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CAVITATION EROSION RESISTANCE OF VACUUM-ARC COATINGS BASED ON TiN

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This review presents an examination of various studies investigating the impact of deposition process conditions and structural characteristics of TiN-based vacuum-arc coatings on their ability to withstand cavitation erosion in water. The structural and phase composition of TiN coatings is influenced by two key technological parameters: the nitrogen pressure in the vacuum chamber and the substrate bias potential. However, it has been observed that vacuum-arc alloy coatings such as TiSiN and TiAlYN exhibit notably lower resistance to cavitation erosion. Additionally, research on multilayer Ti-TiN coatings with varying numbers and thickness ratios of layers has not shown an improvement in resistance to cavitation wear when compared to single-layer coatings deposited under optimal conditions. On the other hand, single-phase stoichiometric TiN coatings deposited at a higher nitrogen pressure of 2 Pa and a bias potential of up to -300 V have demonstrated remarkable resistance to cavitation wear. These coatings could be effectively utilized to protect the titanium alloy Ti-6Al-4V against cavitation damage.

INTRODUCTION

The efficient operation of energy and transportation systems, whose equipment operates in conditions close to extreme, requires a significant increase in the resistance of the materials used to the destructive factors acting on them, one of which is cavitation, especially when working in liquids [1, 2]. The resistance of the surface of materials to fracture can be increased using one or both of two fundamentally different methods. The first method is to reduce the conditions for the formation of cavitation, and the second method is to specially treat the surface, including the application of anti-erosion coatings [3]. An analysis of the methods of forming coatings with the required characteristics showed that the use of magnetron or vacuum-arc discharge plasma is the most promising compared to thermodiffusion, detonation, and plasma methods [4, 5]. The main principles of the use of vacuum-arc discharge plasma for coating deposition are described, in particular, in [6] by the staff of the National Science Center "Kharkov Institute of Physics and Technology".

Vacuum-arc nitride coatings are widely used to significantly increase the resistance of materials to destructive factors in various industries from aerospace to nuclear [6]. However, despite their many advantages, vacuum-arc nitride coatings are not protected against degradation and erosion caused by environmental factors such as cavitation [7, 8].

The erosion of vacuum-arc nitride coatings by cavitation is a complex process that has not yet been fully understood. Several factors can influence the erosion rate, such as the size and frequency of vapor cavities, the corrosivity of the medium, and the mechanical properties of the coating itself [9]. Additionally, the mechanisms by which cavitation causes erosion are still under investigation, with some researchers suggesting that the physical impact of shock waves is the dominant factor, while others believe that the corrosive environment plays a more significant role [10, 11].

Despite ongoing research on the erosion of vacuum-arc nitride coatings caused by cavitation, there are already numerous methods available to mitigate its effects [12–17]. Furthermore, studies on the resistance to cavitation erosion of PVD coatings have demonstrated the superior durability of multilayer coatings when compared to single-layer ones [18, 19]. These investigations have revealed that the cavitation erosion resistance of the PVD coating-steel substrate system is influenced not only by the mechanical properties but also by the thermal properties of both the coating and the substrate [20, 21].

Titanium alloys are widely used in aerospace and power engineering due to their low density, high strength, and corrosion resistance [22]. However, their use in power engineering is limited by their low hardness and erosion resistance [23]. The influence of elemental and phase composition, processing methods, and surface modification on the cavitation resistance of titanium alloys has been widely studied [24, 25]. Increasing surface hardness, for example, by nitriding, reduces cavitation erosion of titanium alloys [24]. Nevertheless, the creation of a nitrided layer in titanium alloys with a thickness of more than 10 μm for long-term erosion resistance requires high temperatures (> 800 °C) and a long time, which can lead to a deterioration in the mechanical properties of the entire product [26]. Deposition of protective coatings of sufficient thickness on the surface of a titanium alloy using the vacuum arc method at moderate temperatures (< 500 °C) can solve this problem. Titanium nitride (TiN) coatings are most widely used in industry to improve the performance of cutting tools, as erosion-resistant, biocompatible, etc. [27]. The use of TiN-based coatings for the effective protection of titanium alloy products from cavitation erosion requires studying the effect of deposition conditions, composition, and structural features of these coatings.

The objective of this study is to review and systematize the impact of structural and technological factors in the deposition of TiN-based vacuum-arc coatings on their protective properties against cavitation in water.

1. MATERIALS AND EXPERIMENTAL METHODS

Using a Bulat-type installation, the scheme of which is shown in Fig. 1, and two metal plasma sources, coatings were deposited on samples of titanium alloy (Ti-6Al-4V) and stainless steel (08Cr18Ni10T) at a distance of 200 and 300 mm from the cathode. The temperature of the samples during the deposition of coatings was determined using a chromium-aluminum thermocouple, which was installed in the substrate from the side opposite to the coating at a distance of about 1 mm from its surface. The current of the vacuum arc discharge was varied from 65 to 135 A. A negative potential of 200 V was applied to the samples. The initial pressure in the vacuum chamber was $8\cdot10^{-4}$ Pa. The nitrogen pressure during the deposition of TiN coatings was varied from 0.05 to 3 Pa. The thickness of the deposited coatings was in the range of 10 to 15 μm.

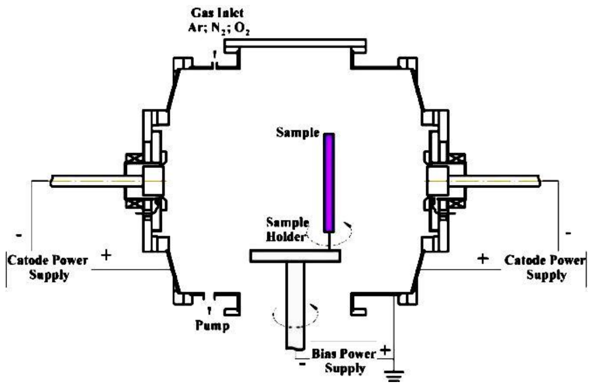


Fig. 1. Scheme of the Bulat-type setup with two metal plasma sources and a planetary sample rotation device

The microhardness of the coatings was measured using a PMT-3 microhardness tester with a Vickers diamond pyramid at a load of 1 N.

The study to determine the resistance of coatings under cavitation was carried out on two ultrasonic devices, the general view of which is shown in Fig. 2. The main difference between these installations is the area of the cavitation zone: in the NSC KIPT design installation, the diameter of this zone is ~ 5 mm, and in the Hielscher-UP400St installation, it is ~ 16 mm.

Fig. 2,a shows a schematic diagram of the NSC KIPT installation, where it can be seen that the bath and vibrator are placed in a soundproof chamber and can be moved relative to each other by a special mechanism. The installation includes a power supply and water cooling system mounted in the center of the chamber. An ultrasonic generator, control and measurement instruments and a control panel are mounted directly under the chamber. This arrangement makes it easy and convenient to carry out experiments. A UZVL-0.4 ultrasonic transducer with a resonant frequency of 20.5...23 kHz and a power of 400 W, driven by a UZG3-0.4 ultrasonic generator, was used as the magnetostrictive vibrator. A set of interchangeable 1X18H10T steel acoustic concentrators was used to increase the amplitude of the vibrations transmitted to the bath. The concentrators had an exponential profile which provided both the required amplitude level (30...45 μm) and durable operation due to insignificant destruction during operation. The diameter of the concentrator at the point of attachment to the magnetostrictor is 65 mm, and the diameter of its radiating surface is 5 mm. Such an elastic transducer is attached to the magnetostrictor by means of a screw connection. We studied plane-parallel samples of rectangular shape 15×15 mm and in the form of discs with a diameter of 20 mm and a thickness of about 5 mm.

Cavitation above the sample surface is produced by a vibrator operating at a frequency of 20 kHz with an oscillation amplitude of up to 140 μm. Fig. 3 shows the voltage oscillograms recorded by a 2×2 mm sensor with a thickness of 6.37 mm [10] placed in the center of the cavitation zone. It can be seen (see Fig. 3,b-d) that in each cycle of the ultrasonic wave the cavitation cavity is closed for several microseconds. Stress peaks are recorded, the magnitude of which depends on the amplitude of the ultrasonic vibrations of the emitter.

Our calculations show that there is a non-linear relationship between these values, as can be seen in Fig. 4.

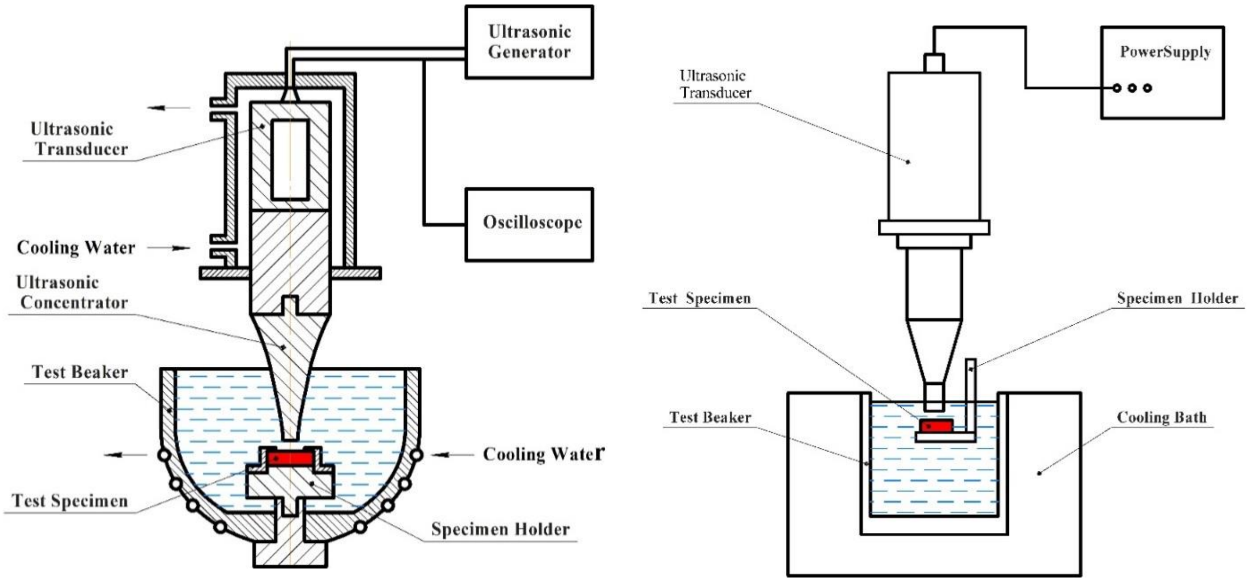
The data in Fig. 4 shows that the average stress amplitude (σ) is related to the vibration amplitude (A) by a ratio:

$$\sigma = cA^{1/3}, \tag{1}$$

where *c* is 200.3 MPa·μm$^{-1/3}$. The experimental points do not differ by more than 5% from the curve reflecting this ratio, and only for A=50 μm does the difference reach 9%. In contrast to symmetrical closure, asymmetrical cavity closure produces microjets up to 10 μm in diameter which induce stresses of the same magnitude in the solid. The magnitude of these stresses can reach 600…700 MPa with a vibrator amplitude of 30...50 μm.

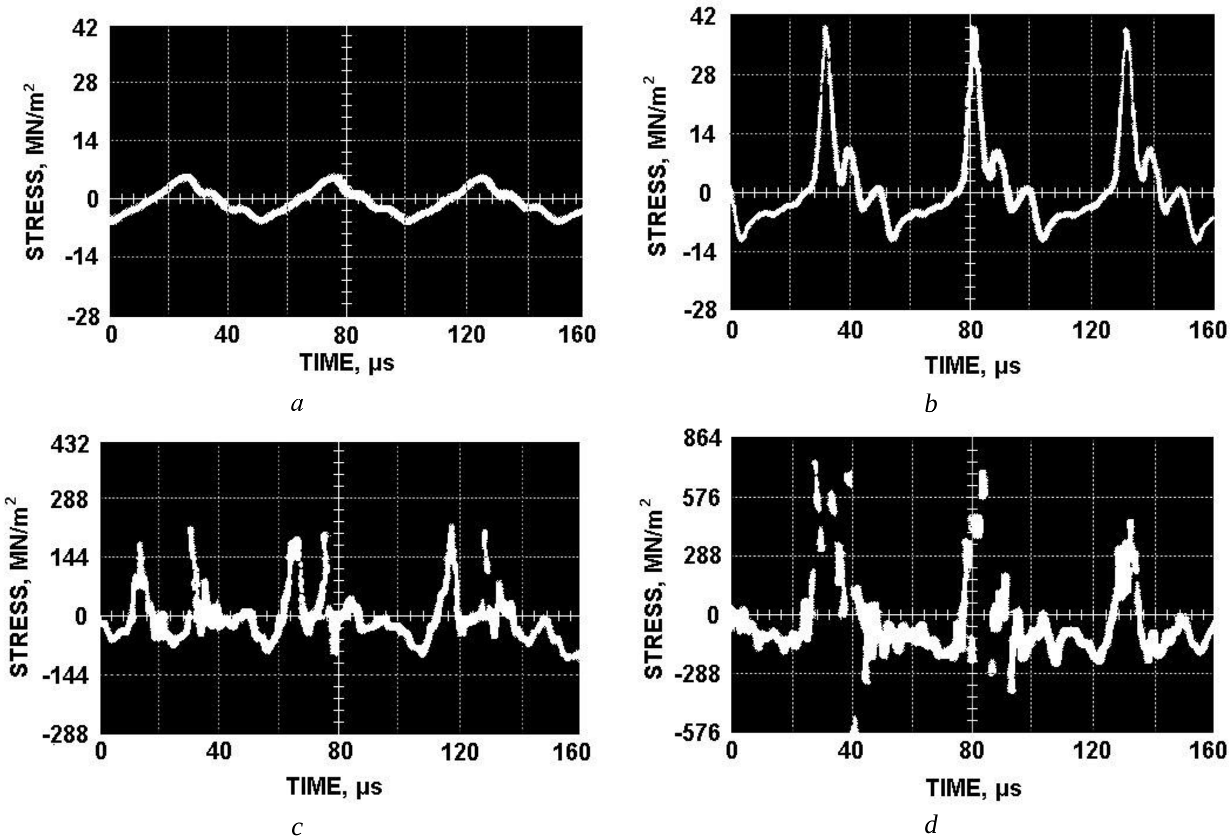
Cavitation tests for comparison were performed in distilled water using a Hielsher-UP400St instrument shown in Fig. 2,b at a temperature of 70 °C, when cavitation wear in water is maximal [25]. The distance from the vibrator to the sample surface was 0.05 mm, the oscillation amplitude was 50% at a frequency of 23.76 kHz and a power of 100 W.

Cavitation erosion of materials and coatings was measured by weight loss of the samples after a fixed test time (mg/h or μm/h). The cavitation erosion resistance (CER) of coatings was determined as the reciprocal of the cavitation erosion value (h/μg).



a *b*

Fig. 2. General view of the test bench and scheme of cavitation zone generation on NSC-KIPT device (a) and Hielscher-UP400St (b)



a *b* *c* *d*

Fig. 3. Oscillograms of the voltage occurring in a quartz sensor during cavitation in distilled water. The oscillation frequency of the vibrator is 20 kHz:
a – low vibrator amplitude, no cavitation;
b–d – cavitation of varying intensity

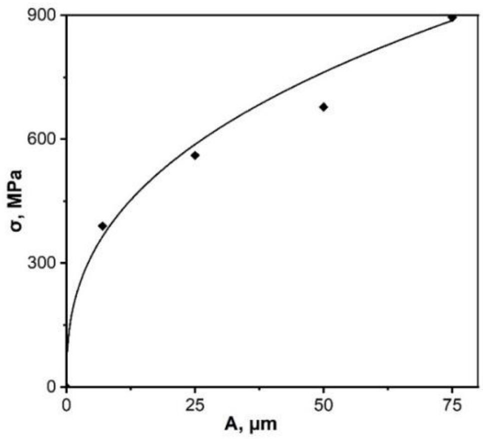


Fig. 4. Dependence of the average stress (σ) in a solid under cavitation on the amplitude (A) of the transmitter oscillations

2. PROPERTIES OF VACUUM ARC TiN COATINGS

Due to the fact that the formation of coatings by vacuum arc discharge occurs as a result of the interaction of the erosion flow from the cathode with the interelectrode medium, followed by the deposition of this flow on substrates, a significant part of the research is devoted to the study of the properties of all the components of the process. Thus, in [6, 28–30], the erosion from the cathode of a stationary vacuum arc was studied. Cathode erosion was studied on an installation with auto-stabilisation and containment of the cathode spot, the diameter of the cylindrical water-cooled cathode was 64 mm [6]. The length of the cathode was 25...40 mm. The erosion coefficient was determined by measuring the mass loss during the arc burning time (t) at a current (I):

$$\chi = \frac{\Delta m}{t \cdot I}. \quad (2)$$

The coefficient χ determines the total losses in the form of ions, neutrals, and macroparticles.

Results of studies on the influence of Ar and N_2 pressure on the cathode erosion coefficient at a current of 110 A and a temperature of 390 and 800 K (1, 2, and 3 respectively).

Fig. 5 shows that increasing the N_2 pressure in the chamber significantly reduces the erosion coefficient of the titanium cathode at both low and relatively high temperatures. The introduction of Ar into the interelectrode space does not significantly change the erosion coefficient. When the vacuum arc discharge current is increased by a factor of 2, χ decreases by a factor of 1.3. The cathode erosion rate increases from 39 μg/K at a cathode temperature of 390 K to 76 μg/K at a temperature of 800 K. The increase in the coefficient χ is mainly due to an increase in liquid metal droplets ejected from the melt zone of the cathode spot and a decrease due to the formation of films of chemical compounds on the cathode surface which are more refractory than VT1-0. Therefore, it is advisable to apply protective coatings with a minimum content of macroparticles at a nitrogen pressure higher than 0.1 Pa. The study of the chaotic motion speed of the cathode spot showed that it varies from 1 to 10 m/s, which is significantly lower compared to pulsed and quasi-stationary discharges.

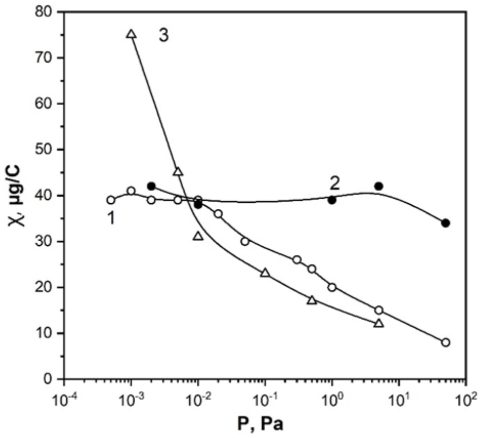


Fig. 5. Dependence of the erosion coefficient (χ, μg/K) on the pressure of nitrogen (1, 3) and argon (2). The cathode temperature is 390 (1, 2) and 800 K (3) [adapted from 6]

One of the components of the erosive flux coming from a titanium cathode that influences the properties of the resulting coatings is the ions component. Quantitatively, the ions of different charge are Ti^+ – 27%; Ti^{+2} – 67%; Ti^{+3} – 6% at a current of 100 A and a pressure of $3 \cdot 10^{-4}$ Pa [6]. The charge composition of the plasma changes with increasing gas (nitrogen) pressure as a result of recharging processes. In the pressure range of 1…10 Pa, the activation mechanism (excitation and ionisation) of metal ions and atoms (Ti) has been observed [31]. Excited atoms and ions of the cathode material Ti^*, Ti^+, Ti^{2+}, and the working gas N_2^*, N_2^+ are formed in the vacuum arc discharge plasma. The synthesis of TiN coatings on a substrate takes place under conditions of intense ion bombardment of the deposited coating surface by metal and gas ions, so the substrate potential has a significant effect on its temperature and on the elemental and phase composition of the coating. The substrate potential and its temperature determine the level of internal stresses in the coating [32], which can reach values of up to 8 GPa. Internal stresses above a certain critical value in the substrate-coating system can significantly reduce the cavitation resistance of the material.

Phase composition measurements showed that the coatings have different phase compositions depending on the nitrogen pressure in the vacuum chamber. Thus, at a pressure of less than 10^{-2} Pa, the composition of the coating corresponds to α-Ti + Ti_2N, at $P \geq 6.6 \cdot 10^{-2}$ Pa, TiN + α-Ti, and at $P \geq 0.3$ Pa, only the TiN phase with a lattice parameter of 0.4244…0.4237 nm is detected, which correlates with the maximum of nitrogen molecules in the AΣ state. The stoichiometric composition of the TiN layers and the corresponding lattice parameter are observed at P ~ 0.3 Pa, and the presence of an axial texture [111] along the normal to the surface can be noted. From the point of view of the use of the coatings, the structure obtained is optimal. Accordingly, we measured the microhardness and fracture rate of these coatings under cavitation. Fig. 6 shows typical kinetic curves of the cavitation erosion of titanium coatings as a function of the nitrogen pressure in the vacuum chamber.

The data obtained show that the erosion rate is higher in the interval up to 1.8 ks compared to the interval greater than 1.8 ks. The effect of the cavitation medium (water or 3% NaCl solution) on the erosion rate is insignificant (curves 3 and 5).

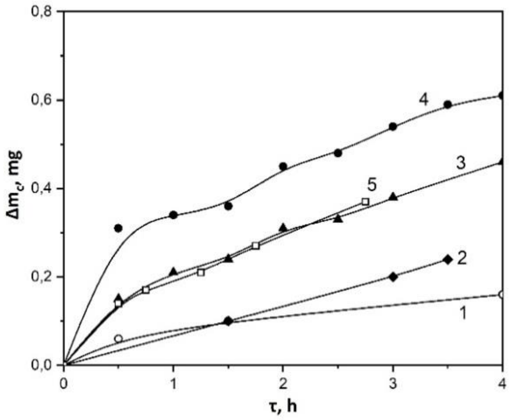


Fig. 6. Time dependence of weight losses of coatings under the influence of cavitation: 1 – P = 0.3 Pa; 2 – 0.9 Pa; 3, 5 – 0.07 Pa; 4 – 0.1 Pa; 1, 2, 4 – cavitation in water; 5 – cavitation in 3% NaCl

From the kinetic curves shown in Fig. 7, the destruction rates of the coatings obtained at different formation parameters were determined and their microhardness was measured. The microhardness of the TiN coatings is in the range of 18…39 GPa (see Fig. 7).

The data in Fig. 7 shows that as the microhardness increases, the erosion rate of TiN coatings increases exponentially:

$$V_C = 0.10445 + 0.00319 \cdot \exp\left(0.1054 \cdot H_\mu\right). \quad (3)$$

The dependence of the microhardness and the cavitation erosion resistance (CER) of the coatings on the nitrogen pressure in the chamber during TiN formation at different discharge currents is shown in Fig. 8.

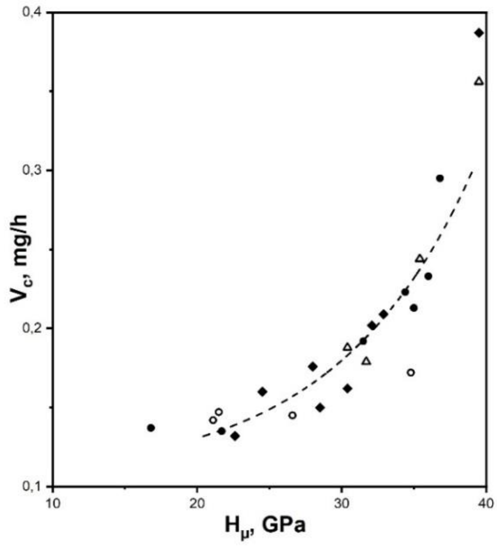


Fig. 7. Relationship between cavitation erosion rate of coatings (V_c) and microhardness (H_μ)

The data obtained show that as the nitrogen pressure increases, CER and $H_\mu^в$ change in opposite directions. In the range of P from 0.01 to 0.1 Pa, the cavitation resistance is minimal at the maximum values of microhardness, and in the range of 0.3...0.6 Pa, the pattern of change of these values is opposite.

The obtained dependence of CER and $H_\mu^в$ on nitrogen pressure (P) is related to the structural phase state of the coatings: up to P < 0.01 Pa, coatings are formed which are a solid solution of the embedding atoms in α-Ti, in the range from 0.01 to 0.1 the coating changes to α-Ti + Ti_2N + TiN, and then to TiN of stoichiometric composition, at which H_μ has a maximum value.

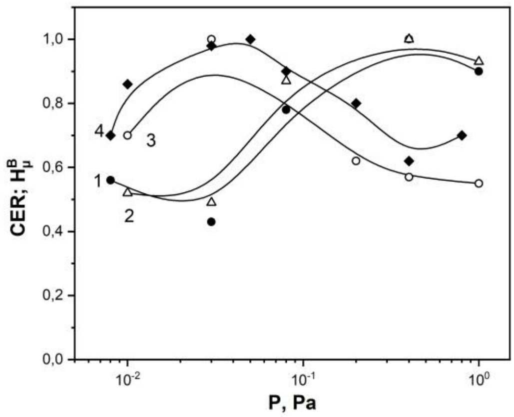


Fig. 8. Relationship between cavitation resistance ($Z_m^в$) and microhardness ($H_\mu^в$) of coatings for different values of nitrogen pressure in a vacuum chamber. The index "B" means relative to the maximum value: 1, 4 – at I_d = 200 A, U_b = 200 V; 2, 3 – I_d = 65 A, U_b = 200 V; 1, 2 – CER; 3, 4 – $H_\mu^в$

The properties of TiN coatings during their deposition under the conditions of simultaneous operation of a vacuum arc discharge and an RF power source of the substrate have been studied as a function of nitrogen pressure [33].

It has been found that the microhardness of coatings obtained with an additional RF field on the substrate is higher than that formed by a standard vacuum arc discharge and is equal only at nitrogen pressures above 1 Pa (I_d = 100 A; U_b = -100 V). The abrasive wear of RF field coatings obtained in the N_2 pressure range of 0.1 to 0.5 Pa is 1.25...2 times lower than that of coatings without RF field. The wear resistance of coatings without an RF field under air-abrasive (AE) and cavitation (CE) erosion is shown in Table 1.

The table shows that the values of the incremental stability divided by the maximum values vary in a symbiotic way with the nitrogen pressure under cavitation and air-abrasive blowing. We observe an increase in their stability up to a maximum value reached at a pressure of 0.3 Pa, followed by a decrease with a further increase in nitrogen pressure. At the same time, the position of its maximum does not coincide with the relative maximum for microhardness.

Table 1
Resistance to air-abrasive erosion (AER) and cavitation erosion (CER), microhardness (H_v) of TiN coatings deposited at the RF potential of the substrate as a function of nitrogen pressure

Type of erosion	Nitrogen pressure, Pa				
	$1·10^{-2}$	$2·10^{-2}$	0,1	0,3	0,9
AER, a.u.	0.032	0.11	0.3	1	0.43
CER, a.u.	0.57	0.42	0.8	1	0.96
H_v, a.u.	0.765	1	0.6	0.63	0.61

Thus, the addition of an RF power source to the substrate does not significantly increase the resistance of TiN coatings to cavitation wear.

The use of elevated nitrogen pressure during the deposition of TiN coatings not only reduces defects in the coatings due to the reduced number of macroparticles generated at the cathode, but also results in an increase in the deposition rate of these coatings in the range of nitrogen pressures from 2 to 10 Pa [34]. This may be due to a change in the spatial distribution of condensed particles in the coating deposition area. The coatings obtained at elevated nitrogen pressure are characterised by high mechanical properties: nanohardness of 25 to 28 GPa and Young's modulus of 450...500 GPa.

In [35] the cavitation resistance in distilled water of Ti-6Al-4V alloy with TiN and CrN vacuum arc coatings deposited at a vacuum arc current of 100 A and an elevated nitrogen pressure in the range of 1.5...2 Pa was investigated. A constant negative bias of 300 V was applied to the samples during the deposition process. It has been shown that coatings with high mechanical properties significantly reduce cavitation wear of the alloy, prolong the incubation period of cavitation erosion and reduce mass loss. Preliminary ion plasma nitriding of a titanium alloy results in the formation of a hard transition layer under the coating, which improves the adhesion of the coating to the metal, thereby increasing its resistance to cavitation erosion.

Fig. 9 shows the relationship between cavitation exposure time and sample weight loss. Samples with the same coatings were tested on two different cavitation testers. This was done to validate the approach to measuring cavitation wear of coated materials.

As can be seen from Fig. 9, TiN and CrN coatings with a thickness of 3…4 µm prolonged the incubation time before fracture by 3…4 h and reduced the mass loss of the specimens by a factor of seven compared to the Ti-6Al-4V alloy over the same time period of the test. However, the application of a 10 µm thick CrN coating to the surface of the titanium alloy had no effect on the rate of sample mass loss compared to the uncoated alloy. Preliminary ion plasma nitriding of the titanium alloy and deposition of 10 µm thick TiN coatings (see Fig. 9, TiN+N_2) significantly reduced the erosion rate of the Ti-6Al-4V alloy. Furthermore, cavitation erosion measurements on two different machines clearly confirm the result.

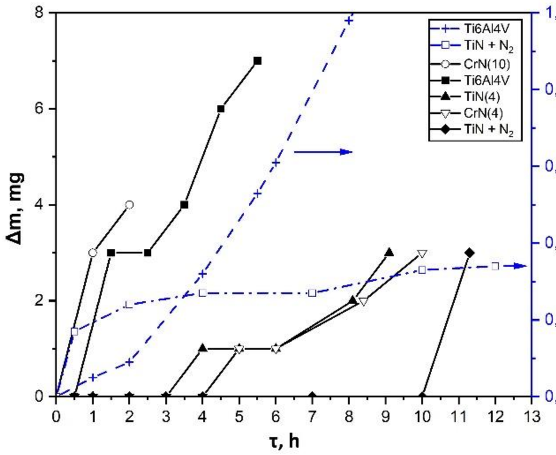


Fig. 9. Cavitation erosion of Ti-6Al-4V alloy with coatings. On the left the measurement was carried out on a Hielscher UP400St [35], on the right on the NSC KIPT. The thickness of the coatings is given in brackets

The high protective properties of TiN coatings deposited at an elevated nitrogen pressure of 1...3 Pa allowed us to select and justify the composition and conditions for the synthesis of the optimal coating for strengthening steam turbine blades made of Ti-6Al-4V alloy [36]. The parameters of the coating deposition process on blade models were worked out and a pilot technological process for the deposition of coatings resistant to cavitation wear was created. Samples of VT6 (Ti-6Al-4V) alloy with selected coatings were tested under simulated conditions close to operational conditions. The deposition rate of the TiN coating on the blade mock-up with dimensions up to 1300 mm and weight up to 30 kg was ~ 10 µm/h.

It is known [37] that an important deposition parameter that can influence the number and size of droplets (defects) in coatings is the bias voltage on the substrate during deposition. In [38] the effect of a high constant substrate bias voltage ranging from 300 to 1300 V on the structure and cavitation resistance of titanium nitride coatings deposited at a nitrogen pressure of 2 Pa was investigated. The best cavitation wear resistance was observed for coatings with the preferential orientation (111) deposited at -300 V. When the bias voltage is increased to -800 V, the cavitation wear rate of TiN coatings increases exponentially with voltage. This means that the most dynamic wear is characteristic of the predominant orientation (220) coatings obtained at a bias voltage ≥ 800 V.

Based on the above results of studies of the effect of deposition parameters on the cavitation erosion of TiN coatings, it is found that coatings deposited at elevated nitrogen pressure (> 1 Pa) and a constant bias voltage of up to -300 V are the most resistant.

3. PROPERTIES OF TiN COATINGS ALLOYED WITH Si AND Al

Multicomponent coatings based on different metallic and non-metallic elements combine the advantages of the individual components, leading to further improvements in coating properties [39]. Alloying additives such as Cr and Y significantly improve oxidation resistance, Zr and V improve wear resistance

[39], while Al and Si increase the hardness and thermal stability of TiN coatings [40].

Research shows that the mechanism of cavitation erosion of TiAlN and AlTiN magnetron coatings depends on brittleness, which may be related to fatigue processes that cause film fracture and internal decohesion as the flakes split, leading to coating delamination and substrate exposure [41]. Compared to the stainless steel reference sample, PVD coatings exhibit excellent resistance to sliding and cavitation erosion. However, for NiCrAlTi magnetron multicomponent coatings, the introduction of nitrogen showed a negative effect on the resistance to cavitation erosion [42].

We have previously shown that vacuum arc titanium and alloy coatings of the TiAl and TiNi systems can be used to protect steel products from cavitation wear [43]. To determine the possibility of increasing the resistance of TiN coatings under the influence of cavitation, their properties were studied when doped with Si, Al, and Y [44–47]. The "Bulat" installation was used with cathodes of the following composition: VT1-0, Ti-Si, Ti-Al-Si, Ti-Al-Y for deposition of the TiSiN and TiAlYN coatings. The arc current was 100 A, the negative bias potential was 100…200 V, and the nitrogen pressure in the chamber was 0.09…0.16 Pa. The sum of the concentrations of titanium and silicon (aluminum, yttrium) in weight % was taken as 100%. Data on the mass losses of TiSiN coatings under the influence of cavitation are shown in Fig. 10 [46].

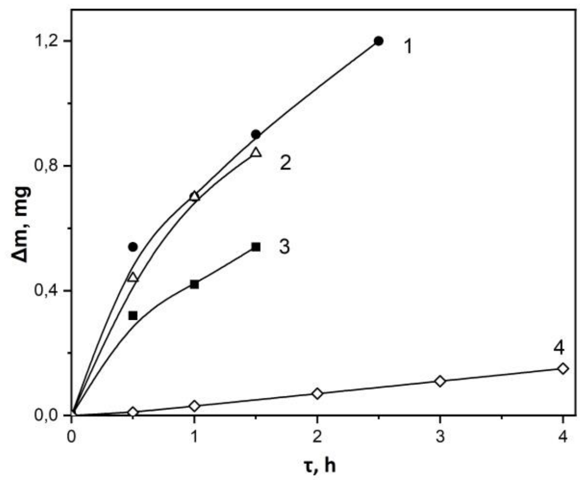


Fig. 10. Kinetic curves of the erosion of TiSiN coatings under the action of cavitation: 1 – (Ti-2.4Si)N; 2 – (Ti-1.8Si)N; 3 – (Ti-1.0Si)N; 4 – TiN [46]

The kinetic curves demonstrate that the doping of TiN vacuum-arc coatings with silicon in the range from 1 to 2.4 wt.% significantly increases the mass loss of samples (see Fig. 10).

Table 2 shows that the addition of Si to the coatings results in a 1.07-fold increase in microhardness, a 1.4-fold increase in strength, and a 4.5-fold decrease in cavitation resistance.

The presence of high internal stresses in TiSiN coatings can limit the ultimate thickness of this films due to the occurrence of surface delamination ("shooting") [46] and reduce cavitation resistance.

The results of the study of the properties of TiN coatings doped with Al and Y are presented in Table 3 [47].

Table 2

Effect of Si concentration on the mechanical properties of TiSiN coatings [46]

Coating	H_μ, GPa	E, GPa	H^3/E^2, GPa	CER, a.u.
TiN	33.3	486	0.16	1
(Ti-1.0Si)N	34.5	445	0.21	0.274
(Ti-1.8Si)N	35	490	0.18	0.174
(Ti-2.4Si)N	35.7	481	0.20	0.182

Analysis of the data in Table 3 shows that Ti-Al-Y-N coatings have a 2-fold lower resistance to cavitation erosion than TiN and a slightly higher resistance than TiSiN coatings. Comparison of the fractographic data for the coatings shows that the higher resistance to cavitation is inherent in coatings with a denser columnar structure created under the influence of some compressive stresses.

Table 3

Effect of Al and Y concentration on the mechanical properties of Ti-Al-Y-N coatings [47]

Coatings	H_μ, GPa	E, GPa	H^3/E^2, GPa	CER, a.u.
TiN	33.3	486	0.16	1
Ti-26Al-0.5Y	37.1	487	0.22	0.56
Ti-22Al-3.5Y	35.1	440	0.22	0.27
Ti-20Al-4.5Y	31.8	394	0.21	0.42

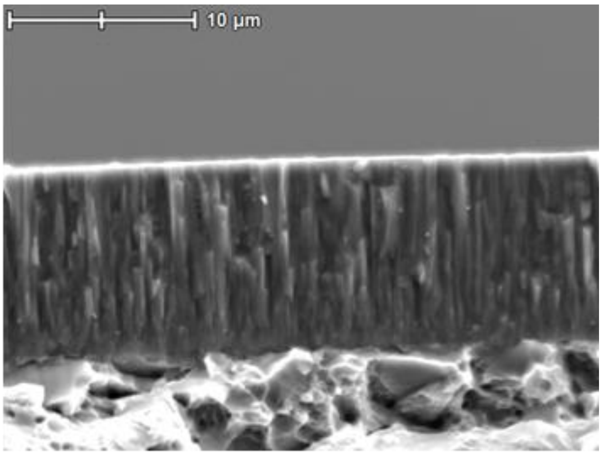
The destruction of such a structure occurs with an increase in the amount of yttrium, causing a corresponding decrease in its cavitation resistance. This explains the higher stability of the TiN coating without impurities [47].

4. MULTILAYER Ti-TiN COATINGS

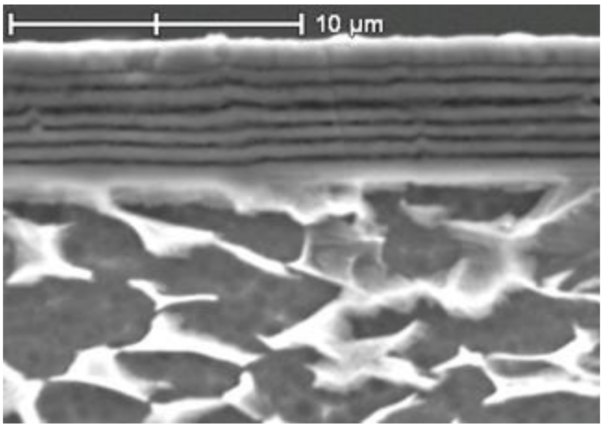
The results of studies on magnetron deposited coatings show excellent adhesion and high erosion resistance of the CrAlYN/CrN multilayer coating (the erosion rate is 14 times lower than that of the Ti-6Al-4V substrate) [48]. In [18] multilayer Ti/TiN coatings (4, 12, and 40 layers) were deposited on the surface of X6CrNiTi18-10 steel by vacuum arc deposition PVD. The coated samples showed better resistance to cavitation erosion than uncoated stainless steel. As the number of layers increased, the cavitation erosion resistance of the multilayer Ti/TiN coating was lower. It has been shown experimentally that a Ti/TiN coating with a number of layers of 4 provides the best protection against cavitation erosion [18].

In [49] we carried out comparative studies of the cavitation resistance of single layer TiN and multilayer Ti/TiN coatings. The transverse fracture structures of these coatings are shown in Fig. 12. A columnar structure is clearly seen in the TiN coating (see Fig. 11,a). The width of the columns is in the sub-micron range. There are no cracks or through-holes. In the multilayer coating, the columnar structure is not clearly visible (see Fig. 11,b), the width of a titanium layer is 0.2 μm and the width of the titanium nitride layer is 1 μm. The top layer in the coating is titanium nitride.

The nanohardness and Young's modulus of these coatings were 31 and 438 GPa, 29 and 380 GPa respectively. The use of a multilayer Ti/TiN structure with layers of relatively soft titanium resulted in a reduction of the Young's modulus to 380 GPa while maintaining a high hardness of 29 GPa. This in turn results in a higher H^3/E^2 ratio of 0.17 GPa compared to 0.16 GPa for a single layer coating. Despite the higher H^3/E^2 coefficient, the cavitation resistance of the multilayer coating is only 0.25 of that of the single-layer TiN coating [45]. This may be due to the sub-optimal choice of the ratio of the thickness of the metal and nitride layers.



a



b

Fig 11. SEM images of cross sections of TiN coatings (a) and Ti/TiN×6 multilayer coatings (b) on Ti-6Al-4V alloy

In [49] an investigation was made to study the effect of the ratio of the thickness of Ti and TiN layers of 1:10, 1:3, and 1:1. The coatings were deposited at a pressure of $2.7 \cdot 10^{-3}$ and $6.7 \cdot 10^{-1}$ Pa for Ti and TiN, respectively. Coatings with different thicknesses and a total number of 10 to 30 layers were also deposited. Table 4 shows the main characteristics of the multilayer Ti-TiN coatings.

It can be seen from Table 4 that some coatings increase the cavitation resistance by a small amount.

A number of studies have also been carried out with other systems and metals forming multilayer coatings [48]. The erosion rate of multilayer vacuum arc coatings as a function of microhardness is shown in Fig. 12. The erosion rate of coatings under the action of an abrasive corresponds to curve A and the erosion rate under the action of cavitation corresponds to curve B.

Table 4

Mechanical properties of Ti-TiN coatings as a function of the number of layers n [49]

Thickness ratio, Ti:TiN	H_μ, GPa	H^3/E^2, GPa	n	CER, a.u.
1:10	36	0.435	20	1.5
1:3	25	0.200	7	0.76
1:1	24	0.204	30	0.77

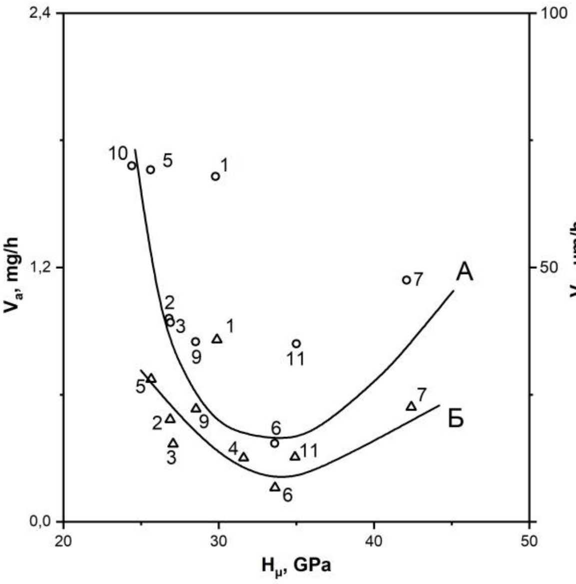


Fig. 12. Dependence of the erosion rate under the action of abrasive (V_a) and under the action of cavitation (V_c) in the depth of the erosion zone. Curve A – V_a; curve B – V_c.
The markings correspond to the coatings:
1 – Zr-ZrN-Zr; 2 – Ti-TiN-Ti;
3 – Cr-CrN-Cr; 4 – Mo-MoN-Mo; 5 – Cr-Cr-Cr;
6 – TiMo-TiMoN-TiMo; 7 – ZrCr- ZrCrN-ZrCr;
8 – TiCr-TiCrN-TiCr; 9 – TiZr-TiZrN-TiZr;
10 – ZrMo-ZrMoN-ZrMo;
11 – MoTiAlV-MoTiAlVN- MoTiAlV [49]

The erosion rate under cavitation decreases for samples with a microhardness (H_μ) of 20 to 32 GPa. The maximum resistance (minimum V_a or V_c) is provided by coatings containing Ti, Mo and their nitrides. However, the results of [49] do not demonstrate the superiority of multilayer coatings over single layer TiN coatings in terms of cavitation resistance.

A comparison of the resistance to cavitation erosion of TiN-based coatings as a function of their microhardness is shown in Fig. 13. The cavitation wear data have been obtained over many years of research at the same facility (see Fig. 2,a) and are compared with the titanium alloy Ti-6Al-4V. Additional alloying of TiN coatings with elements such as Si, Al, and Y or the formation of multilayer coatings does not significantly increase their cavitation resistance.

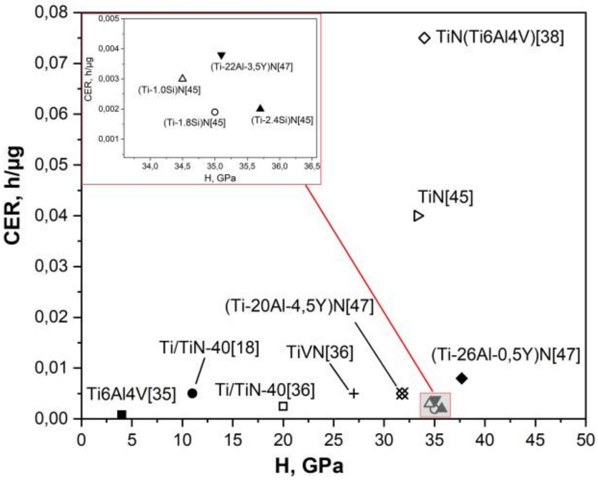


Fig. 13. Cavitation erosion resistance (CER) of TiN-based coatings as a function of their microhardness

Thus, of all the vacuum arc coatings studied, TiN coatings deposited at elevated nitrogen pressure and a substrate bias potential of -300 V are the most resistant to cavitation erosion in comparison to the Ti-6Al-4V titanium alloy [35].

CONCLUSIONS

The influence of technological conditions of deposition and structural features of TiN-based vacuum arc coatings deposited without plasma filtration of macroparticles on their protective properties under the influence of cavitation in water is reviewed.

It has been shown that the main technological conditions affecting the cavitation resistance of TiN coatings are the nitrogen pressure in the vacuum chamber and the substrate bias potential. Single phase stoichiometric TiN coatings deposited at a nitrogen pressure of > 0.3 Pa and a bias potential of -100...-300 V have the highest resistance to cavitation wear. The use of an additional RF power source to the substrate does not significantly increase the resistance of TiN coatings to cavitation wear.

Additional doping of the TiN system with elements such as Si, Al, and Y leads, under the formation conditions studied by the authors, to the synthesis of TiSiN and TiAlYN coatings whose cavitation resistance is 5...10 times lower than that of unalloyed coatings.

The study of multilayer Ti-TiN coatings with different numbers and thickness ratios of layers did not show any significant increase in cavitation wear resistance compared to single-layer coatings deposited under optimum conditions.

Further research to improve the cavitation wear resistance of TiN coatings may be aimed at identifying the optimum coating thickness to ensure the required service life of specific products under cavitation.

ACKNOWLEDGEMENTS

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СТІЙКІСТЬ ДО КАВІТАЦІЙНОЇ ЕРОЗІЇ ВАКУУМНО-ДУГОВИХ ПОКРИТТІВ НА ОСНОВІ TiN

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Проведено огляд досліджень по впливу технологічних умов осадження та структурних особливостей вакуумно-дугових покриттів на основі TiN на їх стійкість до кавітаційної ерозії у воді. Технологічні параметри, що визначають структурно-фазовий склад покриттів TiN, є тиск азоту у вакуумній камері та потенціал зміщення підкладки. Вакуумно-дугові складнолеговані покриття TiSiN та TiAlYN, що отримані у досліджених умовах формування, мають значно меншу стійкість до кавітаційної ерозії. Дослідження багатошарових покриттів Ti-TiN з різною кількістю та співвідношенням товщини шарів не виявили збільшення стійкості до кавітаційного зносу у порівнянні з одношаровими покриттями, осадженими за оптимальних умов. Високу стійкість до кавітаційного зносу мають однофазні стехіометричні покриття TiN, осаджені при підвищеному тиску азоту 2 Па, та потенціалі зміщення до -300 В, які можна використовувати для захисту титанового сплаву Ti-6Al-4V.