

# THE MAIN DIRECTIONS AND WAYS TO IMPROVE THE TECHNOLOGY OF LEATHER AND FUR

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## STRUCTURE AND PROPERTIES OF NITRIDES ON THE SURFACE OF COLLAGEN

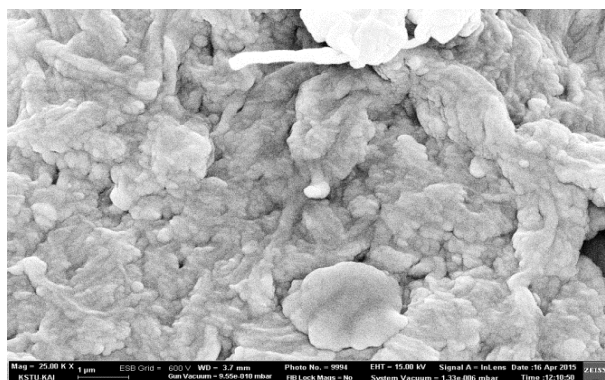
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Nanostructured, superhard nitride coatings are condensed from the plasma phase by magnetron sputtering and cathodic arc deposition. Some condensates, for example, hafnium inhibit the growth of the pathogenic microflora, and may be used in medicine (Bactericidal coating material. Patent № 2554773 RU).

Of particular interest are hafnium nitride coatings on a natural collagenic substrate – the orthopedic leather. They could be used to produce orthopedic products. Leather is the main structural protein and polymer with  $\text{NH}_2$  and  $\text{COOH}$  active groups. It has porous nanostructure formed by microfibrils. It is different from the metals of low thermostability (up to  $100\text{ }^\circ\text{C}$ ), high moisture content (18-20%) and dielectric properties. 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 new nanostructured coatings are known to inhibit the growth of pathogenic microflora and microfungus. They are based on hafnium nitrides and condensed from the plasma phase in nitrogen atmosphere. Before condensation the leather is kept at a pressure of 0.01 Pa. 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. Main characteristics of the leather with coatings satisfy the requirements of national standards.



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

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 microsized with elements having a nominal diameter of 1-3  $\mu\text{m}$ .

The reason of this hilly relief of coating was revealed by changing the condensation regime. Figure 2 shows the nanowhiskers with length of 5-6  $\mu\text{m}$  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.

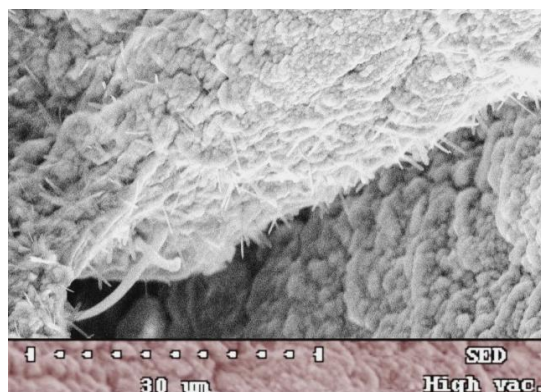


Figure 2 – SEM image of nanowhiskers

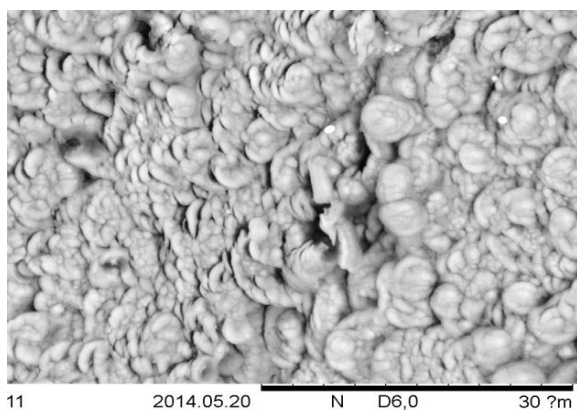


Figure 3 – SEM image of the scaly structure of nitride coating on the leather

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  $\mu\text{m}$ . 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.

Interest is the study of composition of the individual scales. Hafnium-titanium coatings on the polycorundum substrate were studied by X-ray fluorescence analysis on such spectrometers as Bruker «Tornado» and «Picofox». Studies on depths up to 60  $\mu\text{m}$  showed the ratio of hafnium and titanium in equal parts with  $\pm 20\%$  variation. The distribution of elements on the electron energy spectrum was investigated at workstation «Auriga» by Carl Zeiss using secondary electrons with the energy dispersive spectrometer INCA (Figure 4). 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. 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.

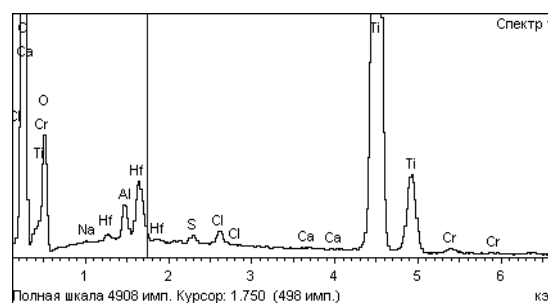


Figure 4 – The distribution of elements on the electron energy spectrum