Corrosion resistance of ultrafine-grained pseudo-α titanium alloy PT-3V

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Abstract. Ultrafine-grained (UFG) samples of PT-3V pseudo-α titanium alloy were subjected to diffusion welding through spark plasma sintering. It has been shown that the destruction of welded UFG samples under hot salt corrosion (HSC) is two-staged: first, intercrystalline corrosion (ICC) is manifested, which then graduates to pitting corrosion. It has been established that the corrosion resistance of the weld joints is determined by the concentration of vanadium at the grain boundaries, the size and volume ratio of the β-phase particles, and the presence of pores in the weld joints. It has been shown that welded UFG samples possess a higher hardness and resistance to ICC than coarse-grained samples.

1. Introduction

Today, titanium pseudo-α Ti-Al-V alloys are widely used in shipbuilding, nuclear power engineering, etc. [1-2] Forming an ultrafine-grained (UFG) structure in titanium alloys by severe plastic deformation represents one of the promising ways to improve their performance. UFG titanium alloys are characterized by increased strength and better creep resistance and fatigue strength [3, 4]. One of the industrial application challenges for UFG titanium alloys is their welding behavior. The commonly used argon-arc or electron-beam welding will not preserve the UFG structure.

One of the worst hazards for titanium alloys in nuclear power engineering and naval aviation is hot salt corrosion (HSC) [4, 5]. This type of corrosion occurs when salt deposits are formed on the surface of equipment operating at elevated temperatures. HSC in titanium alloys is a multi-stage deterioration process under exposure to elevated temperatures, corrosive mediums (salts), and oxygen [4, 5].

The purpose of this work is to study the deterioration behavior of weld joints in samples made of PT-3V UFG alloy when exposed to HSC and, in particular, to study the impact that microstructure parameters of welded samples have on the HSC resistance.

2. Methods and materials

The object of the study was the pseudo-α titanium alloy PT-3V (Ti-4.73%Al-1.88V). The UFG structure was processed by Equal Channel Angular Pressing (ECAP) (TECAP = 450 °C, NECAP = 4, Bc mode).

Spark plasma sintering (SPS) [6, 7] is one of the latest techniques for solid state welding of structural materials, including titanium alloys [8, 9]. An important advantage of SPS is the ability to
implement high heating rates (up to 2500 °C/min), which will preserve the UFG structure with high mechanical properties in titanium alloys. A Dr. Sinter SPS-625 spark plasma sinterer was used for diffusion welding of the samples. Heating rate (Vₜ) varied from 10 to 350 °C/min, applied pressure (P) from 50 to 100 MPa, welding time from 0 to 90 min. Welding was performed in the α-phase field (600 °C), near the α-β-phase boundary (700 °C), at the beginning of the two-phase (α+β)-field (800 °C), and in the β-phase field (1030, 1140 °C). Welding was performed in a vacuum, without molds, which caused tangent stresses, perpendicular to the uniaxial pressure axis.

A Jeol JSM-6490 scanning electron microscope and a Jeol JEM-2100 transmission electron microscope were used for microstructural studies. A Shimadzu XRD-7000 diffractometer was used for average grain size in CG samples (Table 1) with an α/α’-structure near the weld joints, where β-phase (600 °C), near the α-β-phase boundary (700 °C), at the beginning of the two-phase (α+β)-field (800 °C), and in the β-phase field (1030, 1140 °C). Welding was performed in a vacuum, without molds, which caused tangent stresses, perpendicular to the uniaxial pressure axis.

A Duramin Struers 5 durometer with a load of 2 kg was used for microhardness (H) microscope were used for microstructural studies. A Shimadzu XRD-7000 diffractometer was used for X-ray diffraction analysis (XRD). A Duramin Struers 5 durometer with a load of 2 kg was used for microhardness (H) measurements. HSC tests were performed in a 300:1 mixture of NaCl and KBr crystal salts at 250 °C during 500 hours with oxygen access. A Leica DM IRM metallographic microscope was used to assess corrosive damage to the surface of samples.

3. Experimental results
Macrostructure studies show incomplete fusions of ~50-70 μm at the edges of coarse-grained (CG) samples welded under low pressures, at low temperatures, or high heating rates. At the top of the macrodefects, large pores are observed, the volume fraction of which decreases farther from the edge of the sample (away from the areas of the maximum tensile stresses). The remaining larger area of the weld joint has micropores, the volume fraction of which depends on the welding mode. It should be noted that low volume fractions of macro- and micropores are observed in the case of diffusion welding of CG samples over an interval of 700-800 °C and under low stresses (50 MPa).

There are virtually no macrodefects in the weld seams of UFG alloys, the volume fraction of macropores and micropores is small and is observed chiefly after welding at low temperatures (600 °C) or under high pressures (70-100 MPa). Varying basic SPS parameters has little effect on the average grain size in CG samples (Table 1) with an α/α’-structure near the weld joints, where β-phase particles vigorously precipitate along the boundaries of elongated grains of the α'-phase.

Table 1. Parameters of microstructure of the PT-3V alloy specimens after the diffusion welding

| Welding regime | Coarse-grained alloy | UFG alloy |
|----------------|----------------------|-----------|
| initial state  | 10-100 3-15 - 2.0-2.1 0.5 - - 3.1-3.2 | |
| 600            | 16 3.2 H 2.5 2.4-2.5 4.8 2.4 H 3.0 3.0-3.1 | |
| 700            | 17 3.0 M 2.5 2.5-2.6 5.9 3.0 L 2.8 2.8-2.9 | |
| 800 100 10 50  | 18-19 5.1 M 2.3 2.3-2.4 6.9 3.3 M 3.2 3.2 | |
| 1030           | 12 - L 2.5 2.4 - - - | |
| 1142           | 10 16-18 5.0 L 2.6 2.5 6.8 3.1 H 2.5 2.5-2.6 | |
| 700 50 10 50   | 17-18 3.5 M 2.6 2.4-2.3 5.5 3.3 M 2.7 2.8-2.9 | |
| 100 18-19 3.0 M 2.4 2.5 5.9 3.0 L 2.7 2.7-2.9 | |
| 350            | 18 3.0 H 2.4 2.5 3.8 3.3 L 2.9 3.0-3.1 | |
| 50 18-19 3.5 L 2.5 2.4-2.6 5.9 3.3 L 2.7 2.8-2.9 | |
| 700 100 10 70  | 15 3.2 H 2.7 2.6-2.7 5.3 2.6 H 2.7 2.9-3.0 | |
| 100 10 2.9 H 2.7 2.5-2.6 4.9 2.5 H 2.7 3.0-3.1 | |
| 0 18-19 3.5 H 2.5 2.5-2.6 4.7 2.0 H 2.9 2.9-3.1 | |
| 700 100 10 50  | 18-19 3.0 H 2.4 2.4-2.5 5.9 3.3 M 2.7 2.8-2.9 | |
| 50 16-17 2.0 H 2.3 2.3-2.6 9.1 3.5 L 2.6 2.8 | |
| 90 12-13 2.0 W 2.4 2.4-2.6 9.3 3.5 L 2.5 2.5-2.6 | |

Note: The volume fraction of macropores and micropores: H – High, M – medium, L – low
Table 2. Results of the corrosion testing of the welded joints of the PT-3V alloy

| Welding regime | Coarse-grained alloy | UFG alloy |
|----------------|----------------------|-----------|
|                | HSC character | Zone I | Zone II | h<sub>max</sub>, μm | h<sub>ср</sub>, μm | HSC character | Zone I | Zone II | h<sub>max</sub>, μm | h<sub>ср</sub>, μm |
| 600            | ICC          | ~600   | ~400    | C, P, IGC | 223 | 162 ± 43 | C, P, IGC | 188 | 124 ± 34 |
| 600            | ICC          | ~600   | ~400    | C, P, IGC | 223 | 162 ± 43 | C, P, IGC | 188 | 124 ± 34 |
| 700            | C, P, IGC   | 235    | 231 ± 39 | -        | 420 | 273 ± 62 |
| 800            | C, P, IGC   | 280    | 265 ± 48 | C, P, IGC | 400 | 285 ± 59 |
| 1030           | -           | 358    | 184 ± 35 | -        | -      | -          |
| 1142           | -           | -      | -       | C, P, IGC | 557 | 211 ± 45 |
| 50             | C, P, IGC   | 238    | 182 ± 45 | -        | 171 | 132 ± 24 |
| 700            | C, P, IGC   | 235    | 231 ± 39 | -        | 420 | 273 ± 42 |
| 350            | C, P, IGC   | 444    | 220 ± 92 | -        | 451 | 189 ± 36 |
| 50             | C, P, IGC   | 290    | 215 ± 49 | -        | 130 | 110 ± 30 |
| 700            | C, P, IGC   | 132    | 108 ± 21 | -        | 138 | 113 ± 28 |
| 50             | C, P, IGC   | 246    | 178 ± 77 | -        | 163 | 93 ± 40  |
| 700            | C, P, IGC   | 390    | 211 ± 82 | C, P, IGC | 385 | 249 ± 58 |
| 50             | C, P, IGC   | 358    | 184 ± 75 | -        | 358 | 184 ± 55 |
| 90             | C, P, IGC   | 163    | 125 ± 62 | -        | 512 | 297 ± 47 |

Note: P – pitting corrosion, IGC – intergranular corrosion, C – crevice corrosion

Varying the basic welding parameters has little effect on the average grain size in CG samples. The structure of the alloy structure near the weld joints has a coarse-grained α/α'-structure. The most vigorous precipitation of the β-phase is observed along the boundaries of α'-phase elongated grains, with the volume fraction of β-phase particles in the weld joint being greater than in the initial CG alloy (Fig 1). Increased heating rate, pressure, or time of exposure reduce the average size of β-phase particles in CG alloys.

It should be noted that the grain size in the UFG samples is 3-4 times less than in the CG samples, while occasional β-phase particles of 2-3 μm are observed at grain boundaries. Increasing welding temperature from 600 °C to 800 °C raises the average grain size in UFG alloys from 4.8 to 6.9 μm. Higher welding temperatures and longer times increase the size of β-phase particles and grain size. Heating rates have no marked impact on the size of β-phases but lead to smaller UFG grains.

Salt deposits on the surface of the samples after HSC tests are mixtures of NaCl, titanium oxides (TiO<sub>2</sub>, TiO), and alumina, as well as vanadium-based constituents (VO<sub>1.15</sub>, V<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>) and Al<sub>3</sub>V. Corrosion products (salt deposits) on the samples produced by SPS at temperatures above 1000 °C also consisted of NaCl, TiO<sub>2</sub>, TiO, and aluminum oxide, with aluminum constituents (TiAl<sub>2</sub>Cl<sub>8</sub>, AlTi<sub>3</sub>) and traces of VO<sub>2</sub> detected instead of vanadium-based constituents (VO<sub>1.15</sub>, V<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>, Al<sub>3</sub>V). It is important to note that XRD detected vanadium oxide peaks in corrosion products of CG samples while vanadium oxide was not found in the corrosion products of the UFG samples.

The macrostructure studies demonstrate the difference in corrosion mechanisms in the weld joints and outside. In the area of CG alloy joints, there is a combination of pitting and crevice corrosion, and the depth of crevice corrosion along the weld joint is determined by porosity of the seam. The corrosion depth in highly porous seams produced under suboptimal welding modes can exceed 300 μm. Farther away from weld joints in CG alloys, there is a combination of intercrystalline corrosion (ICC) and pitting corrosion. The largest corrosion pits were evenly distributed over the sample area. The worst corrosion failures are observed in the α'-phase area with an increased volume fraction of the...
β-phase particles. This can explain a heterogeneous distribution of corrosion pits across the surface. ICC can be observed under large corrosion pits. Consequently, ICC sets in fine-grained α'-phase fields during the first stage of HSC, and pitting corrosion develops next. The pressure rates and SPS time have the highest impact on corrosion depth in weld joints of CG samples (Table 2). It should be noted that the size of corrosive defects in CG samples is smaller than in alloy in its initial state (see [2]).

![Image](a)

![Image](b)

![Image](c)

![Image](d)

**Figure 1.** Microstructure of the CG alloy after welding at P = 50 MPa for t = 10 min and heating rate to temperatures of: (a) 50 °C/min, 600 °C; (b) 50 °C/min, 800 °C; (c) 100 °C/min, 700 °C; (d) 350 °C/min, 700 °C

UFG samples manifested crevice corrosion only in weld joints with higher porosity. Farther away from the welding line, a combination of ICC and pitting corrosion is observed, as in the case of CG samples. An increase in SPS time and temperature leads to an increased corrosion depth in UFG alloys weld joints (Table 2). For lower welding temperatures, heating rates, or pressure, corrosion was quite shallow without exceeding the ICC depth in post-ECAP UFG alloys (see [8]). Welding at 700 °C, near the (α + β)-phase boundary under low pressure (50 MPa) and a heating rate of 10 °C/min proves to be optimal – with an average corrosion depth of 110-130 μm and no crevice corrosion in weld seams. It should be emphasized that for these SPS modes, an average pitting depth in UFG samples was 1.5-2 times less than that in CG samples. Hence, it can be concluded that UFG samples have a higher corrosion resistance as compared to CG samples.

The HSC tests on UFG samples demonstrate that an increase in the SPS temperatures from 600 to 800 °C leads to an increase in the average depth of corrosion pits from 124±34 μm up to 285±59 μm, with the maximum corrosion depth growing from 188 up to 400-420 μm. An increase in the heating rates
from 50 to 350 ºC/min reduces the average corrosion depth from 304±51 down to 189±36 μm. The applied pressure and time of exposure had low-to-no impact on the corrosion depth in the UFG samples.

Figure 2. The nonuniform distribution of large corrosion pits at different sides of the joint line of the coarse-grained titanium alloy Ti-5Al-2V after HSC testing

Hardness studies have suggested that SPS modes have little impact on H_v of seams and the parent metal in CG samples. The hardness of CG samples is 2.4-2.6 GPa. The higher hardness of the samples versus the PT-3V alloy in its initial state (~2.1-2.2 GPa) may be due to its deformation hardening. This finding is indirectly confirmed by seam H_v increasing to 2.7 GPa when welded under a pressure of 100 MPa (Table 1). The hardness of the seams and parent metal in UFG samples is higher than that of CG samples by ~0.4–0.8 GPa. The highest seam hardness (~3.0–3.2 GPa) is observed in UFG samples obtained at low temperatures, high heating rates, and fast times of exposure. Increasing heating rates to 350 ºC/min can form a high-density seam with a UFG structure and high hardness (2.9–3.1 GPa).

A model has been offered to describe the impact of microstructure parameters on the susceptibility of UFG titanium alloys to HSC. It has been shown that the following has the biggest impact on the alloy susceptibility to HSC: (i) the concentration of corrosive alloying elements (AE) – vanadium, most of all – at grain boundaries, (ii) the presence of β-phase particles at grain boundaries, (iii) pores in weld joints. According to [8], the formation of grain-boundary segregations of corrosive AE and the presence of β-phase particles with a high concentration of β-stabilizing elements (vanadium) can cause microgalvanic couples that accelerate electrochemical corrosion and can lead to an accelerated chemical corrosion of grain boundaries. The negative impact of pores is primarily manifested through an increase in the available surface area involved in chemical or electrochemical reactions.

4. Conclusions
UFG samples have been shown to have better weldability than CG ones, the weld joints of which manifested incomplete fusions that cause crevice corrosion. There were virtually no seam macrodefects in UFG samples while seam porosity was very low, which ensures high resistance of the weld joints to crevice corrosion of the UFG alloy.

The corrosion resistance of welded CG samples is higher than that of PT-3V alloy in its initial state. Corrosive defects on the surface of CG samples are primarily concentrated in the field of the fine-grained α'-phase, the grain boundaries of which manifest a higher volume fraction of the β-phase.
Destruction of CG samples under HSC is two-staged: first, ICC is manifested, which then graduates to pitting corrosion.

Corrosion resistance of UFG samples depends mainly on the concentration of vanadium at the grain boundaries, the presence of β-phase particles at the grain boundaries and pores in the weld joints. It has been established that increases in the concentration of vanadium at migrating grain boundaries as SPS temperature and time grow, adversely affect the resistance to HSC. It has been shown that diffusion welding in the high-speed heating mode (350 °C/min) up to a temperature close to the phase boundary (700 °C), under a pressure of 50 MPa without holding facilitates the formation of a fine-grained structure with increased hardness and better corrosion resistance.

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