Thermal Stability of Ti-C-Ni-Cr and Ti-C-Ni-Cr-Al-Si Nanocomposite Coatings

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Abstract. The results of the microstructure, mechanical and tribological properties investigations of Ti-C-Ni-Cr and Ti-C-Ni-Cr-Al-Si nanocomposite coatings based on amorphous carbon in the initial state and after the annealing to 900 °C are presented. The effect of annealing temperature on the microstructure, tribological and mechanical properties of Ti-C-Ni-Cr and Ti-C-Ni-Cr-Al-Si nanostructured coatings is discussed.

1. Introduction

Recently, wide attention is focused on the composite materials because of the possibility of creation a protective surface layer having a combination of such properties as high hardness, wear resistance, thermal stability and low coefficient of friction [1].

A promising area of research in this field is development of the coatings based on amorphous carbon (a-C), which are used as the solid lubricant, and nanoscale carbide crystalline particles and (or) nitride phases. These coatings are of the type DNG / AM, (dispersed nanograins in amorphous matrix) and have low internal stresses. These stresses are associated with the decreasing of volume fraction of sp³ bonds (diamond-like) and increasing proportion of sp² bonds (graphite-like) as a result of doping amorphous carbon, for example, by the elements such as Cr, Si, Al, Ti [3].

Coatings of this type can be used to improve the strength properties and reducing the friction coefficient of some manufactures in friction units.

In the present paper the thermal stability, namely, the influence of annealing temperature on the structure-phase state, tribological and mechanical properties of Ti-C-Ni-Cr and Ti-C-Ni-Cr-Al-Si nanostructured coatings have been investigated.

2. Materials and methods

The Ti-C-Ni-Cr coatings were synthesized in the plasma magnetron-arc facility "Legend" [4] with three graphite cathodes (C₁, C₂, C₃) and one composite titanium-carbide cathode using nichrome as a binder. To form a Ti-C-Ni-Cr-Al-Si coating, one of the graphite cathodes was replaced by an AlCrSi cathode. Deposition parameters are given in table 1. The substrates were made from VT1-0 titanium alloy, WC₀ hard alloy (tungsten-cobalt) and molybdenum.

Investigation of samples by transmission electron microscopy was performed on microscope Philips CM-12 at an accelerating voltage of 120 kV. Microhardness of the resulting coatings was measured by the Vickers method using a special attachment to a Neophot-21 optical microscope.
Tribological tests have been carried out in a high-temperature tribometer in a ball-on-disk mode with a normal load of 2 N on the spherical indenter. On the studied coatings anneals at temperatures up to 900 °C under a high vacuum of $2 \times 10^{-5}$ Torr have been made.

### Table 1. Regimes of coatings synthesis.

| Coating          | P (kW) | $U_s$ (V) | $T$ (°C) | t (min) | $P_{Ar+N}$ (Torr) |
|------------------|--------|-----------|----------|---------|-------------------|
| Ti-C-Ni-Cr       | TiCNiCr| C1 0.9    | C2 0.9   | C3 0.9  | 50 450 60         |
| Ti-C-Ni-Cr-Al-Si | TiCNiCr| C1 0.4    | C2 0.9   |         | 50 450 60         |

3. Results and discussion

Transmission electron microscopy (TEM) investigations reveal the presence in the Ti-C-Ni-Cr coating of nanocrystalline (TiC and NiCr) phases and the amorphous phase (a-C). The diffraction pattern contains a diffuse halo corresponding to the amorphous phase, and the diffraction rings corresponding to the crystalline phase TiC with a small crystallite size and brighter reflections corresponding to relatively large NiCr particles (figure 1 b). It is assumed that chromium in this coating is partially dissolved in the amorphous phase (up to 20 at. %). In the diffraction patterns, these particles (the particles conglomerates) give some brighter reflexes (figure 2 b).

Titanium carbide particles are dispersed in an amorphous matrix sufficiently homogeneous. As areas of high-density particles, where the distance between the particles is comparable with their sizes, as areas, in which the distance between the particles significantly exceeding these sizes, are observed. In the diffraction pattern (figure 1 b) rings of the phase TiC are broadened, that indicates about the small size of the crystallites. Estimates of sizes by the half-width of the diffraction peak component 1/25 Å⁻¹ for reflex $g = [111]$ TiC gives the values of $\approx 2.5$ nm, which are consistent with the analysis data of dark-field images.

Investigations of coatings cross-sections have revealed features in the distribution of nanoscale particles. At a distance of more than 0.5 microns from the substrate, a structure of coating is homogeneous. It is represented by an amorphous phase (a - C) with uniformly distributed particles of TiC and NiCr (<10 nm) [5]. At a distance of less than 0.5 microns from the substrate a particles (or conglomerates) NiCr sizes up to 30 nm are observed.

![Figure 1](image)

**Figure 1.** Dark-field image (a) and microdiffraction pattern (b) of Ti-C-Ni-Cr coating after deposition.
Investigation of the microstructure of the coatings Ti-C-Ni-Cr after the annealing up to $T = 900 \, ^\circ\rm{C}$, 1h by transmission electron microscopy revealed that sizes of the nanocrystalline phases (TiC and NiCr) are reserved (figure 2). The formation of new phases did not found.

![Figure 2](image1.png)

**Figure 2.** Dark-field image (a) and microdiffraction pattern (b) of Ti-C-Ni-Cr coating after the annealing at 900 °C.

Ti-C-Ni-Cr-Al-Si coatings after deposition have a microstructure similar to coating Ti-C-Ni-Cr, but different elements content. In Ti-C-Ni-Cr-Al-Si coating the carbon content is significantly less. It should be noted that in crystalline nanoparticles Al and Si did not found. Therefore these elements are dissolved in the amorphous carbon matrix.

Investigations of the microstructure of the Ti-C-Ni-Cr-Al-Si coatings after the annealing up to $T = 900 \, ^\circ\rm{C}$, 1h by the methods of TEM also revealed the stability of amorphous and nanocrystalline phases (TiC and NiCr).

The values of the coefficient of friction for Ti-Ni-Cr-C coatings after deposition are in the range $\mu \approx 0.14 - 0.16$, for titanium alloy $\mu \approx 0.5 - 0.6$. These values of the coefficient of friction are retained at the annealing up to 700 °C.

Increasing the annealing temperature up to 900 °C leads to higher values ($\mu \approx 0.4 - 0.5$, figure 3 b) of friction coefficient of Ti-C-Ni-Cr coating, which is comparable with the coefficient of friction of the titanium alloy without coating ($\mu \approx 0.5 - 0.7$). The increasing of the coefficient of friction is caused the formation of oxide phases on the surface of the coating that was confirmed by X-ray analysis.

![Figure 3](image2.png)

**Figure 3.** Dependence of the coefficient of friction on the distance traveled by the indenter on the Ti-C-Ni-Cr coating. (a) – after deposition, 1h, (b) – after the annealing 900 °C, 1h.
From the analysis of dependency of the friction coefficient from the distance traveled by the indenter at different annealing temperatures for Ti-C-Ni-Cr-Al-Si coating, it follows that the value of this coefficient after the annealing at T = 900 °C is practically identical with the initial value (μ ≈ 0.34). However, the nature of this dependence is varied considerably. The coefficient of friction achieves this value almost from the beginning of the test (figure 4 b). The changing of the nature of this dependence may indicate on degradation of the coating structure as well as the possible formation of new phases, which increase the coefficient of friction.

![Figure 4](image)

Figure 4. Dependence of the coefficient of friction on the distance traveled by the indenter on the Ti-C-Ni-Cr-Al-Si coating. (a) – after deposition, 1h, (b) – after the annealing 900 °C, 1h.

Investigations of mechanical properties of the samples of titanium alloy with Ti-C-Ni-Cr coating showed that the microhardness of the composition retains its value up to T = 900 °C. Moreover, there is some increase in hardness from ≈ 14 GPa in the initial state to ≈ 18 GPa after the annealing. These values of microhardness are in ≈ 5 - 7 times higher than that of titanium alloy (2 GPa).

It should be noted that at increasing of load the penetration depth of the indenter reaches a value close to the value of the coating thickness. Thus, is actually determined the microhardness of composition "substrate + coating".

Ti-C-Ni-Cr-Al-Si coatings on samples of titanium alloy already after deposition have a somewhat lower hardness (10.7 GPa). The annealing of these coatings causes a reduction of microhardness values up to ≈ 9.4 GPa (900 °C). At present the physical causes of such behavior microhardness do not clear.

| Coating                  | Load, g | Hμ before annealing, GPa | Hμ after annealing 900 °C, GPa |
|-------------------------|---------|--------------------------|--------------------------------|
| Ti-C-Ni-Cr              | 20      | 13.9±0.9                 | 18.3±0.9                       |
| Ti-C-Ni-Cr-Al-Si        | 20      | 10.7±1.5                 | 9.4±1.1                        |

4. Conclusion

Multielement nanocomposite coatings Ti-C-Ni-Cr and Ti-C-Ni-Cr-Al-Si, having a sufficiently high (11 - 18 GPa) hardness, low (μ <0.2) the coefficient of friction and high thermal stability of the microstructure and properties up to 700 °C, were obtained. After the annealing at 900 °C the coefficient of friction increases, which can be connected to form an oxide film on the coating.

Coating structure is represented by the amorphous matrix with dissolved Al, Si, Cr, Ni metal elements and nanosized particles of crystalline phases (TiC and NiCr).

The high values of microhardness are caused the structure of amorphous carbon and nanosized particles. The tribological tests have shown that the Ti-C-Ni-Cr coatings have low values (μ < 0.2) of the coefficient of friction, which is necessary for antifriction applications. These values are ensured by
the amorphous carbon matrix that plays the role of a solid lubricant. The resulting combination of properties demonstrates the possibility of applying the considered coatings on the manufactures of titanium alloys.

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