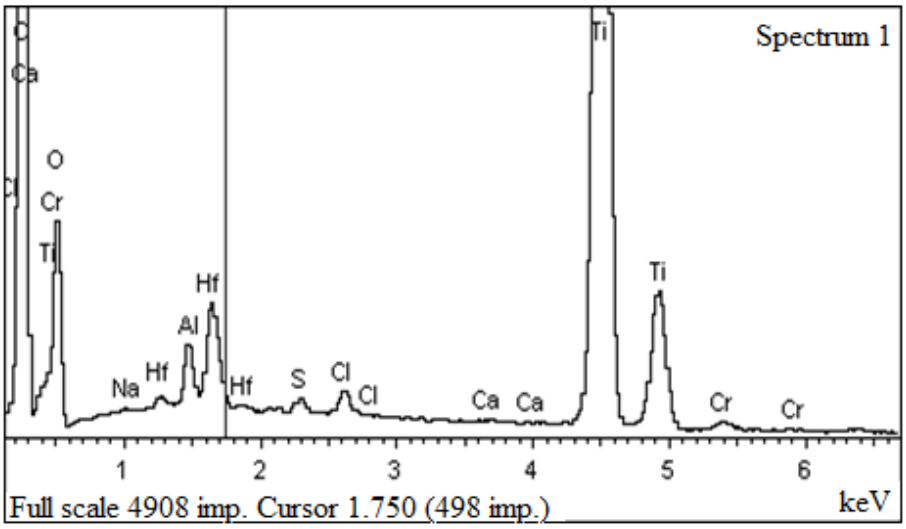

Figure 5. The distribution of elements on the electron energy spectrum.

Probably the atmospheric oxygen and water from collagen are oxidized the outer layers from nitrides to oxides. This is due to the large difference in the value of the standard enthalpy of formation of 88 and 265 kcal/mol, respectively.

Hafnium-titanium coatings on the polycorundum substrate were studied by X-ray fluorescence analysis on such spectroscopes as Bruker «Tornado» and «Picofox». Studies on depths up to 60 μm showed the ratio of hafnium and titanium in equal parts with ± 20% variation.

The columnar crystals are viewed in scales structure. It is typical for nitride condensates. The crystals have a length equal to the thickness of the coating and a diameter of 20-50 nm. Growth of crystals in the columnar direction is not interrupted by a transition of metal vapor-plasma phase to

another. However, a thin interface between the phases TiN and HfN is viewed in the electronic image (figure 6).

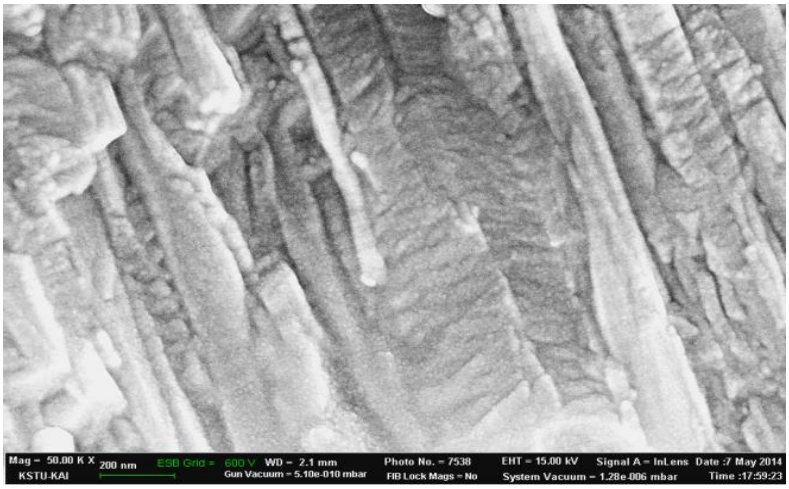

Figure 6. SEM image of the structure of scales.

It is found that the coating of hafnium nitride doesn't degrade the properties of the leather. It gives to the front surface of biocompatibility with human tissues and inhibits the growth of pathogenic microflora and microfungi [2]. Main characteristics of the leather with coatings are given in table 1. They satisfy the requirements of national standards [3].

Table 1. Properties of the leather with coatings.

	Welding temperature (°C)	Tensile strength (MPa)	Relative extension (%)	Moisture content (%)	Biological activity
HfN	92.5	12.3	28.0	10.6	Bioactive, non-toxic
TiN	92.0	12.0	42.5	8.8	Bioinert

Characteristic relief of nitride coating with thickness of 1-3 μm is formed on the leather during the growth of whiskers with a length of 5-6 μm a diameter of 40-80 nm.

The composition of the nanostructured titanium-hafnium nitride coating on depths up to 60 μm has the ratio of hafnium and titanium in equal parts with ± 20% variation. Unlike the composition of outer layer of scaly coating at depths of several atomic layers showed the presence of hafnium oxide and titanium in a ratio of 1:4.

The scaly structure of covering with thickness in 200 nm and the presence in the composition of Ti and Hf allow saving gas permeability, elasticity of the leather, and also inhibits the growth of pathogenic microflora and slow the migration of chromium ions 35 times.

The use of leather with titanium-hafnium nitride coatings is planned in the production of leather-metal prostheses of lower extremities.

References

[1] Patent RU 2 554 773 (2015).
[2] Veinov V P, Bayazitova L T, Haldeeva E V, Mironov M M and Grebenschokova M M 2016 *Sientific session 2016* (Kazan: KNRTU) p 489
[3] Mironov M M, Khramov E N and Grebenschikova M M 2016 *Bulletin of the Technological University* vol **12** pp 108-110