Nitriding of Commercially Pure VT1-0 Titanium and VT6 Alloy in Low Pressure Discharges[1]

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Abstract – Results of research nitriding process of technically pure titan VT1-0 and alloy VT6 in non-self-maintained glow discharge plasma with the hollow cathode and arc discharge are presented. It is shown, that operational properties of the nitrided titanium essentially depend on additives in nitrogen of gases with high ionic-molecular reactions cross-section of atomic nitrogen formation (in particular He).

1. Introduction

At the present time the method of diffusion saturation by nitrogen in gas discharge plasma is used for surface hardness, wear resistance and corrosion resistance increasing of titanium alloys. In most cases nitriding is carried out at high temperatures 700–1000 °C [1–3], pressures 100–1000 Pa and durations up to several tens of hours. At that the surface hardness increases up to 6 times, and nitrided layer depth reaches 100 μm for technical pure titanium and up to 250 μm for titanium alloys. However at high temperatures over $\alpha \rightarrow \beta$ transformation temperature nitriding can lead to microstructure changing, crystals growth and decrease of treated material tribological properties. Often for microhardness increase and modified layer depth increase at nitriding argon is extended with nitrogen to the discharge gap. Depending on nitrogen and argon ratio in the mixture and process temperature, the hardness on a surface or nitrited layer depth increases [4–6]. Argon introduction to the electron cyclotron resonance discharge [7] changes physical-mechanical properties of the nitride coating significantly due to atomic nitrogen increase in plasma.

Influence of argon additive to the working mixture on the microhardness is the most interesting and insufficiently investigated phenomenon. From other side as the analysis of ion-molecule reactions given in [8] shows the atomic nitrogen formation takes a place also in another ion-molecule reactions in particular with neon and helium ions participation, which provide at energy of tens and hundreds eV higher cross-sections of nitrogen atoms and atomic ions formation. This paper aim is showing up of VT1-0 titanium and VT6 alloy modification regularities in process of saturation by nitrogen at using of different gas mediums.

2. Investigation methods

Nitriding of commercially pure VT1-0 titanium was carried out in non-self-maintained glow discharge with a hollow cathode, which provides relatively high current densities (at some mA/cm^2) at low (at some Pa) work gas pressures also at low pressures self-maintained arc discharge plasma. The installation scheme (Fig. 1) and analysises of nitrited samples are considered in detail earlier in [5].

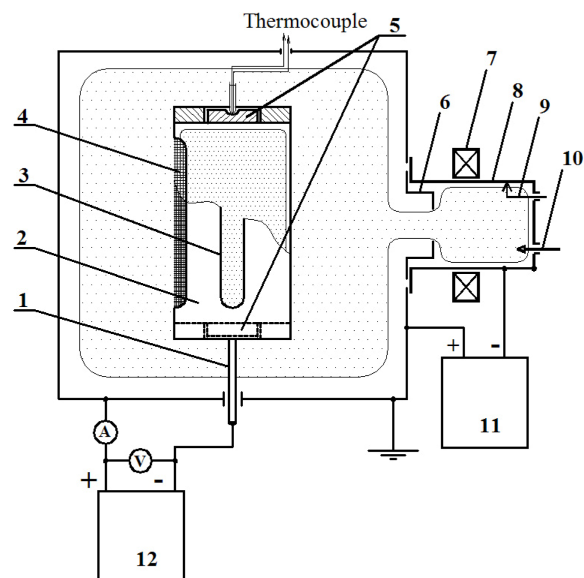

Fig. 1. Experiment scheme: 1 – holder; 2 – hollow cathode; 3 – window; 4 – window closed by fine-structure mesh; 5 – samples; 6 – arc arrester; 7 – short magnetic coil; 8 – hollow cathode; 9 – trigger; 10 – gas lead-in; 11 – arc discharge power supply; 12 – source of high voltage

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3. Nitriding in the glow discharge with a hollow cathode

Nitriding process was conducted in the next succession. At argon pressure in vacuum chamber $p=3\cdot10^{-2}$ Pa, negative bias $U=-600$ V and generator current of gas discharge plasma $I=50$ A cleaning, heating and training of a hollow cathode were conducted during 10–20 min. Than working gases mixture was at ratio of 50:50 % let in plasma generator. VT1-0 titanium samples with diameter of 26 mm and thickness of 5 mm were placed inside of cylindrical hollow cathode, and the negative bias $U=(1-1.5)$ kV relatively to vacuum chamber walls was given to it. Nitriding process can be realized at ion current densities $j_i=(1.5-4)$ mA/cm^2 on the samples surface due to bias voltage changing and in small bounds of pressure $p=(0.1-1)$ Pa.

To prevent the development of grain enlargement process due to recrystallization nitriding was conducted at temperatures not over 650 °C.

The results of VT1-0 titanium nitriding at temperature of 600 °C and during 2 hours in different gas mediums (at ratio of 50:50 %) are given in Table I.

Table I. The dependence of microhardness on the VT1-0 titanium surface on gas medium composition

Gas medium	Microhardness ($HV_{0,5}$), GPa	
	Right side	Backside
N_2	6.5	4.6
$Ne+N_2$	8.0	4.7
$Ar+N_2$	10.0	7.5
$He+N_2$	14.5	9.5

As Table I shows, in these experiments at nitriding in neon-nitrogen and argon-nitrogen mixtures the microhardness on the surface increased approximately for 20 % and for 50 % accordingly in comparison with nitriding in pure nitrogen. At the same time injection of helium to the mixture allows to increase microhardness at almost 2.5 times. Consequently it is possible to get a high microhardness on the surface or to decrease nitriding time significantly in helium-nitrogen mixture.

As that is shown on Fig. 2, time process of saturation by nitrogen occurs irregularly. Firstly saturation occurs with high speed, and then slows down. As that is shown in [5], it occurs as a result of formation in surface layers of nitrides and titanium oxides which complicate nitrogen penetration. It results in delay of surface hardness and depths diffusion layer increase. On the backside delay of process occurs stronger therefore TiN – layer does not scattered by high energy ions.

There are nitrited layers profiles on the fig. 3, where it is shown that along with increase of hardness on the surface nitriding in gas mixtures leads to nitriding depth increase. Within 10 μm from a surface the microhardness at nitriding in helium-nitrogen and argon-nitrogen mixtures at 2 and 1.5 times higher accordingly in comparison with nitriding in pure nitrogen.

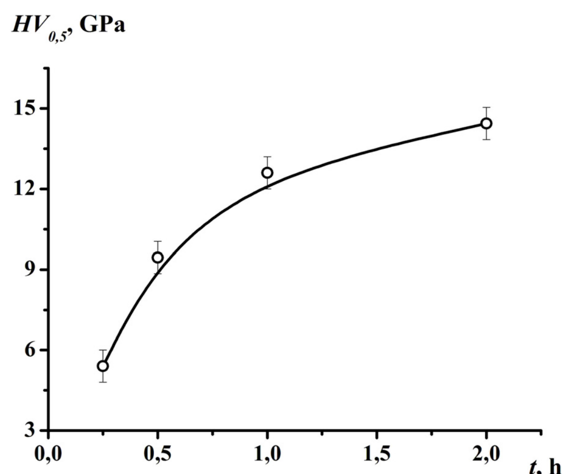


Fig. 2. Dependence of sample surface microhardness on nitriding time in the mixture N_2+He 50:50 %. Nitriding temperature is T=600 °C

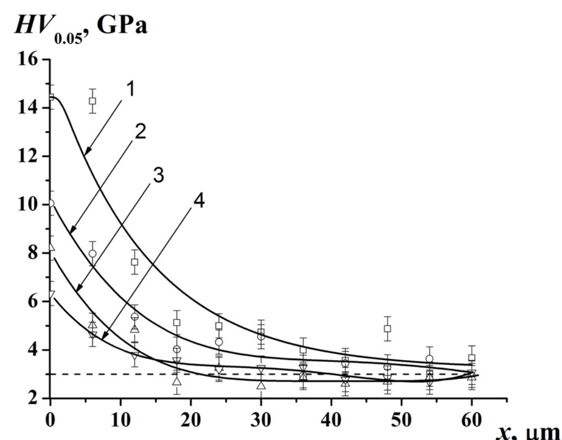


Fig. 3. Nanohardness profile of sample depth after nitriding in different gas mixtures at ratio 50:50 % (curve 1 – N_2+He, 2 – N_2+Ar, 3 – N_2+Ne, 4 – N_2, dotted line shows untreated sample hardness)

High microhardness at nitriding in argon-nitrogen mixture is provided by ionization high cross-section and increased cross-section of ion-molecule reactions at low ion energies. It is, perhaps, connected with TiN layer formation on the sample surface. This layer prevents nitrogen from penetration to the diffused layer. From the side facing to a discharge this layer is sputtered partly by fast ions accelerated in cathode drop and neutrals formatted due to recharge.

At nitriding in helium-nitrogen mixture the roughness of facing to discharge surface decreases. That is stipulated by fewer surfaces etching due to sputtering ration of titanium by He ions is fewer for 2 orders than by Ar [9] ions in energy range (50–1500) eV. At low temperatures and short nitri-

ding time as in [1] microhardness on the sample backside is fewer than on the right side. Obviously that is connected with a fact that on the right side in atoms and atomic ions take part saturation process by nitrogen; and on the backside just atoms.

4. Nitriding in arc discharge plasma

At nitriding we used plasma generator with cold hollow cathode, where arc discharge operates in crossed electric and magnetic field (Fig. 1). At work in a wide pressure range p=(10^{-2}–10) Pa generator at discharge voltage (30–60) V provided discharge current up to (10–100) A and plasma density in vacuum chamber n=(10^9–10^{10}) cm^{-3}. VT1-0 titanium samples and VT6 alloy samples with a thickness 10 mm and size of 25×25 mm were mounted in vacuum chamber on distance of 10 cm from generator outlet.

As it was shown above at nitriding in glow discharge with a hollow cathode in helium-nitrogen medium due to ion-molecule reaction type $He^{+}+N_2 \rightarrow N^{+}+N^{0}+He$ it is possible to increase process efficiency in comparison with nitriding in pure nitrogen, neon-nitrogen and argon-nitrogen mixtures, that's why further there are investigation results of VT1-0 titanium and VT6 alloy just in gases mixture N_2+He 50:50 % for comparison.

The results of nitriding during 2 hours at pressures p=(1–4)·10^{-1} Pa and bias voltage U=–500 V are given in the Table II. Temperature changing was fulfilled due to changing of ion current going to sample from plasma.

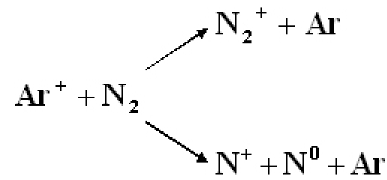
Table II. Dependence microhardness of VT1-0 titanium and VT6 alloy on temperature

Temperature, °C	Current density (j_i), mA/cm²	Hardness ($HV_{0.5}$), GPa	
		VT1-0	VT6
450	2.2	2.4	–
475	2.8	3.8	–
500	3.2	5.3	4.2
550	3.6	7.8	5.6
600	4.0	10.5	7.9
650	3.6	13.5	9.1

As it is clear from table using of nitrogen and helium mixture allows to conduct nitriding at relatively low temperatures not only VT1-0 titanium but also wide using in industry VT6 titanium alloy. At the beginning up to temperature 650 °C hardness increases practically under the linear law, but then this process becomes slower. At average temperatures VT1-0 titanium microhardness exceeds VT6 alloy hardness approximately at 1.2–1.3 times. In comparison with nitriding in nitrogen-argon mixture and pure nitrogen VT1-0 hardness increases at 1.5 times.

5. Results discussion

As it was shown in [6], atomic nitrogen plays defining role in titanium saturation by nitrogen, that's why for the process intensification it is necessary to make conditions at which the maximal number of nitrogen atoms occurs in discharge. There are mainly two channels of atoms formations in glow discharge. Through the first channel atoms formation takes place due to molecules dissociation by electron impact through electron state excitation with cross-section of process $\sigma=1\cdot10^{-16}$ cm^2. Through the second channel due to ion-molecule reactions in gas mixtures, for example nitrogen with argon, neon or helium according to the scheme (for example):



In these reactions the atomic nitrogen formation occurs due to dissociation of molecule nitrogen ion.

According to the dates from [8], in the range of ion energies from 50 up to 900 eV molecules reactions cross-sections with nitrogen atoms formation with helium participation ($\sigma=2\cdot10^{-16}$ cm^2) are higher for an order than with neon participation and for 2 orders than with argon participation.

The comparison of dissociation cross-sections by electron impact and ion-molecule reactions allows thinking that at using of mixture containing helium it is possible to increase at 2–3 times nitrogen atoms and atomic ions intaking to the sample surface and increase microhardness due to it as well on the sample surface as in its volume. High cross-section of nitrogen atoms formation in helium-nitrogen mixture is probably connected with excitation of nitrogen molecule ion during charge transfer process and following dissociation of nitrogen molecule ion. Helium ion has ionization potentials of I_{He}=24.58 eV even at low energies can deliver energy excess $\Delta\varepsilon_{He}$=10.05 eV and move nitrogen molecular ion which has ionization potential of $I_{H_2^+}$=14.53 eV to the excited condition with its following decay at interaction with an electron.

In spite of ion-molecule reaction high cross-section of nitrogen atomic ions and atoms at using of neon-nitrogen mixture the insignificant microhardness increase can be related to a fact, that at discharge voltages mentioned above the ion ionization cross-section is fewer at 2–3 times than argon or nitrogen has.

In spite of low ionization cross-section helium using as additional in gas mixture with nitrogen allows to carry out nitriding process with high efficiency due to higher (about for 2 orders) value of atomic nitrogen formation cross-section in ion-molecule reactions in all range of energies. Besides low ionization cross-section is compensated probably by high

coefficient of secondary ion-electron titanium emission. It results in electron components growth of a discharge current and, as a consequence, to increase in efficiency of atomic nitrogen formation.

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