Surface electrolytic-plasma polishing of Ti-6Al-4V alloy with ultrafine-grained structure produced by severe plastic deformation

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Abstract. The paper deals with the studies on electrolytic-plasma polishing (EPP) of the surface of Ti-6Al-4V alloy with ultrafine-grained (UFG) structure produced by equal channel angular pressing. The electrolyte temperature range and working shift voltages of EPP to ensure the polishing effect in Ti-6Al-4V with UFG structure are discussed. The results of the studies on topography and chemical composition of the alloy surface in coarse grained (CG) and UFG states by scanning electron microscopy are presented. The impact of EPP duration on the surface roughness and metal removal rate of conventional and UFG alloy are demonstrated. The perspectives of the EPP process applied to a surface treatment of medical implants and items for mechanical engineering are discussed.

1 Introduction

Ti alloys are widely used in medicine, mechanical engineering and aircraft. All these application areas impose high requirements to service life of items and, therefore, to quality of their surface. Polishing techniques with employment of felt discs with abrasives, chemical and electrochemical polishing techniques are used presently in order to reduce surface roughness. However the polishing with felt discs with abrasives is restricted to flat surfaces with a large bending radius. Chemical and electrochemical polishing is connected to necessity to use concentrated acids. All the described techniques are characterized by low productivity and technology complexity. Today one of the promising techniques of surface treatment is electrolytic-plasma polishing (EPP) [1-3]. This technique is most widely used to polish items from stainless steels [4-7]. Parts processed by this technique have a surface roughness up to $Ra 0.01 \mu m$ and microscopic defects as stripes and a defect layer with foreign inclusions are removed from the surface. In works [4, 7] surface polishing by EPP is shown to lead to increase of fatigue strength and corrosion resistance of stainless steels. The authors of [6] give examples of effective use of EPP to polish medical items from different alloys, including Ti ones. It is shown that the EPP process can be used for small-sized and complex geometry parts. Alongside, the regularities of EPP of Ti alloys and its impact on physical and chemical state of the processed surface have not been studied sufficiently.

The recent experiments on EPP of Ti alloys in [7-9] show that physical and chemical processes in them are similar to those taking place in chrome steels during polishing in solutions of inert salts. In particular, depending on processing regimes (shift voltage and electrolyte temperature), during EPP of two-phase Ti-6Al-4V alloy, conditions are created for surface oxidation, heating and polishing. However, as compared to steels, oxidation in Ti alloys occurs more intensively with formation of thin but rather dense oxide films, which obstructs electrochemical reactions directed at
surface smoothing. This impacts the physical and chemical state of the item surface. Moreover fluoride-salt-based electrolyte for polishing does not settle the problem of oxidation resistance, which requires studies on electrochemical behavior of Ti alloys during EPP.

As it is known Ti alloys have different types of microstructure depending on thermomechanical treatment. Microstructures differ in ratio of β- and α-phases, their shape and sizes, state of grain boundaries, etc. and, therefore, in electrochemical activity [10, 11]. Comparative analysis of EPP processes and further surface formation in Ti-6Al-4V with ultrafine-grained (UFG) structure produced by severe plastic deformation are of special interest. The recent decade studies show that formation of bulk UFG structure in Ti alloys allows increasing its service and technological properties (strength, fatigue resistance, superplasticity, etc) [10], which is urgent for promising items in medicine and mechanical engineering.

The main goal of the present work is to study the features of EPP and physical and chemical state of the surface of two-phase Ti-6Al-4V alloy with regular globular-plate and ultrafine-grained structure produced by equal channel angular pressing (ECAP).

2 Experimental methods

Ti-6Al-4V alloy of following chemical composition in wt.% (Ti- base, Al – 6.6 %; V – 4.9 %; Zr – 0.02 %; Si – 0.033 %; Fe – 0.18 %; C – 0.007 %; O – 0.17 %) is used to perform the research. The initial coarse-grained (CG) structure of the alloy is mixed globular plate structure consisting of primary α-phase grains (the average size is about 15 μm, the fraction of which is about 30%), and zones with (α+β) thin-plate structure (Figure 1 a). Billets with a diameter of 20 mm and 100 mm long are subjected to ECAP on the die-set with the angle of channels intersection of 120° via route Bc at T=650°C, 6 passes. The total accumulated strain after ECAP is the equivalent strain degree ε=3. In the microstructure of ECAP-processed billets low-deformed grains of primary α-phase with the average size of about 10 μm are observed (Figure 1b), and in the zones with α+β structure UFG structure is formed, the average size of grains/subgrains of α and β-phases is about 350 nm (Figure 1c).

![Figure 1. Microstructure of Ti-6Al-4V alloy with coarse-grained globular-plate structure (a); ultrafine-grained structure (b, c).](image)

The EPP of samples is implemented in electrolyte composition applied to conventional Ti-6Al-4V [8], including from 4 to 6 wt. % of hydroxylamine hydrochloride and from 0.7 to 0.8 wt.% of sodium or kalium fluoride [8]. The samples are dipped in the bath of the EPP-50EM set to a depth of 50 mm from the electrolyte surface. The bath walls are cathodes; the treated samples are anodes (Figure 2). The voltage is supplied before the parts are dipped in the electrolyte. In these conditions when the parts are dipped in the electrolyte, the electrolyte starts boiling intensively round the anode, thin steam-gas shell forms (Figure 2).

The studies on the peculiarities of EPP applied to two-phase Ti-6Al-4V with CG and UFG structures include:
- the impact of shift voltage on EPP applied to alloy with UFG structure at 260 and 280 V and the electrolyte temperature 90+5°C;
- the impact of EPP duration on roughness change and metal removal rate.

The surface state and chemical composition are studied with the help of a scanning electron microscope (SEM) JEOL-6490VL with an X-ray microanalyzer Oxford Instruments. The
roughness is measured with the help of a profilometer SurfTest SJ-210 (Mitutoyo Corporation). The rate of metal removal from the surface during EPP is estimated through measuring the thickness of samples with the help of a caliper CD-15AX (Mitutoyo Corporation).

Figure 2. Scheme of electrolyte-plasma polishing and steam-gas shell formation.

3 Results

3.1 Influence of voltage during EPP on the polishing effect of samples surface
In this work it was experimentally established that for an UFG alloy the polishing effect was observed at a temperature \( T = 90 + 5 \, ^\circ C \) as well as for a CG alloy. Therefore, in the course of further studies this parameter did not change.

As is known that the process of EPP for a conventional Ti-6Al-4V alloy is usually carried out at a shift voltage of 280 V [8]. The polishing process of UFG samples surface at this voltage led to the etching of the surface and the formation of etch pits (Figure 3a). The shift voltage reduction up to 260 V for UFG alloy allows achieving highly polished effect to reach the surface of the mirror (Figure 3b and c).

Figure 3. SEM image of surface topography (a) in UFG Ti-6Al-4V samples after EPP via the regimes of CG alloy processing (U=280 V, T=90 °C); samples surface after EPP and a voltage: a) 280V, b) 260V.

3.2 The impact of EPP duration on chemical composition and surface roughness
The results of the studies on chemical composition of the surface of UFG Ti-6Al-4V after mechanical polishing and after EPP treatment are displayed in Table 1.

It is seen from Table 1 that electrolytic-plasma polishing in the electrolyte containing fluoride components results in some change of chemical composition of the surface as compared to conventional mechanical polishing. In particular, alongside with alloying elements fluoride ions are observed in the sample surface. It is known that fluohydric acid HF is in majority of solutions applied for etching of Ti alloys. The Ti surface treatment by fluohydric acid solutions disturbs the stability of initial oxide film \( \text{TiO}_2 \) and results in its subsequent dissolution. Oxide layer that forms
after chemical etching is more homogeneous in thickness and composition as compared to initial layer [12].

Table 1. Chemical composition of sample surface with UFG structure after mechanical polishing and after EPP (wt. %).

| State         | Ti    | Al    | V     | Fe   | F       |
|---------------|-------|-------|-------|------|---------|
| Mechanical polishing | 89.11 | 5.60  | 4.50  | 0.32 | -       |
| EPP           | 88.82 | 5.99  | 5.08  | 0.40 | 0.48    |

The results of measurement the parameter $Ra$ in the EPP process as a function of the polishing time for the Ti-6Al-4V alloy with a CG and UFG structure are shown in Figure 4. It can be seen that a decrease in the surface roughness with a UFG structure from $Ra 0.2...0.25 \mu m$ to $Ra 0.05 \mu m$ occurs in 2 minutes, whereas similar values of $Ra$ for a CG alloy were achieved only after 4 minutes of polishing. Further increase of polishing time does not lead to significant change of roughness: a maximally achievable value of the $Ra$ is $0.040...0.045 \mu m$ for both CG and UFG alloys.

Figure 4. The surface roughness of Ti-6Al-4V samples with UFG and CG structure during EPP against polishing duration.

3.3 Impact of EPP duration on rate of metal removal from the surface

Figure 5. The thickness of CG and UFG samples during polishing after 1 minute (a); for 2 to 10 minutes (b).
It is established experimentally that during the first minute of polishing the thickness of samples reduces most intensively, when the metal removal rate from the surface of conventional and UFG alloy is 0.01 and 0.05 mm/min, respectively (Figure 5a). When the polishing duration increases to 10 minutes, the rate of metal removal decreases and gains some constant value of 0.03...0.04 mm/min (Figure 5b). Such behavior is typical also during chemical etching of surface of Ti and Ti alloys in solutions with fluorhydric acid, which is conditioned by formation of stable protective passivation film on the surface. This effect strengthens in the conditions of ultrafine-grained structure of material [11, 13].

4 Discussion
The experiment results obtained in this work testify to the fact that the previously developed electrolyte for CG Ti-6Al-4V [8] with fluoride salts is effective for EPP of UFG alloy surface, as formation of UFG structure in alloy does not change its chemical composition. The main difference in the EPP regimes applied to Ti alloy with UFG structure is in achievement of the polishing effect at lower voltage values, as compared to those applied to CG alloy (at 260 and 280 V, respectively). Taking into account that the shift voltage during EPP determines the energy of ions in the steam-gas shell, one may conclude that lower energy of ions is required for polishing of alloys with UFG structure. This allows assuming that lower energy consumption of EPP applied to Ti alloys with UFG structure is connected with increase in its electrochemical (corrosion) activity [11, 13]. The mentioned effect of electrochemical activity enhancement can be explained by intensification of surface substructure heterogeneity and its thermodynamically instable state [13]. Moreover, transition of metal in the UFG state, for which high density of high-angle boundaries and defects is typical, is reflected in increase of electrons activity and enhancement of a diffusion coefficient in grain boundary area. Taking into account that the EPP occurs with formation and subsequent dissolution of oxide films, both described effects could impact the increase of the UFG structure alloy surface dissolution, which was observed in the experiment.

Special attention should be paid to the change in the chemical composition of the alloy surface after EPP in the electrolyte containing fluorhydric acid. Fluoride ions in the surface can be assumed as a positive effect of EPP, for example, for medical items (implants) which remain in a human body for a long period. In particular, according to the authors of [14, 15] change of the oxide layer properties during surface treatment by HF solutions has a positive impact on the surface biocompatibility. Formation of TiF groups contributes to formation of new bone tissue on the implant surface.

The main target of the electrolytic-plasma polishing is reduction of surface roughness in items and achievement of the set values of Ra. Such task is topical for different items applied in medicine and mechanical engineering. In this work the surface roughness in samples during EPP changes exponentially depending on the process duration (Figure 6). Such change in roughness is typical of many previously studied alloys. It is connected with distribution of material over the height of micro-roughnesses; there is less material at the top of micro-roughnesses than at their base. So at a constant dissolution rate of the material volume unit during EPP, primary change of the height of micro-roughnesses takes place with a higher rate [1].

In this work, it is shown that the UFG structure helps to accelerate the reduction of micro-roughness on the surface in the first 2 minutes of polishing, whereas the same Ra value in the CG alloy is achieved only after 4 minutes of polishing (Figure 4). A similar behavior was observed when measuring the metal removal rate, when in the first 1 minute of polishing of a CG and UFG surface it was different and amounted to 0.01 and 0.05 mm/min, respectively (Figure 5a). Perhaps this effect is associated with a more active process of metal dissolution on the crystalline defects, including grain boundaries. As is known, the total length of grain boundaries in the UFG alloy is much higher than in the CG. Similar behavior was observed in UFG pure titanium when a passivating film was formed in acid solutions. For example, in [11], the corrosion behavior of commercially pure titanium in UFG and CG states in solutions of hydrochloric and hydrofluoric
acids was investigated. It was found that the increased corrosion resistance of UFG titanium is due to the faster formation of the passivation film. The proof of this effect was a lower density of corrosion currents, more positive corrosion potentials and low critical currents for UFG titanium. Further increase in the EPP duration already depends little on the material microstructure, as can be seen from Figure 4. Perhaps this is due to the consistent formation and entrainment of oxide films. It is obvious that the duration of the EPP process is set depending on the tasks set for a researcher, primarily related to achieving the target roughness parameters. Thus, EPP of parts from Ti alloys with UFG structure is a promising surface treatment technique, which allows achieving high surface quality which could not be achieved by other treatment techniques.

5 Conclusions

1. The electrolyte composition applied for EPP and its temperature ensure creation of conditions for steam-gas shell formation and, as a consequence, enhancement of surface polishing efficiency applied to Ti-6Al-4V with UFG structure. In the UFG alloy due to its enhanced electrochemical activity, micro-roughness sublimation, formation of oxide films and their further removal occur at lower voltages of 260 V as compared to the CG structure alloy, in which these processes take place at 280 V and higher.

2. It is shown that the UFG structure contributes to the acceleration of the reducing the surface micro-roughness in the first 2 minutes of the polishing process in comparison of CG alloy, which is due to the high density of grain boundaries and defects in the crystal structure. The total duration of the polishing process to achieve the specified roughness parameters (0.0040 ... 0.045 μm) constituted about 6 minutes for the CG and UFG states of the alloy.

Acknowledgements

The work was conducted with the support of the Russian Science Foundation under grant No. 16-19-10356 in USATU.

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