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Glow discharge assisted oxynitriding of the binary Ti6Al2Cr2Mo titanium alloy

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Abstract

The paper presents the results of glow discharge assisted oxynitriding of binary titanium Ti6Al2Cr2Mo carried out in an N_2 + air atmosphere. An oxynitrided diffusion layer is thus produced of the $TiO_2 + TiN + Ti_2N + \alpha Ti(N)$ type with a hardness of 17 GPa. The outer zone of the layers contains the TiO_2 phase. This layer slightly decreases the corrosion resistance of the substrate of the alloy. An increase of the process duration and, thus, of the thickness of the individual zones of the layer, in particular the TiN zone, increases the resistance of the layer to frictional wear, but only slightly affects the fatigue properties of the titanium alloy.

Keywords: Plasma oxynitriding; Titanium alloy; Corrosion resistance; Wear resistance; Fatigue limit

1. Introduction

Titanium and its alloys, materials with particular chemical and physical properties, are finding increasing application in industry. They are characterized by a low specific gravity, a good corrosion resistance, and a high relative strength. They also show a good biocompatibility in the environment of human cells and tissues, which is of crucial advantage in the fabrication of reconstructional parts, prosthetic implants and endoprostheses, and in joining human bone fractures [1–3]. The drawbacks of these materials are their low hardness and low frictional wear resistance. To eliminate these drawbacks, various surface treatment techniques are applied, such as thermal spraying, PVD methods, anodic oxidation, ion implantation, laser treatment, and glow discharge assisted treatments [4–6]. The most attractive methods seem to be those that consist of producing surface layers under glow discharge conditions. These methods, enable full control of the growth of the layer, i.e. its structure and chemical composition and thus its properties, and in addition permit the treatment of parts with complicated shapes. Among these methods we

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can mention glow discharge assisted nitriding, which is a widely used treatment [7–9], and carbonitriding carried out in an electrically activated gaseous medium [10,11].

An essential feature of titanium and its alloys is their high affinity to oxygen and nitrogen, which permits these two elements to be introduced simultaneously into the surface layer of the titanium alloy during the process, and thereby to modify its performance properties. Within the temperature range from 700 to 1000 °C, the diffusion coefficients of oxygen and nitrogen in titanium are similar, but in Ti(α) their diffusion rate is smaller and their diffusion activation energy is greater than in Ti(β) [12].

The oxide layers produced on titanium and its alloys have a low electrical conductivity and are thermodynamically stable. The passive layer, which forms spontaneously, is compact and its morphology is homogeneous. Its thickness does not exceed 10 nm. This thin oxide layer ensures the high corrosion resistance.

When analysing the free enthalpies of the formation of titanium oxides and nitrides, we can see that, at both low and elevated temperatures, the affinity of titanium to oxygen is higher than that to nitrogen. This is confirmed by the literature reports according to which the values of the bonding energy of the TiN and TiO phases are 2.27×10^{-19} and 1.87×10^{-19} J, respectively, and the values of the diffusion activation energy are 4.00×10^{-19} and 3.45×10^{-19} J, respectively [13].

The paper describes how the glow discharge assisted oxynitriding process parameters affect the structure and the properties of the $Ti_6Al_2Cr_2Mo$ titanium alloy. The available literature reports compare only the results obtained for the Ti6Al4V titanium alloy subjected to glow discharge nitriding and oxynitriding [15].

2. Examination methods

The material examined was the Ti6Al2Cr2Mo titanium alloy. The oxynitrided layers were produced under glow discharge conditions in an atmosphere composed of 96 vol% of nitrogen and 4% of air at a temperature of 900 °C. The operating pressure was 3.5 hPa. The process duration was 3, 6 and 12 h. The metallographic cross-sections were etched using a reagent based on the aqueous solution of HNO_3 and HF, and then observed in Neophot 2 metallographic microscope. The surface microhardness of the layers was measured using the Vickers method. The values are arithmetical means from the 10 measurements. The standard deviation is 0.45 GPa. The phase composition was determined with a Philips PW 1830 X-ray diffractometer using a CoK_α source. The frictional wear resistance was measured by the 'three-rollers + taper' method under a unit load of 200 MPa [14]. In this test, friction is applied, under specified conditions, between three fixed 8-mm diameter, cylindrical specimens (rollers) and rotating conical counter specimens (a taper). The linear wear, expressed as the wear depth, was determined by measuring the diameters of the ellipses formed on the surfaces of the individual rollers. The results were then averaged. The counter specimen was made of AISI 45 steel, quench hardened and tempered to a hardness of 30 HRC. The test lasted for 100 min, but it was interrupted at intervals of 10 min at which the worn area was measured. After each interruption, the load was increased to compensate for the increased worn area so as to maintain a constant unit pressure of 200 MPa. The corrosion resistance was examined by the potentiodynamic method in a 0.5 M NaCl environment. The reference electrode was a saturated calomel electrode. The examinations were made within the potential range from −1000 to +3000 mV and a potential variation rate of 50 mV/min using a fully computerized ATLAS'91 instrument. The fatigue behaviour was examined in a bending-rotational machine at a constant bending moment and a load variation frequency of 2200/min. The fatigue strength (Z_{go}) was determined in 24 samples, which were loaded in a stepwise manner. The stress increment was $s = 2\,kg/mm^2$ (~20 MPa). To visualize better, the advantages of oxynitriding, the results obtained for oxynitrided Ti6Al2Cr2Mo samples were compared with those obtained for the Ti6Al2Cr2Mo samples annealed under glow discharge conditions in an argon atmosphere at a temperature of 900 °C for 3 h.