Structure, Mechanical and Electrical Properties of CN_x Coatings ($0\leq x\leq 0.5$) Prepared by Pulsed Arc Sputtering of Graphite Target

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Abstract – CN_x films 1–3 μm thick were deposited on metal substrates by pulsed arc sputtering of graphite in a nitrogen-containing atmosphere at P=10^{-2}–5 Pa. The nitrogen concentration of the coatings was determined by the method of nuclear reactions $^{14}N(d,\alpha_0)^{12}C$ and $^{14}N(d,\alpha_1)^{12}C$. The coating microhardness H_V and internal stresses σ_0 were measured using methods proposed by the authors. The initial (f_0) and stationary (f_{st}) friction coefficients were determined during the reciprocal motion of a WC-Co ball. The surface morphology was examined by methods of scanning and tunnel electron microscopy (SEM and STM). It was found that the hardness and internal stresses sharply decreased in CN_x coatings at x~(0.25–0.35). Coatings with these compositions were sufficiently hard (H_V~50–60 GPa), but they were stressed less than nitrogen-free coatings (σ_0~10–12 GPa at x = 0). Given the same compositions, f_{st}~f_0~0.10–0.05. The STM examination showed that nitrogen-containing coatings had a marked columnar structure. The dependence of the mechanical properties on the nitrogen concentration and the electrical resistance minimum, which was revealed at x~0.3, were interpreted well in terms of the percolation theory if the CN_x condensate was conceived of as a mixture of diamond-like (sp^3) $CN_{x\leq 0.1}$ domains and C_2N domains with sp^2 bonds. At x~0.3 the composition corresponded to equal fractions of these components, i.e. had an extremely developed interface between unlike structural elements and was characterized by a continuous cluster of each of the elements.

1 Introduction

Hard diamond-like (~80 % sp^3 bonds) coatings (DLCs) possess an excellent set of properties for modification of the surface of tools and friction parts so as to extend their lifetime and expand the fields of their practical application. DLCs have the hardness of about 100 GPa and the stationary friction coefficient of not over 0.1 [1]. However, large internal stresses (~10 GPa) weaken their adhesion to the substrate. This factor limits the lifetime of DLCs in real operating conditions primarily because of peeling. Furthermore, surface roughness of DLCs is responsible for large (f_0~0.5) initial friction coefficients [2]. Since the hardness and the wear resistance of DLCs are high, the initial running-in time is longer, the surface of parts in mechanical contact with DLCs deteriorates, unwanted heat is released at the contact point, etc.

These circumstances have stimulated the search for methods providing modification of DLCs and eliminating the factors that limit their applications. In doing so, hardness may be somewhat sacrificed to clear other faults. It was this practical task that we posed ourselves in the present study. We also intended to clarify how the mechanical and tribological properties of condensates, which were prepared by arc sputtering of graphite in a nitrogen-doped vacuum, depended on the condensate structure.

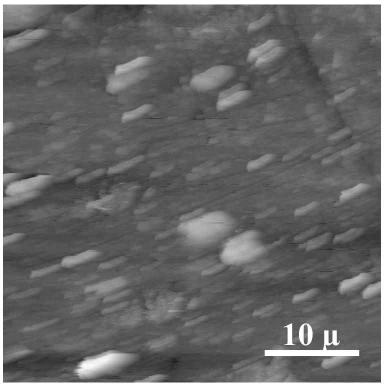
2. Methods

CN_x films 1–3 μm thick were deposited on metal substrates by pulsed arc sputtering of graphite in a nitrogen-containing atmosphere at P=10^{-2}–5 Pa in a UVNIIPA-001 installation. The microhardness of the coating material H_f and internal stresses σ_0 were measured using methods proposed by the authors [3]. The initial (f_0) and stationary (f_{st}) friction coefficients were determined during the reciprocal motion of a WC-Co ball under a load of 2 N. The surface morphology was examined in a Philips 515 scanning electron microscope at the Institute of Metal Physics and a SMM-2000T scanning tunnel microscope. The nitrogen concentration was measured by the method of nuclear reactions $^{14}N(d,\alpha_0)^{12}C$ and $^{14}N(d,\alpha_1)^{12}C$.

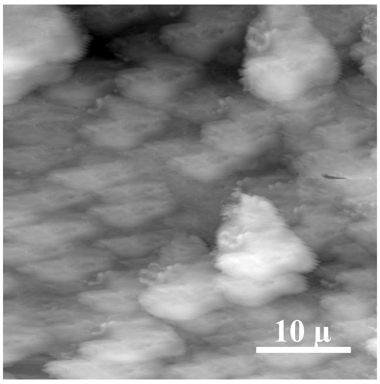
3. Results

We failed, as in [4, 5], to prepare CN_x condensates with the nitrogen concentration of over (33–35) at. %. That is, the limiting composition of the coatings corresponded to the formula C_2N.

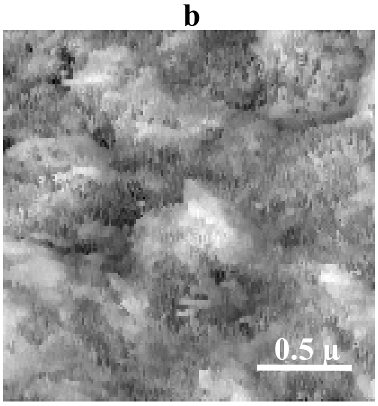
It was shown [6] that the structure of CN_x coatings was formed mainly by an amorphous matrix, which included homogeneous amorphous regions and regions decorated with crystalline precipitates at $0.15\leq x\leq 0.4$. The STM analysis of the surface morphology of the condensates demonstrated that, unlike diamond-like carbon films, the CN_x condensates had a columnar structure with irregularities occurring in 4 to 7μm steps on the average (Fig. 1, *a*, *b*). A detailed examination of the structure of "columns" revealed that they in turn consisted of bunches 0.1–1.0 μm across (Fig. 1, *c*). Furthermore, according to the SEM examination, the surface had sparse spherical formations whose quantity increased with growing concentration of nitrogen in the film (Fig. 2, *a*). The electrical resistance of the spherical formations was higher than the electrical resistance of the basic amorphous structure.



a



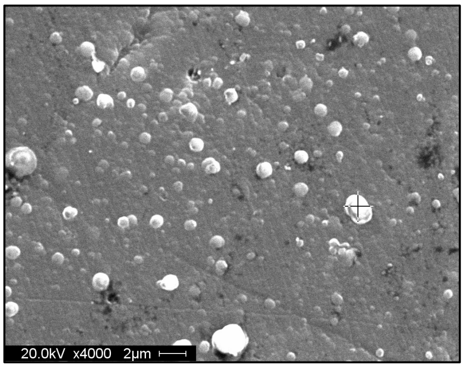
b



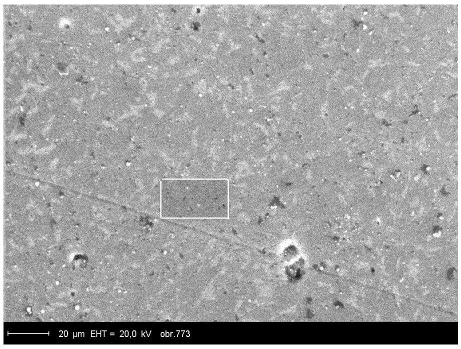
c

Fig. 1. STM images of DLC (a) and $CN_{0.4}$ (b, c)

In addition, the amorphous structure itself was inhomogeneous at $0.15 \le x \le 0.4$. As seen in reflected electrons, the film surface looked like having two phases since light and dark areas were observed (Fig. 2, *b*). Light areas had a higher electrical resistance. This was confirmed by measurements of the spreading resistance using an electron probe and the charge accumulation in these areas. Their size was 0.1 to several micrometers, which was in agreement with TEM [6] and STM (Fig. 1) data.



a



b

Fig. 2. SEM images of $CN_{0.5}$ (a) and $CN_{0.35}$ (b)

The main implication of the structural analysis was that at $0 \le x \le 0.5$ the CN_x condensate represented a mixture of two types of amorphous domains, that is, presumably diamond-like domains with the nitrogen concentration as large as possible for preservation of sp^3 bonds (not over 10 at.% according to [4]) and C_2N domains with sp^2 bonds [5].

The mechanical and tribological properties of the CN_x coatings as a function of the nitrogen concentration are given in Fig. 3.

These dependences can be used for selection of CN_x deposition conditions in different practical applications.

The following points are noteworthy:

– At $x \le 0.15$ the mechanical characteristics σ_0 and H_V remained nearly stable, while the initial friction coefficient sharply decreased (probably because rough peaks were etched with nitrogen ions). Therefore, $CN_{x \le 0.15}$ coatings are preferable in practical terms to nitrogen-free DLCs.

– At $0.25 \le x \le 0.35$ the hardness of the coatings was still sufficiently high (H_f~40 GPa) and they possessed the best functional properties (f_0~f_{st}~0.1).

Considering the observed regularities, we tested CN_x coatings (including those with different compositions) on metal cutting tools. The lifetime of the tools increased at least 2 times. Taps for cutting of thread in blind holes performed especially well.

One more result presenting practical significance was that not only DLCs, but also nitrogen-rich $CN_{0.5}$ coatings had the resistance $R>10^7$ Ohm. Therefore, unstressed C_2N coatings (σ_0~1.5 GPa, Fig. 3) show promise as insulators that readily adhere to various substrates.

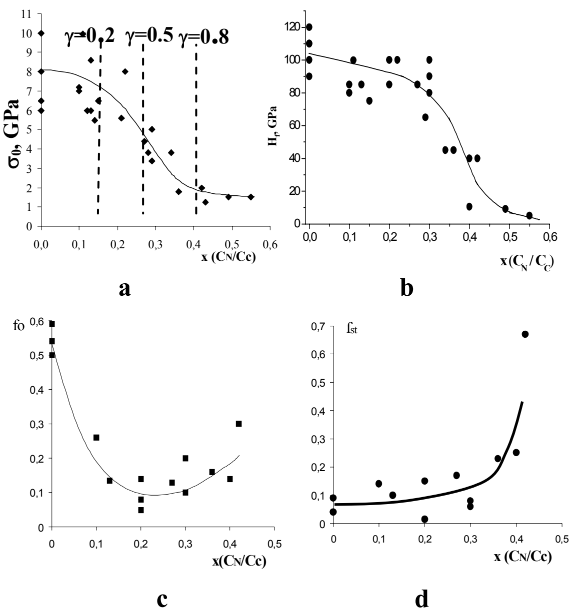


Fig. 3. Dependences of σ_0 (a), H_f (b), f_0 (c) and f_{st} (d) on nitrogen concentration for CN_x coatings

4. Discussion

The analysis of the structure of the amorphous $CN_{0<x<0.5}$ matrix showed that it can be presented as a mixture of CN_{x1} and CN_{x2} domains. In this case, the average nitrogen concentration x is related to the fractionγ of the nitrogen-rich component x_1 by the expression $x=\gamma(x_2-x_1)+x_1$.

It is known from the percolation theory that in the case of a random distribution of two structural elements of the volume, an infinite cluster (the possibility to pass the whole volume along the trajectory that goes through particles of one component only) appears when its volume concentration becomes ~20 % [7]. If we assume x_1=0.05 [4] and x_2=0.5 [5], the infinite cluster from γ=0.2 to γ=0.8 will exist at the average value of x=0.14 to x=0.41 respectively. The concentration x=0.275 corresponds to equal fractions of both components (γ=0.5).

These characteristic values of x are marked in the dependence $\sigma_0=f(x)$ (Fig. 3). It is seen that the CN_x properties remained relatively stable until particles of one of the components were isolated and changed when one of them formed a three-dimensional "framework". The properties changed most dramatically when these components were equal.

The idea that the CN_x matrix represents a mixture of DLC and C_2N domains is well illustrated by the dependence of the electrical resistance R on fraction γ of the nitrogen-rich component (Fig. 4).

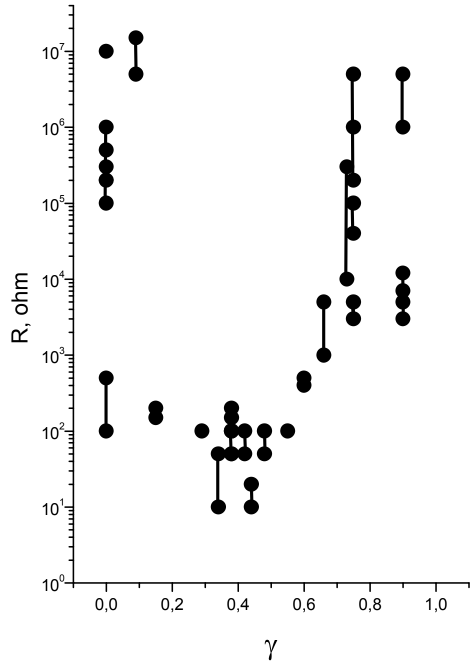


Fig. 4. Dependence of CN_x electrical resistance R on the fraction   of the nitrogen-rich component

It was observed that $R_{0<x<0.5}<R_{0;\,0.5}$. Since DLCs and C_2N undoubtedly had a domain structure, we assumed that the conductivity $1/R$ of the CN_x coatings was due primarily to boundaries between unlike domains. Different models, which are based on the percolation theory [7], give one and the same result: the maximum of the relative fraction of boundaries between unlike components (in our case, the minimum of the electrical resistance) hits the region where the fractions of the components in the structure are equal. We measured R (the coating – the back side of the metal substrate) of samples used for determination of internal stresses σ_0 [3]. These measurements confirmed the expected regularity (Figs. 3 and 4).

5. Conclusion

The study provided experimental data, which can be used to select conditions for deposition of CN_x coatings by sputtering of graphite in a nitrogen-containing atmosphere taking into account their designated purpose.

Considering the obtained results and the data in [4, 5], the structure of $CN_{0\le x\le 0.5}$ coatings was related to their properties by recognizing general regularities inherent in mixtures of two different objects.

The authors hope that this approach to interpretation of properties of coatings may be useful for other inhomogeneous films too.

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