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Plasma nitriding of titanium alloy Ti5Al4V2Mo

Yu.V. Borisyuk, N.M. Oreshnikova, M.A. Berdnikova, A.V. Tumarkin, G.V. Khodachenko, A.A. Pisarev*

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31,115409, Moscow, Russia

Abstract

Nitriding of highly alloyed titanium material Ti5Al4V2Mo was performed at 500, 600,700,800, 900 ºC in the mixture of 50±10% Ar + 50±10% N_2 at 300-450 Pa (3-4.5 mbar) for 3-4 hours. The hardness at the surface increased with temperature, and at 900 ºC it was 1.7 times higher than that of the untreated material. The hardness decreased with the depth, and the thickness of the hardened layer was 30-50 µm at 900 ºC. The phase composition is very complex, comprising various Ti phases, various titanium nitride phases, and titanium dioxide.

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Keywords: plasma nitriding; titanium alloy; glow discharge; hardening; surface modification.

1. Introduction

Titanium and its alloys are widely used in industry and medicine. These alloys are characterized by low specific weight, high corrosion resistance, and biocompatibility. However, low hardness and low wear resistance of these materials are two of the reasons for limiting their wider use. Nitriding of titanium alloys with the purpose of improvement of their wear resistance is an important task. Many works were devoted to nitriding of titanium and

* Corresponding author. Tel.: +7-495-788-5699, ext. 9981.
E-mail address: aapisarev@mephi.ru

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low alloyed titanium (e.g., Avelar-Batista Wilson et al. (2014), Hosseini et al. (2013), Gokul Lakshmi et al. (2004), Sobiecki et al. (2001), Kashaev et al. (2005), de Souza et al. (2014)), but not much is known about nitriding of highly alloyed titanium, which is a promising material for many applications. The superalloy Ti5Al4V2Mo has high strength and corrosion resistance, and it is widely used in industry at medium and high temperatures. Nevertheless, it was not studied in terms of plasma nitriding. This work is devoted to an investigation of nitriding of Ti5Al4V2Mo in argon-nitrogen plasma of the abnormal glow discharge. The glow discharge is used in industry for nitriding of steel, and therefore it was used here.

2. Experimental details

The material used is a titanium superalloy Ti5Al4V2Mo. The chemical composition measured by electron dispersion spectroscopy is given in Table 1. The samples were rods of 14 mm in diameter and 10 mm in length. They were polished and washed in ultrasonic baths of acetone and spirit before nitriding.

Table 1. The chemical composition of the alloy Ti5Al4V2Mo.

Chemical elements	Content, weight %
Ti	84 - 89.3
V	4 - 5
Al	4 - 6.3
Mo	1.5 - 2.5
Cr	0.8 - 1.4
Fe	0.4 - 0.8

The experimental installation for nitriding is shown in Fig. 1. It was pumped by a turbomolecular and membrane pumps to the ultimate pressure of 10^{-5} mbar. The samples were suspended on a titanium holder, which was attached to the cathode. The anode was a system of coaxial cylindrical sheets giving thermal insulation to reach a higher temperature of the sample and make it more uniform over the surface. The abnormal glow discharge between the sample and the cylindrical anode was ignited at pressures of 0.1-10 mbar using a power supplier operated in the pulsed regime to keep the discharge stable.

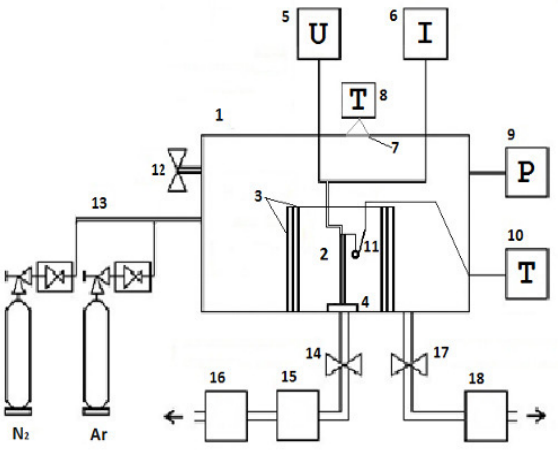

Fig. 1. Scheme of the experimental installation for studying plasma nitriding: 1 – vaclatoruum chamber; 2 – sample holder (cathode); 3 – thermal shields (anode); 4 – ceramic insulator; 5 – power supply unit; 6 – oscillograph; 7 – view window; 8 – infrared pyrometer; 9 – pressure measurement; 10 – multimetr; 11 – thermocouple (type K); 12, 14, 17 – vacuum valves; 13 – the system of gas inlet; 15 – turbomolecular pump; 16, 18 – mechanical pump.

Before nitriding, the samples were cleaned in a glow discharge plasma (gas: argon; pressure 0.5-0.8 mbar, voltage: 250-500 V, duration 15-30 minutes). Nitriding was performed in mixtures of argon and nitrogen 50%-50% in average. Gas compositions and pressures, discharge voltages, sample temperatures, and nitriding durations are given in Table 2.

Table 2. Nitriding parameters.

№	The composition of the gas mixture	Pressure p, mbar	Voltage U, V	Temperature of the sample T, ° C	Duration of nitriding process t, h
1	60%Ar +40%N2	3-3.5	480-550	500	4
2	60%Ar +40%N2	3.5	500-560	600	3.5
3	40%Ar +60%N2	4	550-590	700	3.5
4	50%Ar +50%N2	3.8-4.2	600-640	800	3
5	40%Ar +60%N2	4-4.5	600-640	900	3

3. Results

The samples after nitriding changed their colors. They were in different shades of gray at temperatures 500-800°C and changed color to gold at 900°C . The nitrided samples were cut and polished; and the polished surface was chemically etched in the solution of 33% HF, 33% HNO_3 and 33% glycerol for 1-2 seconds. The cross-section was examined in an electron microscope Hitachi TM1000. The depth profile of the hardness over the cross-section was measured using a FUTURE-TECH CORP Microhardness tester FM-800. Also the hardness was measured normally to the treated surface before cutting the sample. The load applied to the indenter was 50g in all the measurements.

Fig. 2 shows SEM images of the cross-sections of the five treated samples and that of the virgin sample. One can see that the structure of the near surface region drastically changed at the temperature of 900°C (Fig. 2e). One can see a rather pronounced layer of titanium nitride (~ 5 μm of dense nitrides thick) and a rather deep layer of nitride precipitates (about 30 micrometers). At lower temperatures (Fig. 2a-d), there are no thick region of precipitates, but one can tentatively see very thin layers of nitrides on the surface even at the lowest temperature of 500 °C.

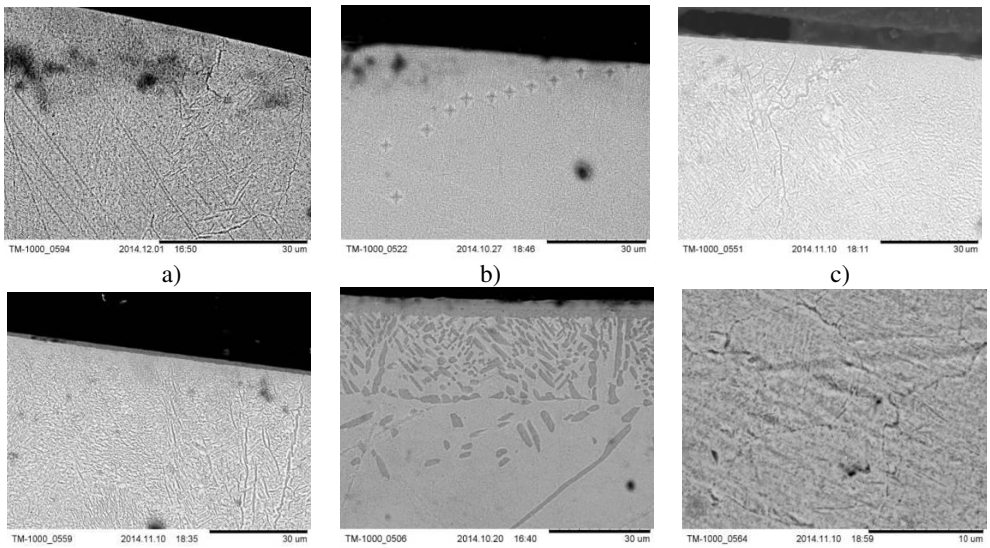

Fig. 2. Cross-sections of the samples. Temperature of processes: a) 500 ºC; b) 600 ºC ; c) 700 ºC ; d) 800 ºC ; e) 900 ºC ; f) the untreated sample.

The hardness as a function of temperature measured perpendicular to the surface of treated samples before their cutting is demonstrated in Fig. 3a. The hardness exceeds the initial value (dashed red line) even at the lowest temperature of nitriding 500 °C and steadily increases with temperature. The maximum hardness was observed if the sample was treated at 900 °C. It was approximately equal to 820 HV, and this was approximately 1.7 times higher than the hardness of the original sample.

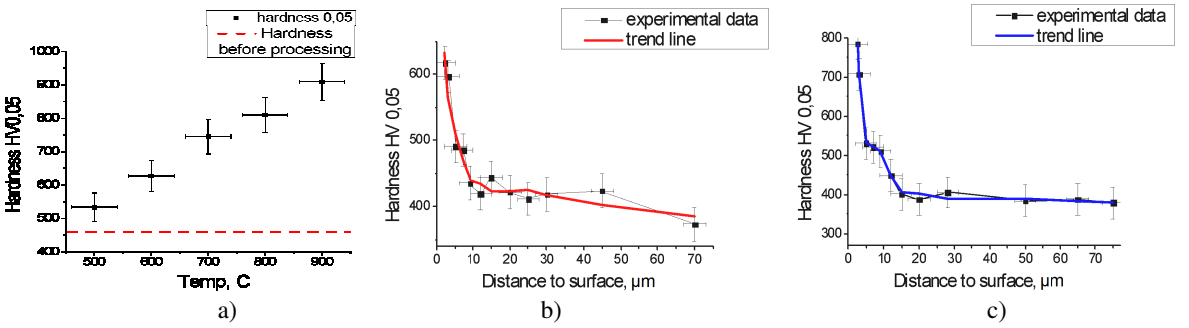

Fig. 3. The hardness of nitrided samples: a) dependence on the nitriding temperatures measured perpendicular to the sample surface; b, c) depth dependencies measured in the cross-sections of the samples nitrided at 600 °C and 900 °C, respectively.

Depth profiles of the hardness for two samples treated at 600 and 900 °C are shown in Fig. 3b, 3c. Similar types of dependencies are observed for other samples. The hardness decreases with depth. The depth of enhanced hardness increases with temperature, and this is not surprising. But one must mention three interesting features of these dependencies. First, this depth is much higher than the thickness of the dense nitride layer at all temperatures used. Second, this depth is less than the thickness of the layer containing nitride precipitates at 900 °C. Third, the core hardness of the samples is less than that of the initial value approximately 1.2 times.

X-ray diffraction analysis was performed using a diffractometer D8 DISCOVER (Bruker) and CuK_{α} radiation. Phase identification was performed using the software Bruker AXS DIFFRAC.EVA v.3.0 and the international database ICDD PDF2. Experimental spectra for the sample treated at 900 °C and identified phases are given in Fig. 4.

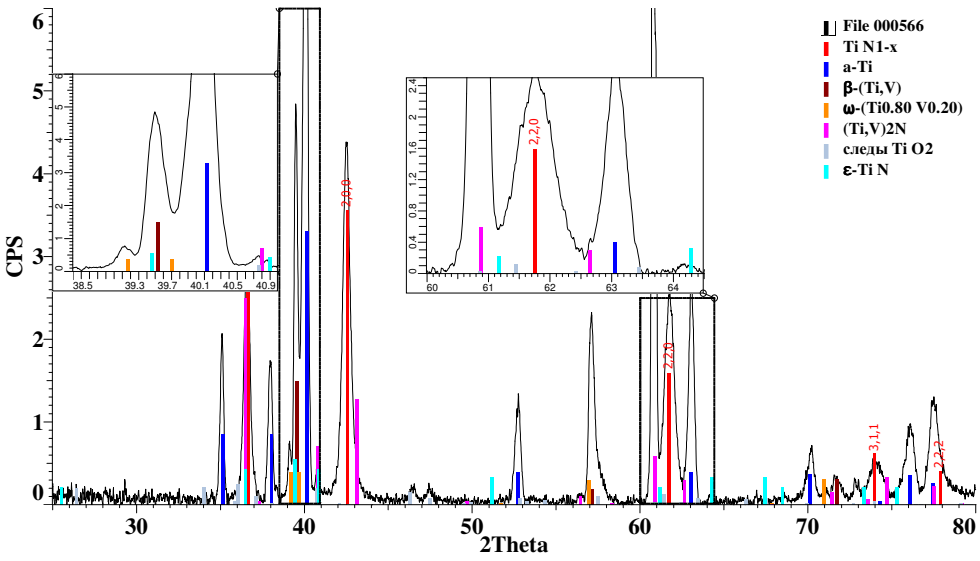

Fig. 4. X-ray diffraction spectra of the sample nitrided at 900 °C. Phases identified are given by vertical lines.

The main phases are α-Ti (hcp) and titanium nitride of variable nitrogen concentration TiN_{1-x}, (fcc). The lines of two phases are asymmetric that is possibly connected with depth nonuniformity of nitrogen concentration. The virgin alloy Ti5Al4V2Mo initially contains two phases (α+β), therefore β-Ti (bcc) is also observed. Additionally, ω-Ti which may be formed in non-equilibrium conditions of plasma implantation was also formed in the sample. Parameters of this phase are slightly different from the table values, and this may be due to the presence of V in the solid solution in the alloy. Additionally, traces of titanium dioxide TiO_2, and tetragonal phases ε-TiN and Ti_2N were also observed. The complex composition can be due to non-uniformity of nitrogen concentration that decreases from the surface to the depth due to diffusion.

4. Conclusions

Highly alloyed titanium Ti5Al4V2Mo was treated in the abnormal glow discharge in a mixture of Ar and N_2 at temperatures 500-900 °C. Bright gold color, which is typical for titanium nitride, appeared at 900 °C. At this temperature, a layer (~ 5 μm) of dense nitrides and a layer (~ 30 ÷ 50 μm) of nitride precipitates appeared, and the hardness at the surface increased 1.7 times with respect to the untreated material. Increase of the hardness, nevertheless, was observed at all temperatures used, including the lowest temperature of 500 °C. The hardness decreases with depth. It was found that at large depths the hardness was 1.2 times less than the initial value. X-ray analysis demonstrated the complex phase composition consisting mainly of α-Ti and TiN_{1-x} with traces of β-Ti, ω-Ti, TiO_2, ε-TiN, and Ti_2N. The complex phase composition is due to the multiphase initial composition, non-uniformity of nitrogen concentration through the depth, and non-equilibrium conditions of plasma impact.

Acknowledgements

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