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) materials 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 materials is much enhanced relative to their coarse-grained polycrystalline counterparts.3,4) As for synthesis of nc materials, methods have been invented since in the early 1980s. Thereinto, K. Lu et al.5) have developed a new approach named surface self-nanocrystallization (SSNC) to prepare bulk nc materials, the nc materials from the technology include a large volume fraction of stored energy and non-equilibrium defective such as dislocations, vacancy, sub-boundary, which may promote chemical reaction of different atoms and enhance atomic diffusion coefficient.6,7) The SSNC has been applied to chemical heat treatment of many metal materials, research results8–13) 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.

However, so far, applying the SSNC to diffusion bonding of metal materials has been rarely reported in many researches. In present work, the SSNC was applied to PPDB of Ti–4Al–2V titanium alloy and 0Cr18Ni9Ti austenite stainless steel rods, aiming at increasing atomic diffusion coefficient, reducing bonding temperature and avoiding formation of brittle intermetallic compounds at bonding surface.

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 $d = 12 \times 30$ mm. The chemical compositions and room temperature tensile properties of samples are given in Tables 1 and 2.

2.2. Surface Self-nanocrystallization Treatment

Before diffusion bonding, end surfaces of Ti–4Al–2V and 0Cr18Ni9Ti rods were treated by means of HESP to
obtain surface nanostructured layer. Figure 1(a) shows a schematic illustration of the HESP treatment set-up used in the present work. Steel balls of 1 mm in diameter impact with high velocity to the end face of sample under peening pressure of about 0.6 MPa. Each peening of the ball will result in local severe plastic deformation on the treated surface (as shown in Fig. 1(b)). Repeated impacting on the sample surface over short period of time (in this work, treatment time is 5 min) leads to a progressive refinement of coarse grains into nanometer regime. Prior to the treatment, the end surface were polished manually with silicon carbide papers to 1000# and then mechanically polished with Al₂O₃ polishing powder to achieve finish surface. It was noted that a restrain sleeve part with 12/H₁₁₀₀₂ 0/H₁₁₀₀₁ 0.5 mm inner diameter was machined to grip the treatment end of sample and impede metal to flow away rim of the surface (as shown in Fig. 1(a)).

Microstructures observations of the treated samples were preformed on a TESCAN VEGA II scanning electron microscope (SEM, operating at a voltage of 30 kV). Meanwhile, microstructure features of nanostructured layer were characterized by using a Philip Tecnai-20 transmission electron microscope (TEM, operating at a voltage of 200 kV). Thin foils for TEM observations were prepared by means of cutting, grinding, dimpling and a final ion thinning at low temperatures. The quantitative X-ray diffraction (XRD) analysis of the surface layer in the HESP treated samples were carried out on a D/max-2400 X-ray diffractometer (12 kW), with CuKα radiation (wavelength λ₁ = 0.154056 nm, λ₂ = 0.154439 nm was eliminated by a graphite monochromator using its (0002) reflection), slit parameters of the diffractometer are 1°–1°–0.30 mm. The average grain size and mean microstrain on the top surface were calculated from line broadening of Bragg diffraction peaks.

2.3. Diffusion Bonding Experiment

After the HESP treatment, the roughness of the treated surface was increased in some short. In order to satisfy the interface condition of diffusion bonding, treated surface were prepared by conventional metallographic technology. The Ti-4Al–2V titanium alloy was etched for 120 s in a solution of 80%HNO₃ + 20%HF, and the 0Cr18Ni9Ti austenitic stainless steel was etched for 10 s in a solution of 15%H₂SO₄ + 15%HCl + 5%HNO₃ + 65%water at room temperature. The samples were then degreased in an ultrasonic bath using acetone and dried in air.

The PPDB experiments were conducted using a Gleeble-1500D system. Nanostructured surfaces of stainless steel and titanium alloy were kept in contact in a fixture and the assembly was inserted in a chamber. Transition joints were prepared at three different temperatures (T), 650, 700 and 750°C for 800 s in a vacuum of 5×10⁻² Pa by electric heating. A uniaxial pulse load of minimum pressure (Pₘᵢₐᵢₙ) and maximum pressure (Pₘₐₓ = 150 MPa) was applied along the longitudinal direction of the assemblies. The cycle (N) and frequency (f) of pulse load were 400 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. 2.

After diffusion bonding, joints were annealed for 1 h at 400°C in vacuum furnace to eliminate bonding stress. Tensile samples were cut into Φ₁₀×₅₀ mm in size, and experimented on the Instron-1342 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% FH + 92%H₂O) and

| Table 1. Chemical composition of tested materials (wt%). |
|----|----|----|----|----|----|----|----|----|----|----|----|
| 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. (a) The illustration of the HESP treatment set-up; (b) the local plastic deformation in surface layer by the peening of the shot.
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, EDS curves of Fe, Ti, Cr and V 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. Microstructure of Surface Self-nanocrystallization Treatment
After HESP treatment of samples, the longitudinal-sectional SEM morphology of titanium alloy shows a plastic deformation layer of about 253.52 μm thickness was generated (as shown in Fig. 3(a)). Plastic deformation was gradually exacerbated with decreasing of depth to the top surface. While the depth was reduced to about 121.81 μm, severe plastic deformation was created due to greater stress and strain. Cross-sectional TEM morphology about 20 μm depth in titanium alloy indicates nanograins with about 50 nm were formed (as shown in Fig. 3(b)), the corresponding selected area electron diffraction (SAED) pattern shows these nanograins have nearly random crystallographic orientation. Within 50 μm below the top surface in the titanium alloy samples, nanograins with below 100 nm were produced after 5 min HESP.

In the 0Cr18Ni9Ti samples, the thickness of plastic deformation layer was about 615.84 μm, and the thickness of severe plastic deformation layer was about 184.56 μm, as shown in Fig. 3(c). Cross-sectional TEM morphology about 30 μm depth shows that equiaxial nanograins with about 60 nm were formed in the 0Cr18Ni9Ti sample, the corresponding SAED pattern reveals nanograins have random crystallographic orientation (as shown in Fig. 3(d)). By TEM observation, nanograins layer about 80 μm thickness was generated in the 0Cr18Ni9Ti after HESP.

On the top surface of treated samples, Full Wave at Half Maximum (FWHM) of diffraction peaks were measured by the MDI Jade5.0 (an X-ray analysis software). The average grain size and mean microstrain on the top surface were calculated from broadening of diffraction peaks, by using formula as follows:

$$\frac{FW(s) \cdot \cos(\theta)}{\lambda} = K + 4 \cdot \varepsilon \cdot \sin\theta \cdot \frac{\sin\theta}{\lambda}$$ ........................(1)

Where $FW(S)^D = FWHM^D - FW(I)^D$ is FWHM of peaks after detracting broadening led by the diffractometer itself; $K$ is a constant, $K=0.89$ here; $\lambda$ is the wave length of the Cu $K_{α1}$ irradiation; $\theta$ is Bragg diffraction angle; $D$ is mean grain size; $\varepsilon$ is mean lattice strain. By performing a least square fit $FW(s) \cdot \cos(\theta)/\lambda$ plotted against $\sin\theta/\lambda$ for all of the measured peaks of a sample, one is able to determine the mean grain size $D$ and the mean lattice strain $\varepsilon$ (as shown in Table 3).

3.2. Tensile Strength of Joints
Joint formed at 650°C fractured while machining, which indicates bonding temperature is on the low side and has not formed effective bonding joint. Figure 4 shows tension–displacement curves of joints formed at 700°C and 750°C respectively while tension test. Tensile strength of joints are summarized in Table 4. The strengths of joints formed
at 700°C and 750°C are respectively 223.3 MPa and 262.0 MPa. From the Table 4, one can know the compressibility of joints is increasing with rising of bonding temperature. The compressibility achieves 16.40% when bonding temperature is 750°C, which indicates the maximum pulse pressure of 150 MPa is on the high side.

### 3.3. Analysis of Joints

The SEM images and EDS curves of the transition joints are given in Fig. 5. The SEM images show grains in the vicinity of diffusion interface are refined and increasing with rising of bonding temperature, and diffusion layers on the titanium alloy sides have been not explicit β-Ti layer which is transformed from α-Ti while bonding temperature is above 800°C. EDS curves of joints indicate Fe and Ti atom both diffused into titanium alloy and stainless steel matrixes respectively after PPDB at 650–750°C. After PPDB at 650°C, diffusion distances of Fe and Ti atom are about 3 μm and 5 μm respectively. With the increasing of bonding temperature, the diffusion distance of Ti atom in stainless steel augments tardily, after diffusion bonding at 750°C, it was added only to 7 μm or so. However, the diffusion distance of Fe atom is increasing rapidly with rising bonding temperature, and achieved about 10 μm at 750°C. It is noted that the diffusion distance of Ti atom is equivalent to that of constant temperature and pressure diffusion bonding (CTPDB) at 850°C, which indicates diffusion of Ti in 0Cr18Ni9Ti nanomicrostructure is remarkable at low temperature.

### 3.4. Analysis of Fractures

After tension test, two sides of joints formed at different temperatures take on same SEM pattern 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 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. It is noted that the dimension of blocky structures on two sides of fractures are far less than that of joints formed at high temperature.
The Fig. 7 is fracture XRD patterns of joint formed at 750°C. The XRD patterns of the fracture surface indicated that the phases on the 0Cr18Ni9Ti side of the interface are austenite and martensite (see Fig. 7(a)), while on the Ti–4Al–2V side the phases found present are $\alpha$-Ti (see Fig. 7(b)). The XRD analysis of fracture shows intermetallic compounds have been formed at the interface of joints formed by PPDB at 750°C, meanwhile, $\alpha$-Ti did not transform into $\beta$-Ti during PPDB.

4. Discussion

In the present work, after PPDB of Ti–4Al–2V and 0Cr18Ni9Ti with nanostructured layer, the diffusion distances of Fe and Ti atoms are equivalent to that of constant temperature and pressure diffusion bonding (CTPDB) at 850°C. And the tension strength of joint formed at 750°C reaches 262.0 MPa which is equal to that of joint formed at 850°C by CTPDB for 1800 s. The XRD analysis of fracture shows intermetallic compounds have been formed at the interface of joints formed by PPDB at 750°C, meanwhile, $\alpha$-Ti did not transform into $\beta$-Ti during PPDB.

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In the present work, after PPDB of Ti–4Al–2V and 0Cr18Ni9Ti with nanostructured layer, the diffusion distances of Fe and Ti atoms are equivalent to that of constant temperature and pressure diffusion bonding (CTPDB) at 850°C. And the tension strength of joint formed at 750°C reaches 262.0 MPa which is equal to that of joint formed at 850°C by CTPDB for 1800 s. During surface self-nanocrystallization by means of HESP, the top surface layer of samples 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 straining causes progressive grain refinement into refined nanograins. Research shows the ultrafinegrained structures provide about 30 vol.% grain boundaries for average grain size of 10 nm, and a few volume percents triple junctions, which can offer fast atomic diffusion channels and facilitate diffusion of atom. In present work, after HESP, bonding interfaces of samples include numerous non-equilibrium grain boundaries, subboundaries, vacancy and dislocation which act as fast atomic diffusion channels during PPDB of Ti–4Al–2V and 0Cr18Ni9Ti. Meanwhile, these numerous non-equilibrium grain boundaries possess higher Gibbs free energy than the conventional grain boundaries, which may facilitates Fe, Ti atoms diffusion along grain boundaries by decreasing the defect formation energy.

In addition, during PPDB, on the one hand, the pulse pressure increases effective contact area between Ti–4Al–2V and 0Cr18Ni9Ti, on the other hand the pulse pressure occur a number of instant dislocations which offer diffusion channel for diffusion atoms. By this token, 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. Ghosh et al. inferred that diffusion bonded joints of titanium to stainless steel contain $\sigma$ phase, $\chi$ phase, Fe$_2$Ti, FeTi and Cr$_2$Ti intermetallic compounds in the diffusion zone when processed at 850°C. In present work, because of bonding temperature at 650–750°C, the energy is low and intermetallic compounds of Fe, Ti, Cr can not be yielded during diffusion bonding of Ti–4Al–2V and 0Cr18Ni9Ti (as shown in Fig. 7). This may improve tension strength of joints also.

5. Conclusion

(1) After HESP, nanostructured surface layer are prepared on the end surfaces of Ti–4Al–2V and 0Cr18Ni9Ti rods. PPDB is applied to bond Ti–4Al–2V and 0Cr18Ni9Ti rods with nanomicrostructure at low temperature for 800 s, and tighten joints with tension strength of 223.3 MPa and 262.0 MPa were formed respectively at 700°C and 750°C.

(2) Combining SSNC by HESP treatment into PPDB reduces diffusion bonding temperature of Ti–4Al–2V and 0Cr18Ni9Ti, and shorten bonding time is remarkably. Intermetallic compounds are not yielded on interface of joints owing to low temperature diffusion bonding, which may improve the tension strength of joints. But, the cleavage fracture takes place along bonding interface while joints are tension test.

Acknowledgement

The authors acknowledge financial support from the National Science Foundation of China (No. 50675234). The author acknowledges financial support from the Great Equipments Opening Foundation of Chongqing University. The author acknowledges financial support from Chongqing University Postgraduates’ Science and Innovation Fund (No. 200801A1B0100269).
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