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Study of mechanical properties and corrosive resistance of ultrafine-grained α-titanium alloy Ti-5Al-2V

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ABSTRACT

The research has been conducted into the impact that structural-phase state of grain boundaries in α-titanium alloy Ti-5Al-2V has on strength, plasticity and susceptibility to intercrystalline corrosion (ICC). It is found that during Equal Channel Angular Pressing (ECAP) performed at elevated temperatures there is a change in local concentration of alloying elements (aluminum, vanadium) along α-Ti grain boundaries. The current study proves that by controlling the structure of α-titanium alloy Ti-5Al-2V through ECAP it is possible to enhance its strength and resistance to hot salt intercrystalline corrosion. Plasticity of ultrafine-grained (UFG) alloy samples at room temperature is comparable with plasticity of a coarse-grained material, while plasticity of an UFG alloy at elevated temperatures is 2–3 times bigger than plasticity of a coarse-grained material.

1. Introduction

Currently, α- and near α-titanium alloys are used as structural materials for atomic energy [1,2], including in production of heat exchange equipment for nuclear power plants (NPP) [3,4]. Such materials shall meet high requirements as to strength, plasticity and corrosion resistance [1–5].

One of the most hazardous types of α- and near-α titanium alloy destruction is hot salt corrosion, which is mostly intercrystalline in nature. Hot salt corrosion of titanium alloys occurs when titanium alloys come in contact with crystalline halide salts (chlorides, bromides, iodides) and water (bound in salt crystalline hydrates, occluded in salt crystals from air atmosphere) at temperatures above 250°C. Hot salt corrosion is mostly triggered by crystalline chlorides of alkali metals and alkaline earth metals. We shall only note that a number of scholars [6–8] believe that hot salt corrosion in titanium alloys is predominantly chemical corrosion, while some authors (see Ref. [9]) state that at certain stages of hot salt corrosion, electrochemical processes contribute greatly to the corrosion rate.

It shall be noted that while operating NPPs on ships or ice-breakers, there might be cases when seawater or brine from a water desalination plant gets into a condensate-feeding system, which may lead to water-insoluble porous salt deposits being formed on the surface of heat-exchange tubes of steam generating units and to further concentration of corrosive components in those deposits: chlorides and bromides of alkali metals and alkaline earth metals. This gives rise to salt deposits generated in pores, which factor in hot salt corrosion of heat-exchange tubing.

Operational experience in naval aviation proves that hot salt corrosion poses a serious threat to products from two-phase titanium alloys, but the operating temperatures in these cases are much higher than the operating temperature of the NPP heat exchange equipment (~250 °C). That is why studies in to fracture mechanisms observed in titanium alloys are usually conducted at 300–400 °C and higher [6,7,9–14], while any findings on the causes

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of destruction in titanium alloys at lower temperatures are very rare. Besides, they are often ambiguous, since researchers focus mainly on titanium alloys for aviation and, as a result, their susceptibility to stress corrosion cracking or corrosion fatigue under hot salt corrosion [6,7,9–14] rather than to hot salt corrosion, which is relevant for heat exchange equipment of nuclear power plants [3].

Thus, studies into susceptibility of α- and near-α titanium alloys to hot salt corrosion are highly relevant from a practical and scientific point of view.

To improve strength characteristics of modern titanium alloys, technologies based on optimization of their composition and different types of thermo-mechanical processing modes are now widely used [1,2,15–20]. One of the most promising ways to improve physical and mechanical properties, as well as performance characteristics of titanium alloys is to form an ultrafine-grained (UFG) structure in them using different methods of severe plastic deformation (SPD) [16,17,20], including the technology known as Equal Channel Angular Pressing (ECAP) [21–27].

It is generally assumed that enhanced strength of metals and alloys achieved through increased structure imperfection reduces corrosion resistance of materials [28]. The reason for that is that in corrosive environments the grain boundary, which is characterized by specific structure and functions as an area of impurity segregation, together with the alloy crystal lattice forms a microgalvanic couple [28–30]. Normally, high volume ratio of such microgalvanic couples in the fine-grain structure shall lead to intensified intercrystalline corrosion (ICC), the mechanisms of which in titanium alloys are understudied [9,30].

Of particular interest is the study into the impact that grain size and structural-phase state of grain boundaries in titanium alloys have on their susceptibility to ICC. Note shall be taken that dependence between the corrosion rate and grain size in titanium and titanium alloys is complex and ambiguous in nature: in case of grain structure refinement, corrosion resistance in the same material is known both to increase and to reduce. For instance [31,32], prove lower corrosion resistance of nano- and fine-grained titanium, while [33–35] give an illustration that fine-grain structure helps to enhance titanium corrosion resistance [36–38], fail to establish an unequivocal link. The reasons for such ambiguity can be explained by the fact that not only grain size, but also local chemical composition of grain boundaries promotes ICC in titanium alloys.

We reckon that reduced impurity concentration along grain boundaries that runs below the threshold value may help to significantly increase ICC resistance of titanium alloys. This reduction may be ensured by means of reducing the average grain size from d_1 to d_2 and respective increasing the total area of grain boundaries, as well as by providing proper conditions under which corrosive impurities are distributed evenly along new grain boundaries. This will help reduce local concentration of impurities on grain boundaries (ΔC_b) proportionally to the increase in the area of boundaries, i.e. ~ $(d_1/d_2)^2$ times.

The above approach becomes operable due to the ECAP technology that provides substantial refinement of the grain structure [21,22] and through selecting the ECAP temperature that would not only ensure grain refinement but also diffusive rearrangement of corrosive impurities along grain boundaries.

The goal of this research is to apply the above method to simultaneously improve strength and corrosion resistance of UFG α-titanium alloy Ti-5Al-2V, used to produce heat exchange equipment for NPPs on ships and icebreakers. We shall also point out that scientific literature is currently lacking any information on susceptibility of UFG α- and near-α titanium alloys to hot salt corrosion, including any results on the impact that grain size and structural and phase state of grain boundaries in α- and near-α titanium alloys may have on their susceptibility to hot salt corrosion.

The key goal of this paper is to study the impact of the structural-phase state of grain boundaries in Ti-5Al-2V α-titanium alloy on its strength and resistance to hot salt corrosion.

2. Materials and methods

Titanium deformable composition Ti-4.73wt%Al-1.88wt%V (Russian industrial titanium alloys PT3V) is the target of this research. The concentration of oxygen, nitrogen, carbon and hydrogen in the alloy was 0.042 wt%, 0.01 wt%, 0.0024 wt% and 0.04 wt%, respectively. The chemical composition of the titanium alloy is provided in Table 1. This alloy is one of the α-titanium alloys, the volume ratio of β-phase in which does not exceed 5% [3,4]. General chemical analysis of the alloy is carried out using a spectrum analyzer "FOUNDRY-Master". Control over concentrations of oxygen, nitrogen, carbon, and hydrogen is maintained through the method of reductive melting using analyzers "ELTRA ON-900" (control over O_2, C, N_2) and "ELTRA OH-900" (control over H_2).

UFG structure in 14 × 14 × 140 mm^3 samples of Ti-5Al-2V was formed using the ECAP method in a device with the intersection angle of the operating and outlet channels π/2. ECAP was carried out at deformation rate of 0.4 mm/s and deformation temperature of 450°C. The number of ECAP cycles was N = 4.

Structure studies were carried out using the scanning electron microscope Jeol JSM-6490 with energy dispersive X-ray spectroscopy (EDS) microanalyzer INCA 350 and the transmission electron microscope Jeol JEM-2100 with EDS microanalyzer JED-2300. To identify the microstructure (in studies conducted with the help of SEM), electrolytic etching was performed at room temperature in a solution of 75% H_2SO_4+15% HNO_3+10% HF (see the results presented in Fig. 1a). When studying the local chemical composition using the method of energy dispersive microanalysis, the diameter of the beam (in the analyzed area) did not exceed 10 nm (in Fig. 1b–d, the areas under study and their size are numbered from 1 to 7). With the given beam diameter, measurements of the concentration of the alloying element (~0.2 wt% in vanadium and aluminum) showed minimum scatter in different areas of the same sample, i.e. the greatest repeatability of research results was ensured. The energy dispersive analysis was carried out both by measuring the local composition of grain boundaries "at a point" and by scanning in the direction transverse to the grain boundary (see, for example, the results presented in Fig. 1e–f).

Fractographic analysis was carried out using SEM Jeol JSM-6490. X-ray diffraction analysis was performed using the automated diffraction meter "Oxford Diffraction GEMINI S".

In order to study mechanical properties, relaxation tests were run to determine such values as macroelastic limit σ_0 and yield strength σ_y [39]. Rectangular samples of 3 × 3 mm and 6 mm high were used to take measurements. Measuring accuracy of σ_0 and σ_τ – ±30 MPa, loading speed – 0.13%/s, loading time – 0.3 s, relaxation time – 60 s. Hall-Petch coefficient is determined by the formula: $K_{HP}=(\sigma_y-\sigma_0)\cdot d^{1/2}$. Alloy microhardness was measured using microhardness tester "Duramin Struers-5" with a 2 kg load. Tensile tests of flat samples shaped as a 'double blade' with working part dimensions of 2 × 2 × 3 mm were performed using the stress machine "Tinius Olsen H25K-S" at deformation rates ranging from

Table 1
Chemical composition of PT3V titanium alloy (wt.%).

Ti	Al	V	Zr	Fe	Si	O_2	N_2	C	H_2
Balance	4.73	1.88	0.019	0.11	0.03	0.042	0.01	0.0024	0.04