Spark plasma sintering for high-rate diffusion welding of a UFG titanium alloy PT3V

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Abstract. This is the first ever paper to address the prospects of using Spark Plasma Sintering (SPS) for high-rate diffusion welding of a high-strength ultrafine-grained (UFG) α-titanium alloy Ti–5Al–2V. The effect of growing diffusion welding intensity in UFG alloys is also described. Welds of a UFG α-titanium alloy Ti–5Al–2V obtained with SPS are characterized by high density, strength, and corrosion resistance. The rate of weld sealing in UFG alloys is shown to be in nonmonotonic (maximum) dependence on the heating rate.

1. Introduction

Besides, α- and near α-titanium alloys are widely used in petrochemistry, shipbuilding, in production of engineering structures operated at freezing temperatures, etc., requirements as to reliability and resources for which are getting stricter day by day. One of the most promising ways to improve mechanical properties of titanium alloys is to form an ultrafine-grained (UFG) structure in them using different methods of severe plastic deformation (SPD). It ensures a unique combination of high strength, ductility, corrosion resistance, superplasticity, etc.

One of the key challenges preventing extensive use of UFG materials is welding. Traditional argon-arc welding or electron-beam welding accompanied by metal melting fail to preserve a UFG structure with high mechanical properties in a weld. Spark Plasma Sintering (SPS) offers high chances of obtaining high-strength welds since the idea underlying this innovative technology involves rapid heating (up to 2500°C/min) in vacuum or inert atmosphere. This is achieved by sending high-power millisecond DC pulses through the specimen along with applying pressure [1–4]. This technology produces high-density structures in UFG materials at lower optimal sintering temperatures. High heating rates and faster diffusion at lower heating temperatures are crucial for restricting grain growth and preserving a UFG structure in the material.

This paper aims at the study of potential that SPS has for diffusion welding of high-strength corrosion-resistant UFG α-titanium alloys used in nuclear engineering.

2. Experimental

The study focuses on Ti–4.73Al–1.88V alloy (Russian industrial name PT3V). A UFG structure in the alloy was formed with ECAP.

Diffusion welding of specimens sized 7 × 7 × 3.5 mm³ was performed using Dr. Sinter model SPS-625. Surface roughness varied as a result of polishing with diamond paste of different dispersion level.
The degree of roughness in specimens was 40–60 µm. Heating rate \( (\dot{V}) \) varied from 10 to 350°C/min, welding temperature \( (T) \) ranged from 600 to 900°C, applied pressure \( (P) \) changed from 50 to 100 MPa. The degree of shrinkage \( (L_{eff}) \) and shrinkage rate \( (S_{eff}) \) were monitored with a dilatometer integrated in Dr. Sinter model SPS-625. Welding was performed in vacuum (6 Pa). To account for the contribution of SPS-625 thermal expansion into experimentally measured shrinkage \( L_{eff} \), shrinkage studies were performed without specimens \( (L_0) \), afterwards true dependence of temperature on shrinkage was calculated using the formula \( L(T) = L_{eff}(T) - L_0(T) \).

Structure studies were carried out using Jeol JSM-6490 SEM and Jeol JEM-2100 TEM. Microhardness \( (H_v) \) measurements were made with Duramin Struers-5. In order to study mechanical properties, relaxation tests were run to determine such values as macroelastic limit \( \sigma_0 \) and yield strength \( \sigma_y \) [5]. Tensile tests of flat specimens shaped as a 'double blade' with working part dimensions of 2 × 2 × 3 mm were performed using Tinius Olsen H25K-S stress machine.

Electrochemical studies were carried out in an aqueous solution of 10%HNO_3 + 0.2%HF with R-8 potentiostat (Russia). Ahead of tests, the surface of the specimen was covered with corrosion-resistant coating except for a 1 × 10 mm² spot (corrosive) located in the center of a cross-section, in the weld area. Prior to electrochemical tests, the specimen was kept in an electrochemical cell in an aqueous solution of 0.2%HF+10%HNO_3 until a stationary potential value was reached (holding time no less than 2 h), after which \( E_{corr}(i_{corr}) \) dependence was surveyed at the scanning rate of 0.5 mV/s.

3. Results and discussion

3.1. Experimental results

The alloy in the CG state is characterized by irregular grain size distribution. The average grain size varies from 10–20 µm to 50–100 µm. The average grain size after \( N = 4 \) ECAP cycles is 0.2–0.5 µm. EDS analysis proves that variation in local concentration of aluminum and vanadium along different grain boundaries is insignificant [6].

In-situ TEM studies performed during stage heating show that recrystallization during annealing of a UFG alloy is observed at 500°C and above. Along with the onset of grain growth, titanium carbide nanoparticles with an average size of 5–15 nm are observed in the structure of a UFG alloy. After heating to 700–800°C, the average size of titanium carbide particles reaches 30–50 nm, the average grain size in a UFG alloy is 7–9 µm. Any significant difference in average sizes and volume fractions of carbide particles Ti–C in coarse-grained and UFG alloys is not observed.

Research into mechanical properties proves that formation of a UFG structure in alloy with ECAP increases macroelastic limit \( (\sigma_0) \) from 400–420 to 730–750 MPa, yield stress \( (\sigma_y) \) from 600–620 MPa to 1020–1050 MPa, and microhardness limit \( (H_v) \) from 2.0–2.1 GPa to 3.1–3.2 GPa, respectively. Research into thermal stability of mechanical properties shows that softening of a UFG alloy starts after heating to 500–550°C, which corresponds to recrystallization temperature. A slight increase in macroelastic limit and yield stress of PT3V alloy at low temperatures \( (T \leq 450–500°C) \) apparently results from precipitation of titanium carbide nanoparticles.

Comparative analysis of mechanical tensile tests at high temperatures shows that UFG alloy specimens at high temperatures are characterized by higher plasticity and lower flow stress. At deformation temperatures rising from 600 to 800°C, the flow stress in a CG alloy goes down from 355–360 to 125–130 MPa, while plasticity \( (\delta) \) grows from 230 to 360%. The results of testing UFG alloy specimens in similar conditions show that \( \sigma_y \) goes down from 165 to 70 MPa, while plasticity \( (\delta) \) goes up from 190 to 470–475% at deformation temperatures growing from 600 to 800°C.

Figure 1a shows dependences of shrinkage on heating time \( L(t) \) for CG and UFG alloy specimens, while figure 1b presents dependences of shrinkage and shrinkage rate on welding temperature (continuous heating) for CG and UFG alloys. (Figure 1a also shows the temperature curve during heating.) The analysis of \( L(T) \) dependences proves that during continuous heating, a monotonic shrinkage increase is observed, while dependences of shrinkage rate on heating temperature \( S(T) \) have
the usual two stages with a maximum that are typical of $S(T)$ dependences observed during sintering UFG materials. As can be seen from the figures, shrinkage (diffusion welding) of UFG specimens under similar heating conditions starts at lower temperatures than shrinkage (diffusion welding) of CG specimens. The degree of shrinkage for UFG specimens is visibly higher than that for CG alloys.

![Figure 1](image1.png)

**Figure 1.** Shrinkage curves (welding diagrams) for coarse-grained and UFG alloy specimens ($V = 100^\circ$C/min, $P = 100$ MPa): (a) dependence of temperature and shrinkage on heating time for coarse-grained (1) and UFG (2) alloy specimens; (b) dependences of shrinkage and shrinkage rate on welding temperature for coarse-grained (1) and UFG (2) alloy.

Generalized results of structural studies corroborate the observed effect of faster weldability in UFG alloys. Electron-microscopic studies show that the average size and volume fraction of pores in UFG specimens are much smaller than in CG materials (figure 2). Note that SPS allows for very thin welds (figure 2b) that account for much higher operational reliability of welded structures. Analysis of histograms presented in figures 2c, 2d that show pore size distribution (corresponding to figures 2a, 2b) proves that a coarse-grained metal weld has bigger pores with an average size of ~ 1.5 µm, while a UFG metal weld has pores with an average size of ~ 0.25–0.5 µm. Studies of mechanical properties suggest that the hardness of welds obtained with SPS at temperatures below recrystallization temperature corresponds to the hardness of the base metal measured at a distance of no less than three widths of a weld wall from the seam edge.

![Figure 2](image2.png)

**Figure 2.** Weld from coarse-grained (a) and UFG (b) alloy obtained at the same welding temperature ($T = 850^\circ$C), heating rate ($V_h = 50^\circ$C/min) and pressure ($P = 50$ MPa). The white arrows indicate pores.
Let us analyze the impact of key factors (temperature, pressure, heating rate, holding time) on microstructural parameters of a welded joint obtained with SPS during high-rate welding of specimens obtained from UFG alloy PT3V. Dependences of shrinkage and shrinkage rate on the above parameters are shown in figure 3. As can be seen from \( L(T) \) and \( S(T) \) dependences, within the range of welding temperatures below \( \alpha \leftrightarrow \beta \) phase transition temperature, maximum shrinkage \( (L_{\text{max}}) \) and maximum shrinkage rate \( (S_{\text{max}}) \) in UFG alloy specimens are several times higher than \( L_{\text{max}} \) and \( S_{\text{max}} \) in specimens produced from a CG alloy PT3V. Within the temperature range of over 1000°C exceeding the temperature of \( \alpha \leftrightarrow \beta \) phase transition, there is no visible difference between \( L_{\text{max}} \) and \( S_{\text{max}} \) for a coarse-grained and UFG alloy specimens. Thus, it can be assumed that at low heating temperatures, the welding intensity in UFG alloy specimens is much higher than that in CG alloy specimens.

This is accompanied by a decrease in the typical scale of diffusion mass transfer \( x \) that is proportionate to grain size \( x = d/2 \), and therefore, by a decrease in the standard time of diffusion mass transfer \( \tau_{\text{diff}} = \delta D_b/\alpha^2 \), where \( \delta \) is the grain boundary width and \( D_b \) is the grain boundary diffusion coefficient. A fine grain size in a UFG alloy dramatically reduces standard time of diffusion mass transfer \( \tau_{\text{diff}} \) required for diffusion controlled dissolution of pores located near non-equilibrium grain boundaries.

Figure 3b shows dependences of shrinkage \( L_{\text{max}} \) and shrinkage rate \( S_{\text{max}} \) on applied pressure \( (P) \). As can be seen from \( L_{\text{max}}(P) \) and \( S_{\text{max}}(P) \) dependences, an increase in applied pressure from 50 to 100 MPa results in an increase in shrinkage rate \( S_{\text{max}} \) from 1.5 \( \times \) 10\(^{-3} \) to 5.8 \( \times \) 10\(^{-3} \) mm/s for a CG alloy and from 1.6 \( \times \) 10\(^{-3} \) to 23 \( \times \) 10\(^{-3} \) mm/s for a UFG alloy. We reckon that the results obtained testify to a big role of plastic deformation processes in diffusion welding of a CG and UFG alloy (for more details see Discussion). This assumption is also corroborated by significant shrinkage of specimens \( (L_{\text{max}} \sim 1–8 \text{ mm}) \) exceeding surface roughness of specimens after their mechanical polishing.

Analysis of \( S_{\text{max}}(V) \) and \( L_{\text{max}}(V) \) dependences presented in figure 3c shows that the dependence of shrinkage and shrinkage rate on heating rate for coarse-grained alloy specimens in monotonically descending: with the heating rate rising from 10 to 350°C/min, shrinkage \( L_{\text{max}} \) goes down from 0.80 to 0.01 mm, while shrinkage rate \( S_{\text{max}} \) falls from 4.0 \( \times \) 10\(^{-2} \) to 1.5 \( \times \) 10\(^{-2} \) mm/s. This effect is obviously attributable to a decrease in standard time \( \tau_{\text{diff}} \), within which diffusion welding of specimens takes place, and consequently, to a decrease in time required for diffusion controlled dissolution of pores in a weld. \( S_{\text{max}}(V) \) and \( L_{\text{max}}(V) \) dependences for a UFG alloy are more complex. As can be seen from figure 3c, with heating rate rising from 10 to 350°C/min, shrinkage \( L_{\text{max}} \) goes down from 2.14 to 1.23 mm, while shrinkage rate \( S_{\text{max}} \) nonmonotonically changes with growing heating rate: with \( V \) growing from 10 to 100°C/min, \( S_{\text{max}} \) increases from 3.8 \( \times \) 10\(^{-2} \) to 1.6 \( \times \) 10\(^{-2} \) mm/s, with heating rate further rising to 350°C/min, \( S_{\text{max}} \) goes down to 0.8 \( \times \) 10\(^{-2} \) mm/s. We assume that such an unexpected result can be explained as follows:
with heating rate growing, the size of recrystallized grain $d$ drops leading to a decline in the typical scale of diffusion mass transfer $x \sim d/2$ and consequently, to a decline in the standard time required to complete metal sealing and dissolution of pores in a weld. With the heating rate further rising, the factor associated with reduced welding time becomes crucial again and the sealing rate decreases.

As shown above, during high-rate low-temperature diffusion welding of UFG alloys, weld hardness is rather high (~3.2–3.3 GPa) and approximates weld hardness of a UFG alloy after ECAP (~3.5–3.6 GPa). Besides, it exceeds weld hardness achieved with argon arc welding (~2.35–2.40 GPa) or electric fusion welding (~2.40–2.45 GPa). Microhardness of weld joints in coarse-grained specimens is ~2.4–2.6 GPa and hardly depends on diffusion welding modes. It is noteworthy that weld microhardness during welding UFG alloys at low temperatures (600–700°C) is 0.4–0.6 GPa less than microhardness of a base metal away from the weld: after diffusion welding of a UFG alloy at 600°C (100°C/min, 50 MPa, holding time $t = 10$ min), weld microhardness is 2.7 GPa, while microhardness away from the weld is 3.0–3.1 GPa. Note also that with temperature rising to 800°C, weld H, goes down to 2.5 GPa, while metal microhardness away from the weld declines to 2.6–2.7 GPa. Thus, it is safe to say that the weld metal obtained after welding UFG alloys is characterized by lower hardness than the base metal away from the weld. Similar results were obtained while studying the impact that the heating rate and applied pressure have on weld microhardness in UFG metals. Analysis of these results shows that with heating rate rising from 50 to 350°C/min, weld microhardness goes slightly up from 2.4 to 2.6 GPa, while microhardness of a base metal away from the weld grows from 2.7–2.75 to 2.9 GPa. An increase in applied pressure from 50 to 100 MPa leads to a slight increase in hardness from 2.4 to 2.5 GPa and to an increase in microhardness of a metal away from the weld from 2.7–2.8 to 3.0–3.1 GPa.

Microhardness of welds in CG specimens equals microhardness of a metal away from the weld or (at low welding temperatures (700°C and below) and low heating rates (not more than 50°C/min)) is 0.1–0.15 GPa more than microhardness of a metal away from the weld. We reckon that increased microhardness of a weld in coarse-grained alloys can be caused by plastic deformation in surface layers of a coarse-grained alloy and consequently their strain hardening (work hardening). Since the defect structure recovery rate in a coarse-grained alloy during high-rate heating is rather low, the hardened layer lasts during low temperature sintering$^1$.

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$^1$ Since the average grain size in the weld in UFG alloys hardly differs from the average grain size of a metal away from the weld (figure 4), the reasons for reduced weld microhardness in UFG alloys are still vague. We reckon that the most probable reason for reduced weld microhardness in UFG alloys is grain boundary recovery leading to reduced density of defects in UFG alloy grain boundaries.
Analysis of weld grain structure parameters shows that welding temperature and heating rate have the biggest impact on the average grain size in a weld joint. As can be seen from grain size distribution histograms, an increase in welding temperature from 600 to 800°C increases an average grain size in a UFG alloy weld from 3 to ~ 5 µm, while an increase in heating temperature from 10 to 350°C/min reduces an average grain size in a UFG alloy weld from 10–15 to 4–6 µm. An average grain size in weld joints in CG specimens within the experimental accuracy corresponds to an average grain size in a coarse-grained alloy.

Let us analyze the level of corrosion resistance in the weld joints obtained. When comparing potentiodynamic dependences for coarse-grained and UFG alloys after diffusion welding, we noted that corrosion current density ($i_{\text{cor}}$) of welds in a UFG alloy appears to be lower than that in a coarse-grained alloy obtained under similar welding temperature and rate conditions. Note that at higher welding temperatures, differences in corrosion resistance between coarse-grained alloy welds and UFG alloy welds grow – after welding at 600, 700, and 800°C, the corrosion current density ratio for UFG alloy welds and coarse-grained alloy welds is 1.6, 1.7, and 2.1, respectively. The analysis of potentiodynamic dependencies shows that faster heating rates result in bigger corrosion resistance of welds. Corrosion current density $i_{\text{cor}}$ in UFG alloy welds obtained at $V_h = 50^\circ$C/min is 0.98 mA/cm², while at $V_h = 200^\circ$C/min, $i_{\text{cor}} = 0.5$ mA/cm². Corrosion potential thus grows by ~ 40 mV from ~490 mV to ~450 mV. Current density $i_{\text{cor}}$ for coarse-grained alloy welds obtained at the heating rates of 50 and 200°C/min is 2.5 and 2.8 mA/cm², respectively. In this case, corrosion potential is essentially independent of the heating rate and remains constant within the experimental error of ±10 mV caused by a specimen-to-specimen spread of properties. Analysis of the dependence of potential on holding time shows that steady potential for UFG titanium alloy welds appears to be somewhat bigger than for coarse-grained alloy welds, which also proves increased corrosion resistance of UFG alloy welds. Thus, it is fair to say that corrosion resistance of UFG alloy welds appears to be higher than that of coarse-grained alloy welds.

Figure 5 shows images of the surface of CG alloy specimens (figure 5a) and UFG alloy specimens (figure 5b) after corrosion electrochemical investigation. As can be seen from figure 5, rather active corrosion decay occurs in the weld during electrochemical investigation. As can be seen from the figures, etching (corrosion decay) is observed during testing in grain boundaries of titanium alloys. This suggests that any changes observed in corrosion properties are primarily due to the processes that occur along grain boundaries during high-rate diffusion welding of specimens.

![Figure 5. Surface of CG (a) and UFG (b) alloy welds after corrosion electrochemical investigation. Welding modes (10°C/min, 50 MPa, 10 min, 700°C).](image_url)
elements along grain boundaries (vanadium) and reduced difference in vanadium ($\Delta C_V$) and aluminum ($\Delta C_{Al}$) concentrations between their concentration in the crystal lattice ($C_i$) and in the grain boundary ($C_b$). The difference in aluminum and vanadium concentration between the crystal lattice and the grain boundary in a CG alloy may reach $\Delta C_{Al} = 5.6$ at % and $\Delta C_V = 12.9$ at %, respectively [5]. Studies of the grain boundary composition in a UFG alloy after ECAP show that $\Delta C_{Al}$ and $\Delta C_V$ approximate $\sim 0.35–0.40$ at % and slightly exceed the range of experimental error in determining the concentration of aluminum and vanadium with EDS ($\pm 0.2–0.3$ at.%). (see also [5]).

While heating a UFG alloy to the temperature exceeding the recrystallization initiation temperature, fast migrating grain boundaries cover atoms of doping elements (aluminum, vanadium) uniformly distributed in the crystal lattice, which again leads to an increase in $\Delta C_{Al}$ and $\Delta C_V$. In this case, the concentration of doping elements in the grain boundary will obviously be proportionate to a standard distance over which a grain boundary moves and consequently, to the size of a recrystallized grain. Thus, a decrease in the migration rate of a grain boundary due to an increase in the heating rate or decrease in the welding temperature is expected to boost corrosion resistance of a titanium alloy as demonstrated experimentally.

4. Conclusions

SPS is shown to allow efficient high-rate diffusion welding of titanium alloys and at the same time to preserve a UFG structure, high hardness and corrosion resistance in a weld. Pores in UFG alloy welds are found to diffuse faster due to highly intensive diffusion processes taking place along non-equilibrium grain boundaries and a small-scale diffusion mass transfer that is proportionate to grain size.

The dependence of weld sealing rate (welding rate) on heating rate is shown to be different for coarse-grained and UFG alloys. An increase in the heating rate in coarse-grained alloys leads to a monotonic decrease in the sealing rate caused by reduced welding time at high heating rates. The weld sealing rate in UFG alloys is in nonmonotonic (maximum) dependence on the heating rate. We reckon that it is due to the fact that with the heating rate growing, the size of recrystallized grain $d$ decreases leading to a decline in the typical scale of diffusion mass transfer $x \sim d/2$ and consequently, to a decline in the standard time required to complete metal sealing and dissolution of pores in a weld. With the heating rate rising up, the factor associated with reduced welding time becomes crucial again and the sealing rate decreases.

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