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Oxidation behavior of titanium alloy under diffusion bonding

Ho-Sung Lee[a,*], Jong-Hoon Yoon[a], Yeong-Moo Yi[b]

[a] *Department of Structure and Materials, Korea Aerospace Research Institute, 45 Eoeun-dong, Yuseong-gu, Daejeon 305-333, Republic of Korea*
[b] *KSLV Technology Division, Korea Aerospace Research Institute, 45 Eoeun-dong, Yuseong-gu, Daejeon 305-333, Republic of Korea*

Abstract

The solid state diffusion bonding of the Ti–6Al–4V alloy was carried out in inert gas environment and the oxidation behavior at high temperatures was investigated. Bonding was conducted in a furnace using selected combinations of temperature ranging from 850 to 950 °C, pressure of 3 MPa for l–3 h in argon gas environment. Good diffusion bonding interface have been observed at relatively low temperature and pressure. The microstructure bonded at 900 °C exhibits oxygen-enriched alpha phase at bonded interface. It is shown that at the optimum condition for diffusion bonding with parent metal, the oxide film becomes unstable and the oxygen is diffused into the bulk. The evidence of nucleation of new grains and microhardness properties at the interface proves the diffusion bonding process is successful.

Keywords: Diffusion bonding; Titanium; Oxidation; Solid state diffusion; High temperature oxidation

1. Introduction

Solid state diffusion bonding is a process that joins component parts together without use of the secondary phases, solvents or liquid. Diffusion bonding involves atomic or elemental movement from one metal to another when two components are in contact with certain temperatures and time to remove asperities from the interface by vacancy diffusion. In this process, it is essential that the metal surfaces are clean and free of any oxide or other films. However, titanium alloys are famous for corrosion resistance due to a stable, protective, strongly adherent oxide film layer. This film may be considered as an impurity during diffusion bonding process. For this reason, it has been generally known that diffusion bonding process of titanium alloys needs to be undertaken in a vacuum to prevent oxide formation. Diffusion bonding involves atomic movement from one metal to another when two components are in contact with certain temperatures and time to remove voids and oxides from the interface by atomic diffusion.

Zhang et al. [1] selected 1010 °C, 3 MPa and 3 h as the best condition for diffusion bonding of Ti–6Al–4V. Typical manufacturing condition is 940 °C, 5–8 MPa and 2 h under vacuum condition. Mutoh et al. [2] also reported the optimum condition for Ti–6Al–4V was 900 °C, 10 MPa for 1 h in which the bonding process was performed in vacuum with mechanical pressure loading. Since maintaining high vacuum condition during the process is not practical in industry application, it is necessary to investigate the oxidation behavior of titanium in inert gas environment. In the literature, most studies on oxidation of titanium alloy are only in vacuum or oxygen environment [3–6].

Diffusion bonding can be obtained by applying a static pressure to achieve intimate contact for certain amount of time at high temperature well below the melting temperature of the metals. It is important to notice the solid state diffusion is a function of temperature, time, the form of pressurization and contact condition of the matched surfaces. Therefore, the oxide film layer and micro voids from asperities must be removed from the bonding interface during diffusion process.

In this paper, the solid state diffusion bonding of the Ti–6Al–4V alloy was carried out in inert gas environment for practical application and the oxidation behavior at high temperatures was investigated.

2. Experimental procedure

The material used in the present study was supplied in a form of a plate by RTI International Metals, Inc. U.S. Ti–6Al–4V alloy is two phase alloy with fine equiaxed alpha phases mixed with transformed beta phase. The chemical composition of this alloy is 6.05Al–3.89V–0.21Fe–0.11O–0.01C–0.007N with less than

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[*] Corresponding author. Tel.: +82 42 860 2512; fax: +82 42 860 2233.
E-mail address: hslee@kari.re.kr (H.-S. Lee).

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0.005Y. β transus of this alloy was determined by DTA (Perkin-Elmer DTA7) at a cooling rate of 10 °C/min. The average grain size at room temperature was about 10 μm. Oxidation experiments were performed in TGA (Perkin-Elmer TGA 6) purging with dry argon gas in 25 ml/min. Oxidation specimens were cut from the plate and polished with 1000 mesh SiC abrasive papers and ultrasonically cleaned in acetone and water and dried. The sample dimension was 5 mm × 5 mm × 2 mm and ceramic container was used. Oxidation was conducted isothermally at 850, 900 and 950 °C for 500 min. This time is chosen based on typical diffusion bonding process time.

Diffusion bonding experiments were conducted in the as-rolled condition in argon gas environment. The fixture made with a high alloy steel was designed to permit simultaneous argon gas pressurization at both sides of the specimen. Since the surface condition is vital for complete bonding, the surface of blanks was carefully prepared for bonding by special procedure [7]. Ultrasonic rinsing in a high-purity solvent, and in distilled water followed. The rinsed surfaces were then air dried with clean filtered air. Immediately prior to diffusion bonding, the specimens were cleaned again with a high-purity solvent. Bonding was conducted in a furnace using selected combinations of temperature ranging from 850 to 950 °C, pressure up to 3 MPa in inert gas environment. Using gas pressure as a loading medium prevents the bonding area from non-uniform pressure application. After heating, the bonding fixture was cooled to room temperature in the furnace. Microhardness across the bonded region was determined with a Vikers indentor applying 300 gf for 5 s. Samples for optical microscopy were sectioned, mounted and polished using standard metallographic techniques, and etched using Kroll's reagent.

3. Results and discussion

Oxidation of Ti–6Al–4V alloy was studied by Mungole et al. [3] at high temperatures of 777–1067 °C in oxygen gas atmosphere. It was shown that 977 °C is a safe upper limit for high temperature applications, since below this temperature the oxidation rate markedly reduced after exposure of 8 h. The activation energy of oxidation of Ti–6Al–4V in oxygen was comparable to that of the formation of TiO_2 from pure titanium. For titanium alloys, it was observed [4] that an oxide scale, consisting of two layers, one growing outward and the other growing inward, had formed. The outward growing part of the scale consisted mainly of TiO_2, while the inward growing part was composed of a mixture of TiO_2 and α-Al_2O_3. Since oxidation was rapid in air, the inert gas was purged during the bonding process.

Normalized weight gain with respect to oxidation time obtained from oxidation experiments is presented (Fig. 1). In the figure, increasing oxidation temperature accelerated the weight gain and the oxidation rate obeyed parabolic. It is interesting to notice the change of weight gain behavior is observed after 250 min at 900 °C. This is more distinctly shown at 950 °C. This indicates there are two different oxidation kinetics governs at 950 °C. In this study, the first oxidation kinetics is considered, since the initial condition of the surface is important in the diffusion bonding process.

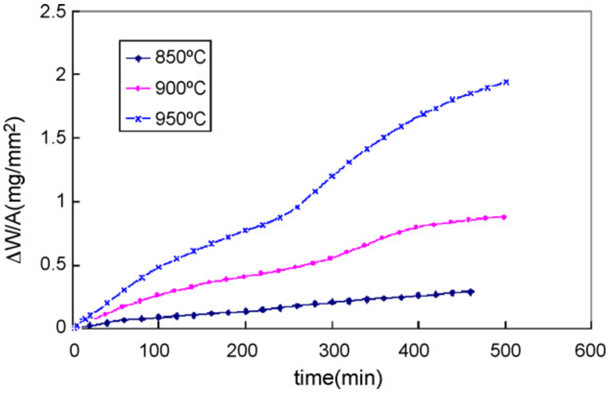

Fig. 1. Normalized weight gain with respect to oxidation time.

Oxidation kinetics can be expressed by the following equation:

$$\left(\frac{\Delta W}{A}\right)^n = Kt \tag{1}$$

where $\Delta W/A$ is the weight gain per unit surface area, K the rate constant, n the reaction index and t is the time. At a constant temperature, the kinetic model is parabolic when $n = 2$.

Fig. 2 shows a plot of $(\Delta W/A)^2$ versus t for determination of the oxidation rate constant. The values of K of the oxidation kinetics are 3.14×10^{-6}, 1.444×10^{-5} and 5.097×10^{-5} kg^2 m^{-4} s^{-1} at 850, 900 and 950 °C, respectively. The corresponding R^2 of K values are 0.98, 0.98 and 0.96.

Since the oxidation rate constant follows an Arrhenius relationship,

$$K = K_0 \exp\left(\frac{-Q}{RT}\right) \tag{2}$$

where Q is the effective activation energy for oxidation, R the gas constant, T the absolute temperature and K_0 is the constant for a given material. The effective activation energy for oxidation was obtained from an Arrhenius plot of K in logarithm scale versus $1/T$ (Fig. 3). The effective activation energy in Ti–6Al–4V for the overall oxidation process is 318 kJ/mol at the present study. This value compares favorably with the effective activation energy of oxygen diffusion in beta titanium, which is 287 kJ/mol [8]. The

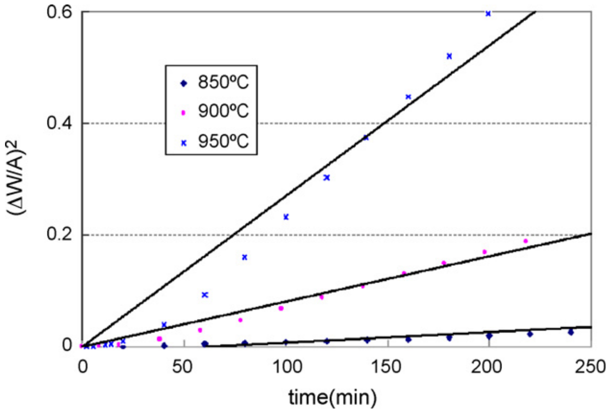

Fig. 2. A plot of $(\Delta W/A)^2$ vs. time for obtaining the oxidation rate constant.

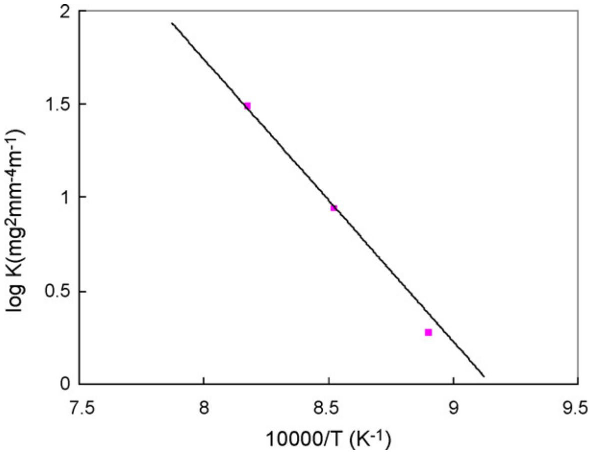

Fig. 3. Arrhenius plot of parabolic rate constant for oxidation of Ti–6Al–4V in the temperature range 850–950 °C.

beta transus temperature was obtained by DTA and confirmed with metallographic observation of microstructure. It was shown that the beta transus temperature of this alloy was 964 °C, which is lower than typical beta transus temperature, which is about 995 °C of grade 5Ti–6Al–4V. The phase ratio is affected by the beta transus temperature and it is assumed that this alloy contains more beta phases than conventional grade 5Ti–6Al–4V at the diffusion bonding temperature.

The initial stage of diffusion bonding starts with plastic deformation at interface, where ridges of the surface asperities deform plastically in such a way that there is no macroscopic deformation in the parts to be bonded. During this process, voids will be produced and aligned at the interface. The voids become isolated and the gas pressure of inside of the voids is equal to the pressure in the furnace. In heating, the surfaces start to absorb the gas and since the voids are isolated, the pressure inside of the void becomes decreased. Recent study of the kinetics of the decrease of the gas pressure in the closed volume at high temperatures [9] shows that at 550 °C, the gas pressure inside of a void of 100 μm is reduced from 7.3 to 3×10^{-4} Pa within several minutes. At 900 °C, the vacuum is expected to form in several seconds. The stability of titanium oxides in the surface region has been investigated in ultra high vacuum [10] and it is shown that all the oxides decompose and the oxygen is diffused into the bulk above 400 °C.

In the case of bonding under hydrostatic pressure, the temperature will raise locally due to the deformation heat, and the temperature increment ΔT can be expressed as [11]:

$$\Delta T = \frac{(1-f)\sigma(\varepsilon_1 - \varepsilon_0)}{C\rho} \qquad (3)$$

where f is the fraction of the work stored depending on the strain, C the specific heat per unit mass, ρ the density, σ the average stress and ε_1 is the true strain. Thus, the diffusion coefficient will increase accordingly and the atomic diffusion is accelerated, which results in the decreasing of interlayer film thickness and increasing of bonding strength.

Fig. 4 shows the microstructure of bonded interface at 850 and 900 °C. The grain size of bonded material is larger than that of the as-received material, due to static grain growth during the thermal exposure and slow cooling rate to room temperature. The microstructure bonded at 900 °C exhibits oxygen-enriched alpha phase at bonded interface, which typical shape is widmanstatten structure. One of the reasons for formation of oxygen-enriched alpha phase at higher temperature is due to the higher diffusion rate of oxygen with presence of oxygen. It is well known that the widmanstatten preform deforms by strain dependent spheroidization while the equiaxed preform exhibits superplastic deformation. Microhardness test reveals that diffusion bonding performed at 850 °C provides structurally integrity bonded interface (220 Hv), since at 900 °C, the bonded interface has lower hardness (200 Hv) comparing to the matrix.

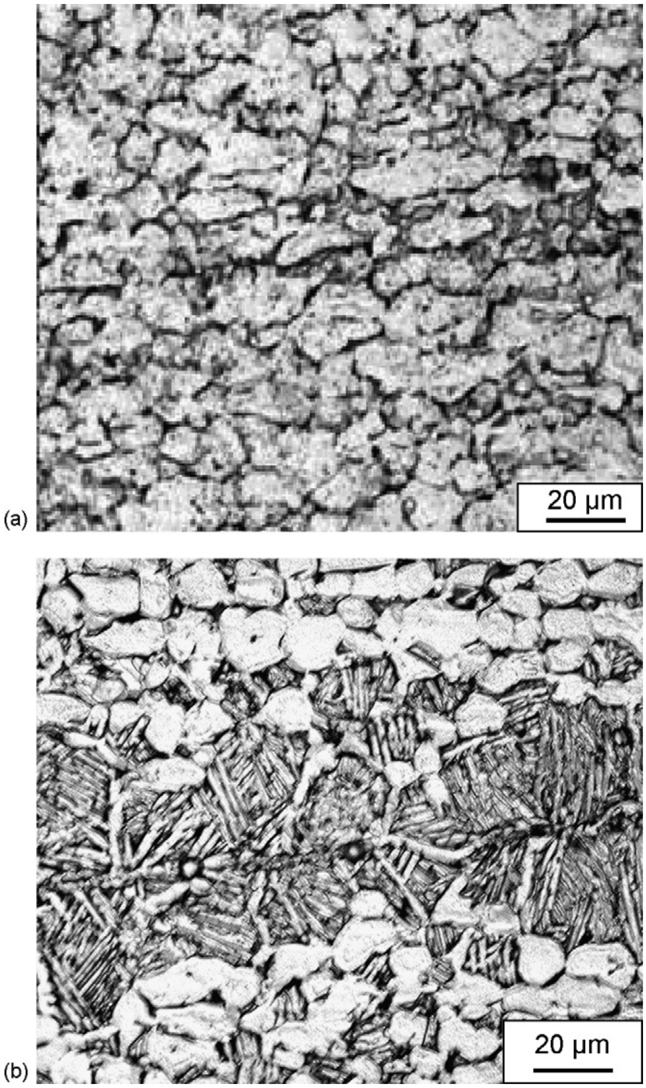

Fig. 4. Microstructure of bonded interface at (a) 850 °C and (b) 900 °C.

4. Conclusion

(1) The oxidation behavior of Ti–6Al–4V alloy at diffusion bonding temperatures obeys the parabolic law in dry argon environment.

(2) The microstructure bonded at 900 °C exhibits oxygen-enriched alpha phase at bonded interface and lower bond strength, while at 850 °C, good diffusion bonding interface have been observed.

(3) The activation energy of Ti–6Al–4V oxidation is estimated to be 318 kJ/mol in diffusion bonding condition.

(4) Good diffusion bonding interface have been observed at 850 °C, applying pressure of 3 MPa for 1 h in argon gas environment, which condition is more practical for industrial application than expensive vacuum condition.

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