Structure and Mechanical Properties of Nanocrystal Coatings on Basis of Titanium Carbide-Nitride

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Abstract – Element and phase composition, microstructure and its effect on microhardness and wear-resistance of the TiC_xN_y based nanocrystalline coatings are researched in dependence of the acetylene and nitrogen reactive gas partial pressures ratio and of the introduction in process of a coating deposition of the ion beam assisting treatment (IBAT). It was shown that TiC_xN_y lattice parameter, internal elastic microstress, (200) texture parameter increases but the mean grain size decreases with ratio of $\rho_{C_2H_2} : \rho_{N_2}$ in coating deposited without IBAT. As a result, the microhardness rises but wear-resistance has little value at $\rho_{C_2H_2} \approx \rho_{N_2}$ and big values at the highest and lowest ratio of $\rho_{C_2H_2} : \rho_{N_2}$. The IBAT improves a wear-resistance of deposited coatings on basis of TiC_xN_y. It permits also to reduce a deposition temperature up to RT.

1. Introduction

Today the hardening nanocrystalline coatings are produced mainly by the deposition in vacuum of multicomponent, polyphase and multilayer gradient materials on the substrates, previously prepared and heated up to required temperature. Despite of advancement in the designing of nanocrystalline coatings, there are considerable problems both in the fundamental comprehension of behavior of systems in nanoscale and in the investigation of their properties. This fact restrains the application of the nanotechnologies in practice.

There are many factors which affect on coating behavior and so the interpretation of properties of nanocrystalline coatings is enough complicated problem [1, 2]. The solving of this problem is impossible without in-depth study of structure, chemical and phase composition. In the present paper the some of the mentioned problems and ways of their solution are considered as applied to the creation of nanocrystalline coatings on the basis of the titanium carbide-nitride.

2. Experimental

A deposition of coatings was made using the DC – magnetron in reactive medium from mix of the argon, nitrogen and acetylene gases under the total operating pressure of 0,10 Pa. The target was made from titanium VT-1-0. The power applied to the magnetron was equal 2.2 kW for all coatings. The substrates were prepared from the austenitic sheet steel of 12H18N10T. The surfaces under coating were parallel to rolling surfaces. A samples was polished to roughness of $R_a = 0.08$ μm.

Four sets of a samples with a deposited coatings containing 4–8 units in every one were prepared. Within the three sets the coatings were deposited at constant temperature 473 K and different ratio of pressures of the acetylene and nitrogen reactive gases (Table 1). Within the fourth set of samples the coatings were deposited at room temperature (RT) under condition of the ion beam assisting treatment (IBAMD method). The composition of gas mixture for ion beam source was the same as composition of working gas mixture for deposition of coatings. Ion beam energy is equal 1 keV, current density of ions is 1 mA/cm^2. The ion-beam treatment for 0.2 s is followed after the deposition of the next 4 nm in thickness layer of coating. There were 1300 cycles of "deposition – ion beam treatment" during all process. The deposition rate was 2.4–2.8 nm/s for all coatings. The thickness of coatings was about 5 μm.

Phase composition and texture were examined by X-ray diffraction analysis using diffractometer DRON-3M. The concentration profiles of elements as function of thickness coating were investigated using mass spectrometer of secondary ions MS-7201M.

The tests for wear-resistance were performance using the 2070SMT-1 machine with counter-body in type of SHH-15 bearing steel with hardness HRC62 polished to roughness of $R_a = 0.08$ μm in condition dry friction slip under a constant load of 49N, the rotation rate is 50 s^{-1}. The total thickness of the coating and wear was determined by the weight method and controlled by a profilometer 296. The data of the two methods coincide within the limits of measurements errors. Microhardness was measured by nanoindentor "NanoTest 600" using Bercovich indenter and microhardnessmeter PMT-3.

3. Results and Discussion

It was determined by phase analysis of the DRON-3M received X-ray diffraction patterns (Fig. 1) the basic phase of all deposited coatings is the TiC_xN_y phase with 94–96% percent amount with the cubic NaCl-type lattice. The little amount of the β-Ti_2N tetragonal

Table 1. Structure characteristics (D means grain size, σ_i – internal elastic stress level, a – crystalline lattice parameter, $I_{(111)}/I_{(200)}$ – X-ray reflection intensity ratio), element composition (I_C^+/I_N^+ – relation of currents of secondary ions of carbon and nitrogen), microhardness $H\mu$ and wear rates of deposited coatings $\Delta m/\Delta t$

No.	$\rho_{C_2H_2}/\rho_{N_2}$	D, nm	σ_i, GPa	a, nm	$I_{(111)}/I_{(200)}$	I_C^+/I_N^+	$H\mu$,GPa	$\Delta m/\Delta t$, mg/hour
1	0.61	10	7.2 ± 0.6	0.4298 ± 0.0001	0.03	1.8	40 ± 2	6.0 ± 1.2
2	0.52	18	3.5 ± 0.4	0.4274 ± 0.0002	0.16	1.0	30 ± 2	30.1 ± 2.3
3	0.22	25	4.1 ± 0.4	0.4255 ± 0.0003	0.63	0.3	23 ± 1	9.0 ± 1.6
4	0.33	20	2.2 ± 0.3	0.4265 ± 0.0001	4.6	0.6	31 ± 1	4.2 ± 1.0

Table 2. Chemical composition of the TiC_xN_y phase in the coatings deposited over substrates of austenite steel 12H18N10T ($\rho_{C_2H_2}$, ρ_{N_2} – partial pressures of acetylene and nitrogen in working gas mixture)

Set of samples	$\rho_{C_2H_2}/\rho_{N_2}$	by X-ray structure analysis	by secondary ion mass spectrometry
1	0.61	$TiC_{0.61}N_{0.31}$	$TiC_{0.64}N_{0.36}$
2	0.52	$TiC_{0.41}N_{0.50}$	$TiC_{0.50}N_{0.50}$
3	0.22	$TiC_{0.14}N_{0.77}$	$TiC_{0.22}N_{0.78}$
4	0.33	$TiC_{0.33}N_{0.58}$	$TiC_{0.38}N_{0.62}$

phase with lattice parameters $a = 0.4945$ nm and $c = 0.3034$ nm is present at all coatings in addition. Increasing of the TiC_xN_y phase lattice parameter owing to growth of the reactive gas partial pressure ratio of acetylene to nitrogen entering into composition of the working gas mixture flowing into a vacuum chamber is observed to investigated modes of the coating deposition (Table 1).

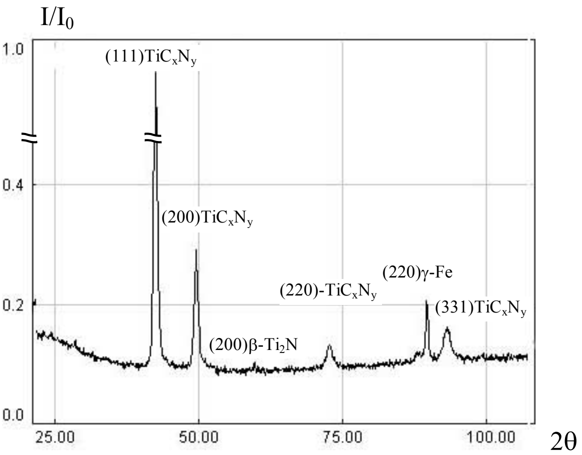

Fig. 1. X-ray diffraction pattern of the TiC_xN_y based coating deposited by IBAMD method at RT

It is known [4] the TiC_xN_y phase lattice parameter is defined a chemical composition of x and y. We can determine a chemical composition of the TiC_xN_y based phase of the 1, 2, 3, 4 coatings by using the lattice parameters (Table 1) received by our X-ray structure analysis (XSA) and the table data about the carbon-nitrogen ratio of the titanium carbide-nitride depending on the lattice parameter [4]. One can see (Table 2) the chemical composition of the TiC_xN_y phase is following hard with the change of the C_2H_2 and N_2 partial pressure ratio. Thus, the $p_{C_2H_2}/p_{N_2}$ ratio is one of basic factor defining a chemical composition of the TiC_xN_y based phase. On the other hand, we can determine a chemical composition by using a values of ratio of the secondary C^+ and N^+ ion currents (Table 1) received with the aid of secondary ion mass spectrometry (SIMS) method due to research of element content along coating profile depth under the Ar^+ ion beam surface sputtering (Fig. 2).

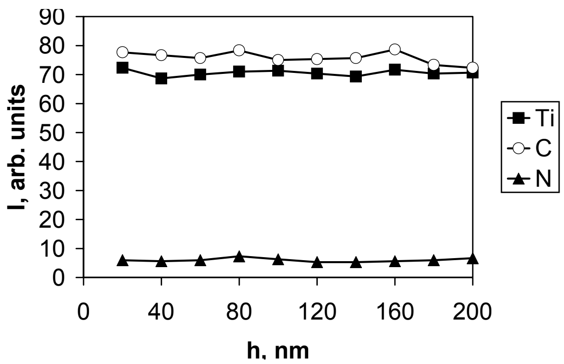

Fig. 2. An element content change with the IBAMD coating profile depth received the SIMS method

If we suppose a sum of the carbon and nitrogen atomic fractions equals 1 that we receive the TiC_xN_y phase chemical composition of the 1, 2, 3, 4 coatings (Table 2) as near to itself received by XSA method vide supra.

Some distinctions of the x and y values received the SIMS method can be stipulated by difference of a sum of the carbon and nitrogen atomic fractions from 1 that can be within $0.33 \le x + y \le 1.04$ [4] depending on experimental conditions.

The mean grain size of the titanium carbide-nitride phase is within 10–26 nm increasing monotonously with reduction of the carbon content (Table 1). The β-Ti_2N phase has constant value of mean grain size equal 5–10 nm for all coatings within a sensitivity of the XSA method. The internal elastic stress magnitude

σ_i reduces with decrease of the carbon content in TiC_xN_y phase (Table 1). The lowest value σ_i is observed for coatings deposited under condition of the ion beam assisting treatment.

The $I_{(111)}/I_{(200)}$ ratio of the X-ray reflection intensities for the TiC_xN_y coatings within the third set of samples (Table 1) is near with 0.75 that has no textured coating on basis the TiC_xN_y phase. The (200) grain-oriented coatings (set of samples 2) were deposited by increase of the carbon content of the titanium carbide-nitride phase with the C_2H_2 and N_2 partial pressures ratio up to $\rho_{C_2H_2} : \rho_{N_2} = 0.52$. The (200) texture of a coating is predominant at the highest carbon content (set of samples 1) (Tables 1, 2). On the contrary the (111) grain-oriented coatings (set of samples 4) were received by means of use of ion beam assisting treatment in process of a magnetron deposition. This type of grain-oriented TiC_xN_y [5] and TiN [6] coatings was observed by deposition under condition of the low partial pressures of reactive gases.

The observed increase of the (200) texture of the TiC_xN_y coatings deposited without use of the IBAMD method with rise of the C_2H_2 and N_2 partial pressures ratio is in accordance with tendency to the observed in [5] increase of the (200) X-ray reflection intensity in coatings on basis the TiC_xN_y phase under condition of rise of the methane reactive gas pressure into a vacuum chamber. Under ion beam treatment a grains of coating grows in this way the most close-packed planes (111) dispose according to normal with the ion beam direction. It is possible condition of essential energy supply for a growth ensuring of the (111) textured grains.

The microhardness measurement of a deposited coatings showed increase from 23 GPa to 40 GPa at rise of the C_2H_2 and N_2 partial pressures ratio (Table 1). It is seen in Table 1 the observed increase of a coating microhardness connected with the carbon content rise into the TiC_xN_y phase and with decrease the mean grain size. This is in accordance with the experimental data [7].

The wear-resistance of the coating (sets of samples 1, 2, 3) deposited without use of the IBAMD method changes no monotonously with rise of the acetylene and nitrogen partial pressures ratio into the working gas mixture of the vacuum chamber. It has the big value due to the low (set of samples 3) and high (set of samples 1) carbon content in the titanium carbide-nitride phase, but it has the little value due to the equal approximately partial pressures of acetylene and nitrogen (Table 1) or the same due to the near about the carbon and nitrogen contents in the TiC_xN_y phase (Table 2). The extreme dependence of a wear-resistance can take place in result of two processes effecting opposite. The first process of the wear-resistance increasing can be due to increase of a coating hardness with rise of the carbon content in the TiC_xN_y phase [7]. The second process of the wear-resistance increasing can be due to decrease the amount of the (200) texture grains in the TiC_xN_y phase. It was shown in [8] the (200) texture grains have a low wear-resistance. Both processes take place with reduction of the carbon content in the TiC_xN_y phase. Thus the competitive effect of these processes can produce the observed extreme change of the coating wear-resistance with the carbon content in the TiC_xN_y phase.

The IBAMD coating have the high content of the most wear-resistant (111) textured grains [8] and the increased microhardness of the TiC_xN_y phase [7] therefore this coating has the highest wear-resistance or the lowest wear rate (Table 1).

4. Conclusions

1. The nanocrystalline coatings with the TiC_xN_y (94–96 p.c.) and β – Ti_2N (4–6 p.c.) phase composition and with the mean grain size within limits from 10 to 25 nm were deposited over the 12H18N10T austenite steel substrates with aid of the DC-magnetron with Ti target at 423 K temperature, 0.1 Pa total pressure of working gas mixture and the C_2H_2 and N_2 reactive gas partial pressures ratio within limits of 0.22–0.61 and by means of the IBAMD method at RT.

2. The TiC_xN_y phase lattice parameter increases monotonously, mean grain size decreases, internal elastic microstress level rises, (200) texture of TiC_xN_y grains appears and increases in value with increase of the C_2H_2 and N_2 partial pressures ratio. In result the microhardness of deposited coatings on basis of TiC_xN_y phase grows incessantly, but the wear-resistance passes through the least value under the about equal of the C_2H_2 and N_2 partial pressures and has the big values under the highest value of $\rho_{C_2H_2}$: p_{N2} and the lowest value of $\rho_{C_2H_2} : \rho_{N_2}$.

3. The change of the TiC_xN_y phase lattice parameter is connected with it chemical composition; the microhardness increase – with rise of the carbon content into the TiC_xN_y phase and reduction of the mean grain size; the wear-resistance change – with effect of the competitive processes stipulated opposite changes of the microhardness and texture of the basic phase.

4. The introduction in the process of a coating deposition of the ion beam assisting treatment made it possible to reduce a deposition temperature up to RT. At the same time it permits to improve a wear-resistance of coatings by means of the more probable growth of the (111) textured grains and decrease the internal elastic microstress level.

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