Pulse Pressuring Diffusion Bonding of Ti–4Al–2V/0Cr18Ni9Ti with Nanostructured Layer Synthesized by Surface Self-nanocrystallization

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Nanostructured surface layer was synthesized on the end face of Ti–4Al–2V alloy and 0Cr18Ni9Ti austenitic stainless steel rods by means of Surface self-nanocrystallization (SSNC). Making treated end surfaces as bonding interfaces, transition joint of Ti–4Al–2V alloy and 0Cr18Ni9Ti stainless steel bars was prepared by pulse pressuring diffusion bonding (PPDB) on Gleeble-1500D tester at 850°C for 80 s, the maximum and minimum pulse pressuring were 8 MPa and 50 MPa respectively, and cycle (N) and frequency (f) of pulse load were 40 times and 0.5 Hz respectively. Bonded joints were tensed on CMT5105 style instron. Microstructure of transition joint was investigated by scanning electron microscope (SEM) and X-ray energy dispersive spectroscope (EDS). The reaction products on the fracture were detected using X-ray diffraction (XRD). Research results showed that the maximum tensile strength reached 384.0 MPa, cleavage fracture took place while tension test of joints. Brittle intermetallic compounds such as Fe2Ti, FeTi and σ phase presented on the fracture, and on the titanium alloy side, α-Ti transformed into β-Ti in the vicinity of interface while diffusion bonding.

KEY WORDS: surface self-nanocrystallization; Ti–4Al–2V; 0Cr18Ni9Ti; pulse pressuring diffusion bonding.

1. Introduction

Due to low density, high specific strength, rich corrosion resistance, the excellent high temperature strength and low-temperature flexibility, titanium and titanium alloy were applied widely to multiple fields such as the aerospace, petrochemical industry and nuclear power. But, due to the low Young’s modulus and poor high temperature creep,1,2) titanium alloy is commonly jointed with stainless steel by means of diffusion bonding to fabricate workpiece used in high temperature. However, the tight joints of titanium alloy and stainless steel can be formed only when bonding temperature is above 800°C. At the same time, there are tremendous physicochemical performance differences for the two materials. The two reasons result in easily formation of brittle intermetallic compounds at bonding interface, growth of grains in the diffusion layer and the increment of joint deformation.

It is well known that nanocrystalline (nc) material exhibits many novel properties relative to their coarse-grained counterparts, such as high strength and hardness, excellent superplasticity at low temperature and good wear property.3) Otherwise, a large number of defective grain boundaries (GBs) in nanostructured materials may act as fast atomic diffusion channels, so that atomic diffusion in nc material is much enhanced relative to their coarse-grained polycrystalline counterparts.3,4) Making use of atomic high diffusion feature in nc material, surface self-nanocrystallization (SSNC)5) has been applied to chemical heat treatment of many metal materials, research results6–11) show that atomic diffusion coefficient is greatly enhanced in the nanostructured surface layer under low temperature, at the same time, heat treatment time is shorten greatly, which inaugurate new path for low-temperature and high-efficiency chemical heat treatment of metal materials. Therefor, bonding interfaces of Ti–4Al–2V alloy and 0Cr18Ni9Ti stainless steel rods were processed by means of SSNC, for increasing of atomic diffusion coefficient in the diffusion layer, shortening of bonding time, reducing of bonding temperature, suppression of intermetallic compound growth in the course of diffusion bonding. Ti–4Al–2V alloy and 0Cr18Ni9Ti stainless steel rods with nanostructured layer on the bonding interface were bonded by constant temperature and pressure diffusion bonding (CTPDB),12) research results showed that applying SSNC into CTPDB of Ti–4Al–2V alloy and 0Cr18Ni9Ti stainless steel bars can increase of atomic diffusion coefficient, suppress of intermetallic compound growth, and advance tensile strength of joints. It was reported that Ti–4Al–2V and 0Cr18Ni9Ti rods with nanostructured layer on the bonding interface was bonded by pulse pressuring diffusion bonding (PPDB) under 800°C,13) result showed that joints of titanium alloy and stainless steel was obtained under 800°C for the first time, and intermetallic compounds was not yielded on in-
Surface of joints, but the maximum tensile strength of joint was only 262.0 MPa. Therefore, the tensile strength of Ti–4Al–2V and 0Cr18Ni9Ti joint demand be advanced by adjusting diffusion bonding technology. In the paper, Ti–4Al–2V and 0Cr18Ni9Ti rods were bonded by PPDB at 850°C after bonding interface were processed for nanostructured layer by SSNC, microstructures and mechanical behaviour of joint were researched.

### 2. Experimental

#### 2.1. Experimental Materials

Commercial Ti–4Al–2V titanium alloy and 0Cr18Ni9Ti austenite stainless steel rods were selected for experiment. The Ti–4Al–2V and 0Cr18Ni9Ti rods were cut into specimens of \( \Phi 12 \times 30 \) mm. The chemical compositions and room temperature tensile properties of samples are given in Table 1 and Table 2.

#### 2.2. Diffusion Bonding Experiment

After the HESP treatment, the roughness of the treated surface was increased in some short. In order to satisfying with interface condition of diffusion bonding, treated surface were prepared by conventional metallographic technology. The Ti–4Al–2V and 0Cr18Ni9Ti rods were cut into specimens of \( \Phi 12 \times 30 \) mm. The chemical compositions and room temperature tensile properties of samples are given in Table 1 and Table 2.

After SSNC by means of high energy shot peening (HESP), about 50 \( \mu \)m and 80 \( \mu \)m thick nanostructured layer were obtained on the Ti–4Al–2V and 0Cr18Ni9Ti treated ends respectively. Nanomicrostructures prepared by the SSNC include a large volume fraction of stored energy and non-equilibrium defective resulting in refining of coarse grains such as dislocations, vacancy, subboundary, which may promote chemical reaction of different atoms and enhance atomic diffusion coefficient.

**Table 1.** Chemical composition of tested materials (mass%).

| Alloy     | Fe   | Ti   | C    | Si   | Ni   | Cr  | S   | Mn  | P   | Al  | V   | N   | H  | O  |
|-----------|------|------|------|------|------|-----|-----|-----|-----|-----|-----|-----|----|----|
| 0Cr18Ni9Ti| Base | 0.29 | 0.04 | 0.47 | 8.37 | 17.22 | 0.02 | 1.21 | 0.034 | –   | –   | –   | –  | –  |
| Ti–4Al–2V | 0.069| Base | 0.01 | 0.04 | –   | –   | –   | –   | –   | –   | –   | 4.5 | 2.2 | 0.023 | 0.003 | 0.05 |

**Table 2.** Tensile properties of base materials at room temperature.

| Alloy     | 0.2% yield strength (MPa) | Ultimate tensile strength (MPa) | Fracture strain (%) |
|-----------|---------------------------|-------------------------------|-------------------|
| 0Cr18Ni9Ti| 196                       | 541                           | 40               |
| Ti–4Al–2V | 660                       | 740                           | 18               |

**Fig. 1.** Technology curve of pulse pressuring diffusion bonding.

**Fig. 2.** Tension–displacement curves of joints formed at 850°C while tension test. Maximum tension of sample 1 joint achieves 18.02 kN, and that of sample 2 joint is 19.29 kN. By conversion, tensile strength of two joints

\( P_{\text{min}} = 8 \text{ MPa} \) and maximum pressure \( P_{\text{max}} = 50 \text{ MPa} \) was applied along the longitudinal direction of the assemblies. The cycle (\( N \)) and frequency (\( f \)) of pulse load were 40 times and 0.5 Hz respectively. During bonding, both initial heating velocity and final cooling velocity were 5°C/s. The technology curve of diffusion bonding is shown in Fig. 1. Three joints were prepared by PPDB, thereinto, two joints numbered sample 1 and sample 2 were used for tensile test, the other one was used for microstructures research.

After diffusion bonding, joints were annealed for 1 h at 400°C in vacuum furnace to eliminate bonding stress. Tensile samples were cut into \( 8 \times 50 \) mm in size, and experimented on the CMT5105 style instron. SEM specimens of joints were prepared by usual grinding and polishing techniques. The titanium alloy and stainless steel sides were etched with Kroll reagent (6%HCl + 2%HF + 92%H2O) and aqua regia (60%HCl + 20%HNO3 + 20%H2O), respectively. Microstructures and fractures of joints were observed by a TESCAN VEGA II scanning electron microscope (SEM, operating at a voltage of 30 kV), meanwhile, curves of diffusion atoms in diffusion layers were measured by X-ray energy dispersive spectroscopy (EDS). The reaction products near the bonding interface on both sides of bulk specimens were detected using X-ray diffraction (Rigaku D/MAX).

### 3. Results

#### 3.1. Tensile Strength of Joint

**Figure 2** shows tension–displacement curves of joints formed at 850°C while tension test. Maximum tension of sample 1 joint achieves 18.02 kN, and that of sample 2 joint is 19.29 kN. By conversion, tensile strength of two joints...
are 358.7 MPa and 384.0 MPa respectively. However, maximum tensile strength of joint was only 321.0 MPa\(^{14}\) after untreated samples were bonded by same diffusion bonding technology. The result shows that the SSNC treated for bonding interface of Ti–4Al–2V and 0Cr18Ni9Ti bars can advance tensile strength of bonded joint.

### 3.2. Analysis of Microstructure

The SEM images and EDS profile of the transition joints are given in Fig. 3. The SEM images show grains in the vicinity of diffusion interface are refined. In the diffusion layer (as shown in Fig. 3(a)), four zones such as A, B, C and D can be divided according to different microstructures feature. Region A is stainless steel matrix consisted of fine grains, region B presents black zigzag groove after etched, region C presents darkish brown and don’t explicit grain boundaries, region D is titanium alloy base. Corresponding line scanning energy spectrum (in the Fig. 3(b)) shows Fe and Cr atoms have diffused into titanium alloy with different distances, and Ti atoms diffused into stainless steel also. Diffusion distance of Fe and Ti atoms are about 10 \(\mu\)m and 4 \(\mu\)m respectively. However, Diffusion distance of Fe atom was no more than 5 \(\mu\)m in the untreated sample, and that of Ti atom was only or so 3 \(\mu\)m (as shown in Fig. 3(c)\(^{15}\)) in the untreated sample. The result showed Fe and Ti atoms diffused to more distances in the SSNCed sample than in the untreated sample while diffusion bonding at same technology.

Concentrations of diffusion atoms such as Fe, Ti, Cr, Ni and Al in the diffusion layer were measured according to the mark in the Fig. 3(a) and summarized in Table 3. According to compositions of samples (as shown in Table 1)

### Table 3. Concentrations of diffusion atoms in diffusion layer (mass%).

| positions | Al  | Ti  | V   | Cr  | Fe  | Ni  |
|-----------|-----|-----|-----|-----|-----|-----|
| S1        | 12.89 | 0.86 | 13.31 | 62.51 | 10.43 |
| S2        | 10.82 | 0.56 | 18.77 | 60.01 | 8.83 |
| S3        | 1.65  | 19.04 | 69.28 | 10.04 |
| S4        | 0.84  | 19.04 | 70.53 | 9.58 |
| S5        | 1.01  | 19.12 | 71.23 | 8.64 |
| T1        | 2.15  | 39.93 | 1.25 | 7.92 | 40.88 | 7.87 |
| T2        | 2.72  | 52.82 | 1.95 | 7.05 | 30.65 | 3.62 |
| T3        | 4.18  | 74.08 | 1.78 | 2.25 | 16.35 | 1.36 |
| T4        | 4.05  | 84.01 | 2.53 | 0.64 | 8.54 | 0.23 |
| T5        | 4.46  | 88.28 | 2.43 | 4.83 |
| T6        | 4.85  | 92.07 | 2.43 | 0.65 |
| T7        | 3.75  | 93.68 | 2.57 |
and concentrations of elements measured in Table 3, region A and D in the Fig. 3 are stainless steel matrix and titanium alloy base respectively. Plotting these datum of Fe, Ti and Cr in Table 3 into curve in the ternary Fe–Cr–Ti phase diagram at 850°C (as shown in Fig. 4). One can see that concentration of Cr cross into \(\chi + \alpha, \chi + \lambda\) three phase zone, with decreasing of temperature, a little of Cr can combine Ti and Mo into \(\sigma\) phase.\(^{16}\) According to Fe–Ti binary phase diagram,\(^{17}\) Fe and Cr can form infinite sodoloid each other. Fe and Cr can but form finite sodoloid while temperature is no more than 830°C. With reducing of Cr concentration, curve of concentration cross into \(\lambda\) consist of \(\text{Fe}_2\text{Ti}\) primarily, \(\text{Fe}_2\text{Ti} + \lambda, \text{Fe}_2\text{Ti} + \lambda + \beta\text{-Ti}, \text{Fe}_2\text{Ti} + \beta\text{-Ti}\) in turn. Herein, curves of Fe and Ti concentrations are crossing each other (as shown in Fig. 3(b)), in the light of definition of diffusion, the zone includes initial interface of bonding materials. Therefore, region B in Fig. 3(a) consists of a little of \(\beta\text{-Ti}\) and brittle intermetallic compounds such as \(\sigma, \text{Fe}_2\text{Ti}\) and \(\text{Fe}_2\text{Ti}\) whose corrosion resistant is poor, and presents black groove after etched. Compositions of region C in Fig. 3 distribute into \(\beta\text{-Ti}\) phase area in Fe–Ti–Cr ternary phase diagram (as shown in Fig. 4), which indicates region C is \(\beta\text{-Ti}\) phase whose corrosion resistant is good. \(\beta\text{-Ti}\) stabilizing element such as Fe, Ni and Cr diffused into titanium alloy base and \(\alpha\text{-Ti}\) transformed into \(\beta\text{-Ti}\) while diffusion bonding, \(\beta\text{-Ti}\) phase did not make phase change and preservation while cooling from bonding temperature to room-temperature quickly. Because of good corrosion resistant, region C did not present explicit boundaries (as shown in Fig. 3(a)).

### 3.3. Analysis of Fractures

Figure 5 is XRD pattern of the fracture surface of diffusion bonded joint. The XRD pattern indicates that phases on the 0Cr18Ni9Ti stainless steel side consisted of \(\gamma\text{-Fe}, \sigma, \text{Fe}_2\text{Ti}, \text{Fe}_2\text{Ti} + \lambda, \text{Fe}_2\text{Ti} + \lambda + \beta\text{-Ti, Fe}_2\text{Ti} + \beta\text{-Ti}\) (see Fig. 5(a)), and on the Ti–4Al–2V alloy side phases are consisted of \(\beta\text{-Ti}, \text{Fe}_2\text{Ti}\) and \(\text{Fe}_2\text{Ti}\) (see Fig. 5(b)). Phases on the fracture surface by XRD are in accordance with that of microstructure analysed in Sec 3.2. \(\beta\text{-Ti, Fe}_2\text{Ti}\) and \(\text{Fe}_2\text{Ti}\) present all on the two sides of fracture. In other words, \(\beta\text{-Ti, Fe}_2\text{Ti}\), and \(\text{Fe}_2\text{Ti}\) are found on both sides of the fracture surface and thus it can be inferred that cracking has taken place somewhere at the interface of the Fe–Ti intermetallic layer and the \(\beta\text{-Ti}\) layer.

After tension test, two sides of fracture take on different SEM patterns respectively. On the stainless side, salient white blocky structures distribute on the gray basal body (as shown in Fig. 6(a)), reversely, blocky gaps mire down in basal body on the titanium alloy side(as shown in Fig. 6(b)). The grains in the basal body region appear isometric and there is no sign of plastic deformation or fracture. By contrast, it can be seen that cleavage fracture took place in the block structures, from which it can be inferred that this
region is where the tensile forces were concentrated. According to analysis of phase and fractography on the structures, the tensile force was apparently absorbed by the $\beta$-Ti layer during the tensile testing (as discussed above), the presence of the Fe–Ti intermetallics led to a lowering of the strength of the bonded joint, indicating that this is the weak point in the impulse pressuring diffusion-bonded joint.

4. Discussion

In the present work, after PPDB of Ti–4Al–2V and 0Cr18Ni9Ti with nanostructured layer at 850°C for 80 s, the diffusion distances of Fe and Ti atoms are equivalent to about 10 $\mu$m and 4 $\mu$m respectively (see Fig. 3(b)). And the tension strengths of two joints both are more than 321.0 MPa which is maximum tensile strength of untreated sample joint prepared by same diffusion bonding technology, and the maximum tensile strength was reached to 384.0 MPa. In other words, tension strength of joint was enhanced enormously later bonding interface was treated by means of SSNC. Increasing of tension strength may result from nanomicrostructure on the bonding interface. In present work, after SSNC treated by HESP, nanostructured layer was formed on the top surface of Ti–4Al–2V and 0Cr18Ni9Ti bars. Research showed that during surface self-nanocrystallization, on the top surface layer of bulk metal material takes place severe plastic deformation, and a great many of non-equilibrium defects, such as grain boundaries, vacancy and dislocation, were introduced into the top surface layer and subdivided coarse grains. Repetitive strain and stress causes progressive grain refinement into refined nanograins. Research showed the ultrafine grained structures provides about 30 vol% grain boundaries for average grain size of 10 nm, and a few volume percent triple junctions, which can offer fast atomic diffusion channels and facilitate diffusion of atom. Meanwhile, these numerous non-equilibrium grain boundaries holding higher Gibbs free energy than the conventional grain boundaries, which may facilitates atom diffusion along grain boundaries by decreasing the defect formation energy. Therefore, when bonded joint of Ti–4Al–2V and 0Cr18Ni9Ti was prepared by means of PPDB, diffusion atoms such as Fe, Ti, Cr and Al may be higher diffusion coefficients in nanostructured sample than in coarse grain sample. Diffusion atoms diffused into opposite matrix as soon as possible and reduced their content in intermetallic compounds, which can advance mechanical behaviour of bonded joint.

In addition, while PPDB, the instant pulse pressure may shatter intermetallic compounds layer, suppress growth of intermetallic compounds, increased effective contact area between Ti–4Al–2V and 0Cr18Ni9Ti, which may result of zigzag compound layer and decrease thickness of compound (see in the Fig. 3). On the other hand the pulse pressure occur a number of instant dislocations which offer diffusion channel for diffusion atoms and promote diffusion of atoms. By this, the SSNC of interface layer and pulse pressure both facilitate atoms diffusion during diffusion bonding of Ti–4Al–2V and 0Cr18Ni9Ti, which may impetus Ti–4Al–2V and 0Cr18Ni9Ti form well-knit joint and improve tension strength of joints. It is well known that the direct bonding between titanium/titanium alloy and stainless steel promotes the formation of various intermetallic compounds, as the solid-solubility of Fe, Cr, Ni and Ti is limited in each other and these intermetallics deteriorate the mechanical properties of the transition joint. The diffusion bonding temperature has pronounced effect on the formation of intermetallic phases. In present work, after bonded Ti–4Al–2V to 0Cr18Ni9Ti at 850°C, $\alpha$ phase, Fe$_3$Ti and FeTi were found on the bonding interface (see in Fig. 4 and Fig. 5). However, intermetallic compounds of Fe, Ti, Cr can not be yielded during diffusion bonding of Ti–4Al–2V and 0Cr18Ni9Ti under 850°C. Ghosh et al. inferred that diffusion bonded joints of titanium to stainless steel contains $\sigma$ phase, $\chi$ phase, Fe$_3$Ti, FeTi and Cr$_3$Ti intermetallic compounds in the diffusion zone when processed at 850°C.

5. Conclusion

(1) Pulse pressuring diffusion bonding is applied to prepare joint of Ti–4Al–2V and 0Cr18Ni9Ti with nanostructured layer at 850°C for 80 s, and tighten joints with maximum tensile strength of 384.0 MPa was formed. Brittle intermetallic compounds shuch as Fe$_3$Ti, FeTi and $\sigma$ phase present on the bonding interface, while diffusion bonding, $\alpha$-Ti transform into $\beta$-Ti because $\beta$-Ti stabilizing element such as Fe, Ni and Cr diffused into titanium alloy base. The cleavage fracture took place along bonding interface while joints were tensed. The tensile force was apparently absorbed by the $\beta$-Ti layer during the tensile testing (as discussed above), the presence of the Fe–Ti intermetallics led to a lowering of the strength of the bonded joint.

(2) Applying SSNC treatment by HESP to PPDB of Ti–4Al–2V and 0Cr18Ni9Ti may promote diffusion of diffusion atoms, shorten bonding time remarkably, suppress growth of brittle intermetallic compounds, which may improve greatly the mechanical behaviour of joints.

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