RESISTANCE OF TITANIUM ALLOYS TO CAVITATION WEAR

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The wear rate of titanium alloys VT1-0, TC5, VT6, VT14, OT4 under the action of microshocks due to cavitation, which is created in distilled water under the surface of the ultrasonic wave emitter, were determined. It was found that the increase in hardness and improvement of cavitation wear resistancefor these alloys depends on the alloying elements, and is also increased after heat treatment and ion-plasma modification of the sample surface. Although no unambiguous correlation was found between the structural class of the alloys and their cavitation wear. Due to ion-plasma modification of alloys, the cavitation wear resistanceis increased by several times, in particular, the VT6 alloy by 3 times. The phase composition of the samples before and after ion-plasma modification was studied and it was found that alloy resistance to cavitation significantly depends on it.

INTRODUCTION

Due to the fact that titanium alloys have low specific weight, high specific strength, and heat and corrosion resistance, their use for the manufacture of parts for various equipment has increased significantly in recent decades [1, 2]. Titanium has two polymorphic modifications: a-Ti with a hexagonal close-packed lattice and high-temperature modification β -Ti with a body-centered cubic lattice. The structure and mechanical properties of the alloy significantly depend on the content of alloying elements, which mainly affect the phase transformations associated with titanium polymorphism [3]. Doped titanium alloys are a promising material for turbine blades and pumps operating under difficult operating conditions, in contact with high-speed microparticle flows, fluid jets, cavitation and liquid droplets moving at speeds greater than 600 m/s [4]. At the same time, the microshock load of the alloy surface is realized, which is characterized by locality, stochasticity, short-term action, significant stresses that can reach the limit of strength of the metal [5].

Increasing the resistance to cavitation and erosion fracture of titanium alloys contributes to increasing the microhardness of its surface [6–8]. This is achieved by doping alloys with other elements, such as Mo or Nb [9]. However, their behavior under the influence of cavitation (microshock load) is still insufficiently studied. The service life and reliability of the equipment are reduced due to the possibility of significant cavitation erosion of the blade surface, which makes it relevant to conduct experimental comparative studies on the erosion resistance of titanium alloys [10].

One of the effective methods to improve the functional properties of titanium alloys is to modify their surface by nitriding, ion-plasma treatment or ion implantation [11-20].

In this paper, the resistance to wear under the action of cavitation for titanium alloys belonging to different structural classes before and after modification of their surface by ion-plasma treatment is studied.

MATERIALS AND EXPERIMENTAL TECHNIQUE

Samples of titanium alloys, the composition of which is similar to the standard GOST 19807-91 were studied. The samples are presented in Table 1.

The samples had the following geometric parameters: disks with the diameter of 18 mm and thickness of 3 mm. In terms of phase composition, VT1-0 is a single-phase α -alloy, and other alloys have a more complex structure, in particular, VT6 has the structure of $(\alpha+\beta)$ -alloy doped with α -stabilizer – aluminum and β -stabilizer – vanadium. VT14 – is an $(\alpha+\beta)$ – alloy additionally doped with molybdenum.

The phase composition was studied using the method of structural analysis on a DRON-3 diffractometer in copper radiation using an active absorption filter (λ (Cu-K α) = 0.154178 nm).

Annealing of samples from VT1-0 alloy was performed in vacuum (10^{-4} Pa) at the temperature of 500 °C for 3 h and irradiated with argon ions by 10 keV and the dose of $1.4 \cdot 10^{18} \text{ cm}^{-2}$. Part of the samples without heat treatment was subjected to ~ 8.5% cold deformation by pressure on the press. Ion-plasma treatment of the samples was performed on a "Bulat-6"type installation at the initial pressure of $1 \cdot 10^{-3}$ Pa and operating pressure of nitrogen and argon mixture of approximately 0.3 Pa. Before ion-plasma modification, the surface of the samples was treated with ions of cathode material (Ti 99.9%) at the negative potential of the sample of 1.2 kV. The ion-plasma modification process was performed at the sample temperature of 650 °C for 15 min. The distance between the cathode and samples was 250 mm. The thickness of the modified layer on the transverse sections was determined using an optical microscope. A number of mechanical characteristics, in particular, hardness and nanohardness of the samples, was studied by the method of nanoindentation using the Nano Indenter G200 at theindenter depth of 500 nm [21] and microhardness tester PMT-3.

Table 1

| | Mass fraction, wt.% | | | | | | | | | | | |
|---------|---------------------|--------|--------|--------|--------|------|------|------|-------|------|------|------------------|
| Marking | Ti | Al | V | Mo | Zr | Si | Fe | 0 | Н | N | С | Other impurities |
| VT1-0 | bal. | _ | _ | - | _ | 0.10 | 0.25 | 0.20 | 0.01 | 0.04 | 0.07 | 0.30 |
| TS5 | | 4.86.2 | 1.52.5 | - | 1.52.5 | 0.15 | 0.30 | 0.15 | 0.01 | 0.05 | 0.10 | 0.30 |
| VT6 | | 5.36.8 | 3.55.3 | - | 0.30 | 0.10 | 0.60 | 0.20 | 0.015 | 0.05 | 0.10 | 0.30 |
| OT4 | | 3.55 | _ | - | 0.30 | 0.12 | 0.30 | 0.15 | 0.012 | 0.05 | 0.10 | 0.30 |
| VT14 | | 3.56.3 | 0.91.9 | 2.53.8 | 0.30 | 0.15 | 0.25 | 0.15 | 0.015 | 0.05 | 0.10 | 0.30 |

The chemical composition of titanium alloys

The samples wear under the action of cavitation was measured using the installation described in [22]. The scheme of the main element for the creation of the cavitation zone is shown in Fig. 1.



Fig. 1. Schematic diagram of the experimental stand for cavitation

The cavitation zone was built under the end surface of the exponential profile concentrator, which is connected to the magnetostrictive transducer, to which signals from the generator are sent. The samples were placed at the distance of 0.55 mm from the end surface of the concentrator in the cavitation zone. The amplitude of oscillations for the concentrator end surface was (30 ± 2) µm, and the frequency was 20 kHz. The weight loss of the samples, which occurs due to their erosion under the action of cavitation, was measured by the gravimetric method with the accuracy of ±0.015 mg. In accordance with the obtained data, kinetic curves were built. Due to these curves, the average rate of sample fracture (V_m) was determined by dividing the weight losses Δm by the value of the exposure time for the sample under cavitation (t). The average linear fracture rate (V_h) in the depth of the sample was also determined.

EXPERIMENTAL RESULTS

The measurement results on the dependence of wearamount (Δm) for the samples VT1-0 on cavitation time (t) are presented in Fig. 2. The samples corresponding in composition to GOST 19807, as well

as the samples after heat treatment and the action of high-energy flows of the charged particles were studied. In accordance with the obtained data, the average rate of alloy fracture in the time interval up to 8 h was determined. In Fig. 2, it is shown that heat treatment of VT1-0 at the temperature of 500 °C for 3 h does not significantly change the wearrate in comparison with the heat-treated sample (curve 1, 2), although the wear rate during the first hour is slightly lower. At the simultaneous action of the temperature and streams of argon ions with the energy of 10 keV at the dose of $1.4 \cdot 10^{18}$ cm⁻², the wear rate is decreased by 1.3 times. At the irradiation by nitrogen ions, the wear rate is decreased by 2.5 times. It is shown that alloy resistance to wear can be increased by its doping with other elements, as well as by increasing the hardness of its surface. It is known [23] that titanium nitride with the hardness higher than the cathode material is formed on the surface of the arc discharge cathode in nitrogen atmosphere.



Fig. 2. Dependence of wear (Δm) for the samples VT1-0 on the cavitation time (t): 1 – initial; 2 – annealed at 500 °C; 3 – annealed and irradiated with Ar ions;
4 – cathode surface (VT1-0) after use in vacuum-arc discharge at 0.1 Pa N₂

The results of the influence, in particular, of VT1-0 (1) doping with Al, Zr, Mo, V (see Table 1) and their subsequent modification on the erosion value under the action of cavitation are presented in Fig. 3.



Fig. 3. Dependence of the average depth of erosion for titanium alloys on the cavitation time:
1 - VT1-0; 2 - TC5; 3 - VT6; 4 - VT14; 5 - OT4;
6-9 - after modification of VT6 and VT14 samples (Table 2)

In Fig. 3, it is shown that both doping and additional modification of doped samples change the course of kinetic curves characterizing the cavitation wear of the samples. Curves 6-8 are the erosion of samples from the modified alloy VT6: 6 - additionally doped with molybdenum in the amount of 1.9 wt.%; 7 – deformed by 8.5%; 8 – after ion-plasma treatment. Curve 9 is the erosion of VT14 alloy after heat treatment. In accordance with Fig. 3, the average wear rates of the samples are calculated. The results are shown in Fig. 4.

VT1-0 alloy has the highest wear rate, which is not changed during three hours of cavitation and is equal to $4 \mu m/h$. Wear of doped and modified titanium alloys



Fig. 4. Average wear rates of samples from different titanium alloys (see Table 2) depending on the cavitation time

occurs at a lower rate. The wear rate for the best of them is 1 μ m/h and less even at ten hours of cavitation.

In Table 2 the mechanical properties of the studied alloys and their resistance to cavitation wear are shown in relation to VT1-0 alloy. In accordance with data analysis in Table 2, adding Al, V, Mo, Zr in different ratios (see Table 1) into the composition of VT1-0 increases the resistance to wear caused by cavitation by 4...5 times (see Table 2, item 1–5). Due to further modification of the samples, the wear resistance is further increased, in particular, VT-6 (item 3) doping with molybdenum – by 1.55 times (item 6), deformation of VT-6 samples by 8.5% - 1.87 times (item 7), ionplasma modification of VT14 (item 4) – by 2.8 times (item 9).

Table 2

| Alloy | VT1-0 | VT6 | VT14 | TC5 | OT4 | VT6+Mo | VT6+deform | VT6+IPM | VT14+heat treatm. |
|--------------------------|-------|-----|------|----------|----------|------------------|------------------|---------|-------------------|
| Structural class | α | α+β | α+β | pseudo-α | pseudo-α | $\alpha + \beta$ | $\alpha + \beta$ | α+β | α+β |
| Hardness, GPa | 2.5 | 4.2 | 4.6 | 4.7 | 4.2 | 4.5 | 4.6 | 20 | 4.3 |
| Young's module, GPa | 113 | 132 | 155 | - | 135 | | _ | 220 | - |
| Relative wear resistance | 1 | 3.9 | 4.3 | 1.88 | 8.8 | 4.7 | 7.3 | 9.7 | 12.1 |

Mechanical properties and relative resistance of titanium alloy samples to cavitation wear

The influence of the ion-plasma modification process on its mechanical properties and resistance to cavitation was studied on the example of VT6 alloy, from which turbine blades for Nuclear Power Plants are made. In Table 3, the results of changes in the mechanical properties of VT6 alloy are presented.

As can be seen from Table 3, 15 min of ion-plasma modification leads to the increase in the nanohardness and Young's modulus, and resistance to cavitation for the samples of VT6 alloy after ion-plasma modification in comparison with unmodified samples is shown by the kinetic wear curves (h_c) in Fig. 5.

In accordance with Fig. 5, the wear of VT6 samples is changed significantly after ion-plasma modification. As a result of 3 h of cavitation action, the wearrate is almost 5 times lower, and with longer cavitation action, the wear rate for the samples with ion-plasma modification remains much lower than that of the unmodified VT6 alloy. In accordance with the data in Fig. 5, the dependence of the wear rate for the samples V_c on the cavitation time is determined, which is presented in Fig. 6.

Table 3

Mechanical properties of VT6 alloy before and after ion-plasma modification

| t _p , min | Hardness (H), GPa | Young's modulus (E), GPa |
|----------------------|----------------------|-----------------------------|
| 0 | 4 | 132 |
| 15 | 22 | 360 |



Fig. 5. Kinetic wear curves for the samples VT6 (h_c) from the cavitation time before and after ion-plasma modification (t_p): $1 - t_p = 0$; 2 - 15 min



Fig. 6. The dependence of the cavitation wear rate for VT6 alloy on the cavitation time for the initial samples and the samples modified with plasma ions for 15 min

It is shown that only the first half hour of cavitation, the wearrate of the modified alloy is higher when the surface layer etched by argon ions is destroyed, and then it is significantly reduced. This can be explained by the formation of a harder nitrided layer during modification.

The results of optical microscopy for the VT-6 alloy cross section after 15-minute ion-plasma modification are shown in Fig. 7.

After ion-plasma modification, a thin 2 μ m modified light layer is formed in VT-6 alloy, under which at the depth of up to 5 μ m, there is a region with fine-grained structure. Modification of VT6 alloy leads to the synthesis of titanium nitrides having different stoichiometric composition (TiN, Ti₂N), and to the formation of a subsurface transition layer having a finegrained smooth structure [23]. This is explained by the alloy structure and modification temperature at which different diffusion processes take place [24]. Thus, as a result of VT6 modification, a transitional harder layer is formed, which affects the cavitation wearresistance.

The change in the phase composition of VT6 alloy surface after 15-minute ion-plasma modification was studied. In Fig. 8, the diffractograms of VT6 alloy is shown in the initial state and after ion-plasma modification.



Fig. 7. Optical microscopy of the VT-6 alloy cross section after 15-minute ion-plasma modification



Fig. 8. Diffractograms of the VT6 sample: a – initial; b – after 15-minute ion-plasma modification

In the diffraction pattern corresponding to the sample in the initial state, the lines of two polymorphic modifications of titanium are shown, namely: α -Ti with hcp structure and β -Ti with bcc structure. The presence of latter can be explained by the presence of vanadium in the alloy, which is an isomorphic β -stabilizer. After 15-minute ion-plasma modification, the intense lines in the diffraction pattern correspond to the same phases observed in the sample in the initial state $-\alpha$ -Ti and β -Ti. At the same time, the lines of these phases become 1.3–1.5 times wider and there is a significant increase in the β -Ti (110) line in comparison with α -Ti lines, as well as the appearance of a strong separate β -Ti (200) line. The α -Ti and β -Ti lines are shifted towards smaller angles, which shows the increase in the parameters of the crystal lattice and can be explained by the formation of a solid nitrogen solution in the crystal lattice of titanium. The size of the coherent scattering region phases after modification is decreased from 65 to 25 nm for α -Ti and from 26 to 18 nm for β -Ti. In addition to intense titanium lines, the diffraction pattern shows weak lines of nitrides – Ti_2N with a tetragonal structure

and TiN with a cubic structure. When the nitride phases appear, the color of the modified sample surface becomes golden.

Therefore, the change in the mechanical properties (see Table 3) and increase of cavitation wear resistanceare caused by the formation of a solid nitrogen solution in the titanium crystal lattice and the appearance of nitride phases after ion-plasma modification.

CONCLUSIONS

It has been experimentally established that cavitation wear resistance is significantly increased due to the doping of VT1-0 alloy with Al, V, Mo, Zr. As a result of 3-hour testing, the wear resistance was increased from 3 to 9 times.

Further modification of already doped titanium alloys by deformation, heat treatment or ion-plasma modification also contributes to the increasing cavitation resistance.

Ion-plasma modification of VT6 alloy results in a significant increase of its mechanical properties and cavitation resistance due to the formation of a layer of nitrogen solid solution and titanium nitrides.

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СТОЙКОСТЬ ТИТАНОВЫХ СПЛАВОВ К КАВИТАЦИОННОМУ ИЗНОСУ

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Определена скорость износа титановых сплавов ВТ1-0, ТС5, ВТ6, ВТ14, ОТ4 под действием микроударов в результате действия кавитации, которая создается в дистиллированной воде под поверхностью излучателя ультразвуковых волн. Установлено, что повышение твердости и улучшение кавитационной устойчивости для этих сплавов зависят от легирующих элементов, а также увеличиваются после термической обработки и ионно-плазменной модификации поверхности образца. Однозначной корреляции между структурным классом сплавов и кавитационным износом не обнаружено. Вследствие ионно-плазменной модификации сплавов стойкость к кавитационному износу увеличивается в несколько раз, в частности сплава ВТ6 в 3 раза. Исследован фазовый состав образцов до и после ионно-плазменной модификации и установлено, что от него существенно зависит стойкость сплава к воздействию кавитации.

СТІЙКІСТЬ ТИТАНОВИХ СПЛАВІВ ДО КАВІТАЦІЙНОГО ЗНОСУ

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Визначена швидкість зношування титанових сплавів BT1-0, TC5, BT6, BT14, OT4 під дією мікроударів у результаті дії кавітації, яка створюється в дистильованій воді під поверхнею випромінювача ультразвукових хвиль. Встановлено, що підвищення твердості та покращення кавітаційної стійкості для цих сплавів залежать від легуючих елементів, а також збільшуються після термічної обробки та іонно-плазмової модифікації поверхні зразка. Однозначної кореляції між структурним класом сплавів та кавітаційним зносом не виявлено. Внаслідок іонно-плазмової модифікації сплавів стійкість до кавітаційного зносу збільшується в кілька разів, зокрема сплаву BT6 у 3 рази. Досліджено фазовий склад зразків до і після іонно-плазмової модифікації та встановлено, що від нього суттєво залежить стійкість сплаву до кавітації.