Studying Corrosion Resistance of Weld Joints of Ultrafine-Grained Titanium Alloys

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

1. Introduction
Currently, forming ultrafine-grained (UFG) structure in titanium alloys by severe plastic deformation (SPD) 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 [1, 2]. Welding of UFG titanium alloys is the most important challenge of their use. The commonly used argon-arc or electron-beam welding will not maintain the UFG structure. Spark plasma sintering (SPS) [3, 4] is one of the latest techniques for solid state welding of structural materials, including titanium alloys [5, 6]. An important advantage of the SPS system is the ability to implement high heating rates (up to 2500 °C/min), which will maintain the UFG structure with high mechanical properties in titanium alloys.

The purpose of this study is to research the decay behavior of titanium near-α alloy weld joints under hot salt corrosion (HSC). It should be noted that HSC is one of the worst hazards for titanium alloys in nuclear power engineering [7]. This type of corrosion occurs when salt deposits are formed on the surface of heat exchange equipment operating at elevated temperatures (250-270 °C).

2. Methods and materials
PT-3V coarse-grained (CG) near-α titanium alloy (Ti-4.73Al-1.88V) is the object of the study. The UFG structure was formed by Equal Channel Angular Pressing (ECAP). A Dr. Sinter SPS-625 spark plasma sintering was used to weld 7×7×3.5 mm samples. Heating rate (Vₜ) was varied from 10 to 350 °C/min, 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 (\(\alpha+\beta\))-field (800 °C) and in the \(\beta\)-phase field (1030, 1140 °C). Welding was performed in a vacuum, without molds, which caused tangent stresses, perpendicular to the pressure axis.

A Jeol JSM-6490 scanning electron microscope were used for microstructure studies. A Shimadzu XRD-7000 diffractometer was used for X-ray diffraction analysis (XRD). A Duramin Struers 5 durometer was used for microhardness \(\left( H_v \right) \) measurements. HSC tests were performed in a 300:1 mixture of NaCl and KBr crystal salts at a temperature of 250 °C over 500 hours. A Leica DM IRM metallographic microscope was used to assess corrosive damage to the surface of samples.

3. Experimental results

Structure studies show incomplete fusions of \(\sim 50–70 \, \mu m \) (Figure 1a,b) at the edges of CG samples welded at low pressures, low temperatures or high heating rates. At the top of macrodefects there are large pores, the volume fraction of which decreases farther from the edge of the sample (away from the areas of the tensile stresses). The remaining larger area of the weld joint has micropores, the volume fraction of which depends on the SPS mode (Figure 1 c,d). A low volume fraction of pores is observed following diffusion welding of CG samples at 700-800 °C and at low pressures (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 at high pressures (70-100 MPa). Varying basic SPS parameters has little effect on the average grain size in CG samples with an \(\alpha/\alpha'\)-structure near weld joints where \(\beta\)-phase particles vigorously precipitate along the boundaries of elongated grains of the \(\alpha'\)-phase.

The volume fractions of \(\beta\)-phase particles in the welded metal are greater than in the original CG alloy. Increased heating rate, pressure or time of exposure reduce the size of the \(\beta\)-phase particles. It should be noted that the grain size in the welded UFG samples is 3-4 times less than in the CG samples while occasional \(\beta\)-phase particles of 2-3 \(\mu m \) are observed at the grain boundaries. An increase in the SPS temperature and time leads to an increase in the particle size of the \(\beta\)-phase and grain size of the UFG alloy. The heating rates have no marked impact on the size of the \(\beta\)-phase particles while producing smaller UFG grains in the alloy.

**Figure 1.** Typical defects in weld joints of CG (a, c) and UFG (b, d) alloys after diffusion welding (50 °C/min, 800 °C, 10 min): (a, b) defective weld, (c, d) micropore
XRD results demonstrate that salt deposits on the surface of the samples after HSC tests are mixtures of NaCl, titanium oxides (TiO$_2$, TiO) and alumina, as well as vanadium-based constituents (VO$_{1.15}$, V$_2$Ti$_3$O$_9$) and Al$_3$V. Instead of vanadium-based constituents, aluminum-containing constituents (TiAl$_2$Cl$_8$, AlTi$_3$) and traces of VO$_2$ were detected in corrosion products of samples welded at temperatures above 1000 ºC.

**Figure 2.** Corrosion defects on the surfaces of CG samples after HSC tests: (a, b) crevice corrosion in Zone I; (c) intercrystalline corrosion in Zone II

The results of the study of weld joints demonstrate that corrosion mechanisms are different in the weld joint and outside it. In the area of CG alloy joints, there is a combination of pitting and crevice corrosion (Figure 2a, b), with crevice corrosion more than 300 μm deep in highly porous seams. Farther away from weld joints, there is a combination of intercrystalline corrosion (ICC) and pitting corrosion. The heaviest corrosion is observed after welding in the α'-phase field with an increased volume fraction of β-phase particles, which leads to a heterogeneous distribution of corrosion pits on the surface of the samples. ICC can be observed under large corrosion pits (Figure 2c). Consequently, ICC sets in fine-grained α'-phase fields during the first stage of HSC and pitting corrosion develops next. The pressure rates and time of exposure have the highest impact on corrosion depth in weld joints of the CG samples. It should be noted that the size of corrosion defects in CG samples is smaller than in the PT-3V alloy in its initial state (see [7]).

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 (Figure 3), as in the case of CG samples. An increase in welding time and temperature leads to an increased corrosion depth in UFG alloys weld joints (Table 2). For lower welding temperatures, heating rates or pressure, the corrosion was quite shallow without exceeding the ICC depth in post-ECAP UFG alloys (see [8]). Welding at 700 ºC, near the (α + β)-phase boundary at low pressure (50 MPa) and a heating rate of 10 ºC/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 welding modes the 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 compared to CG samples.
The results of HSC tests on UFG samples demonstrate that increasing welding temperature 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. Increasing heating rates from 50 to 350 °C/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 corrosion depth in the UFG samples.

Hardness studies have suggested that SPS modes have little impact on Hₜ of seams and the parent metal in the CG samples. Hardness of the CG samples is 2.4-2.6 GPa. Higher hardness of the samples versus PT-3V alloy in its initial state (~2.1–2.2 GPa) may be due to mechanical hardening of the alloys. This finding is indirectly confirmed by seam hardness increasing to 2.7 GPa when welded at a pressure of 100 MPa. The hardness of the seams and parent metal in the UFG samples is higher than that of the 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 °C/min can form a high-density seam with UFG structure and high hardness (2.9-3.1 GPa).

4. Conclusions
UFG samples have been shown to have better weldability than coarse-grained alloys, weld joints of which manifested incomplete fusions, causing crevice corrosion. There were virtually no seam macrodefects in the UFG samples while seam porosity was very low, which ensures high resistance of weld joints to crevice corrosion in the UFG samples.

The corrosion resistance of the CG welded samples is higher than that of PT-3V alloy in its initial state. Corrosive defects are distributed across the surface of CG samples unevenly and 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.

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