Kinetics of thermodiffusion of TZ20 titanium alloy gas-nitride within temperature of 500 °C–650 °C

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ABSTRACT

Surface nitriding is an effective method for improving surface hardness, wear resistant, corrosion resistance etc. surface properties and ensuring effective, safe, and long-term applications of alloys. This work investigated the kinetics of thermodiffusion of gas nitriding and practical nitriding of TZ20 titanium alloy within 500 °C–650 °C. Differential scanning calorimeter was also used to explore nitriding behavior and its activation energy E. Results showed that nitriding on TZ20 alloy within the temperature range of 500 °C–650 °C followed the parabolic law, and E value approximated 186 kJ/mol. Phase analysis revealed that nitride products changed gradually from Ti_2N to Ti_3N_{2-x} + Ti_4N_{3-x} as nitriding temperature increased from 500 °C to 650 °C. The relationship between weight gain and thickness of nitride layer indicated that weight will increase 0.118 mg/cm^2 for each additional millimeter in thickness. Furthermore, surface hardness of TZ20 alloy before and after nitriding treatment was investigated. Surface hardness of specimen after nitriding at 650 °C for 1 h dramatically increased from approximately 400 HV to 870 HV. The findings will not only promote practical applications of new Ti–Zr–Al–V series alloys but also supplement the surface alloying theory.

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1. Introduction

The recently developed Ti–Zr–Al–V (shortened as TZAV) series Ti/Ti–Zr-based alloys have low density, ultrahigh tensile strength, favorable ductility, and ultrahigh specific strength (ratio of tensile strength to density) [1–4]. Thus, this series of alloys exhibits remarkable potential applications in fields, such as aerospace, automotive, and marine engineering. However, as a typical Ti alloy, the TZAV series alloys also display some characteristic shortcomings, such as weak wear resistance, low hardness etc. surface properties, similar to those of Ti alloys [5–8]. Surface treatment is an effective approach to improve surface properties of metal and alloys also containing Ti alloys [9–11]. Accordingly, investigation on surface treatment method and process for TZAV alloys will remarkably promote their practical application.

Surface alloying is an effective method of improving wear resistance [12–14], surface hardness [15], corrosion resistance

[16–18], biocompatibility [19] etc. surface properties of Ti alloys. Among surface alloying processes, surface nitriding widely used on Ti alloys can significantly improve the mentioned surface properties of Ti alloys [20]. Anandan et al. [21] investigated the effect of postnitride annealing on wear and corrosion behavior of Ti–6Al–4V titanium alloy, and their results showed that wear rate of nitrided specimen decreased by an order of magnitude in reciprocating wear experiments and further decreased in annealed samples compared with that of substrate. Li et al. [22] introduced solid-state friction stir processing to surface nitriding on Ti–6Al–4V substrate under nitrogen atmosphere and obtained a nitride layer with microhardness of ~1105 HV0.2 on the top surface. Yang et al. [23] researched the structure and corrosion resistance of vacuum-nitrided coating on TB8 titanium alloy and showed that corrosion rate of TB8 with nitrided film reached approximately 1/175 compared with that of substrate, and no corrosion pits were observed in the film surface. As mentioned previously, surface nitriding on other Ti alloys has been widely investigated, and the corresponding treatment is also comparatively established. However, results concerning surface nitriding on TZAV series alloys are very limited. Gas nitriding is a relatively simple, easy to control, effective, inexpensive, and shape-unrestricted surface-nitriding

process that improves surface properties of Ti alloys [24–27].

This work investigated kinetics of thermodiffusion and surface hardening of gas nitriding on Ti−20Zr−6.5Al−4V (wt.%, shortened as TZ20) alloy within the temperature range of 500 °C−650 °C and its practical process. Obtained findings will be conducive in applying the theory of surface alloying and promoting practical applications of TZAV series alloys.

2. Experimental procedure

TZ20 titanium alloy ingots were prepared by the Northwest Institute for Non-ferrous Metal Research of China by using a vacuum-consumable arc melting furnace. These ingots underwent melting, breakdown, forging. Table 1 summarizes normal production of titanium alloys [28]. Table 1 shows the final compositions. Specimens with size of 10 mm (width) × 10 mm (height) × 70 mm (length) were cut from the ingots and annealed at 500 °C for 2 h to release stress. Subsequently, the specimen was cut and polished into slices with a size of Ø3 mm × 1 mm for nitriding kinetics measurement and into cuboids at 9 mm × 9 mm × 7 mm for gas nitriding treatment. The polishing procedure involved orderly mechanical grinding using 600, 800, 1000, 1200, and 1500 grit silicon carbide papers and further polishing using a 0.25 μm aluminum oxide. Nitriding kinetics was investigated via thermogravimetric analysis (TGA) and measured using a differential scanning calorimeter at temperatures of 500 °C, 575 °C, and 650 °C, according to the test standard ASTM E2402-11. To avoid uncertainty, TGA of each specimen has been performed at least thrice. TGA outcomes corresponded to median result for each group. Based on results of nitriding kinetics, specimens were treated by gas nitriding at various conditions in a tubular furnace to obtain a hardened nitride layer on the base material through inward diffusion of nitrogen. The tubular furnace with specimens was vacuumized into −0.1 MPa. Then, high-purity argon was aerated into the furnace to exclude gaseous impurities. The above process was repeated thrice to reduce gaseous impurities as much as possible. After the exhaust process, the furnace with specimens was vacuumized again into −0.1 MPa again and then heated to a designated temperature and held for 30 min. High-purity nitrogen was aerated into the furnace to −0.05 MPa and diffused into the surface of specimens for a designated time. After thermodiffusion, specimens were cooled in furnace to 300 °C and then air-cooled to room temperature. Table 2 provides thermodiffusion technological parameters of nitriding.

Surface nitriding products were determined by X-ray diffraction (XRD) with Cu Kα radiation. For thickness test of the nitride layer, the nitrided specimens were sectioned in half and mounted in epoxy resin to prevent the nitride layer from breaking during mechanical grinding. The embedded section was also polished as described above. Scanning electron microscopy (SEM) was used to observe and determine thickness of the nitride layer. The exhibited thickness of nitride layers in the present study represents the average value of four edges of tested specimens. Microhardness was tested using Vickers hardness test with a load of 0.1 N. After hardness testing, the diagonal length of indentation was measured using DSX-500-type OLYMPUS 3D automatic optical microsystem because of its small size. The first hardness test position was placed at the nitrided surface. The presented microhardness is the average

Table 1
Actual composition of TZ20 alloy, wt.%.

Element	Zr	Al	V	Hf	Na	Fe	Ti
Content	19.2	6.48	3.86	0.726	0.791	0.22	balance

Table 2
Thermodiffusion technological parameters of nitriding treatment.

Specimen sign	500−2	500−4	575−1	575−2	650−0.5	650−1
Temperature, °C	500	500	575	575	650	650
Holding time, h	2	4	1	2	0.5	1

value of at least six valid results. Weights of specimens before and after nitriding were measured using an electronic analytical balance with a precision of 0.0001 g. The presented weight corresponded to the average value of three specimens.

3. Results and discussion

Thermodiffusion kinetics of nitriding on TZ20 alloy at temperature of 500 °C, 575 °C, and 650 °C was investigated through TGA, and results are shown in Fig. 1. The curves in Fig. 1(a) show that weight gain of the examined alloy after nitriding significantly depended on treatment temperature. Weight increment rate with thermodiffusion time visibly increased with nitriding temperature. After nitriding at various temperatures for 260 min, weight gain is approximately 0.62 mg/cm^2 for 500 °C, 1.67 mg/cm^2 for 575 °C, and 3.67 mg/cm^2 for 650 °C. The relationship between weight gain and treatment time of gas surface thermodiffusion including nitriding treatment can be described using the power function:

$$\Delta W^n = K_p t, \tag{1}$$

where ΔW is the weight gain per unit surface area of nitrided specimen, t refers to thermodiffusion time, n corresponds to an exponent of power function, and K_p is a rate constant. For convenience, Equation (1) can be changed into ln-linear form. Fig. 1(b) plots the new curves based on logarithm values of ΔW-t curves in Fig. 1(a). To investigate the thermodiffusion of nitriding on TZ20 alloy, fitting straight lines of ln ΔW-ln t curves are also shown in Fig. 1(b). Compared with the linear form of Equation (1) and equations of the fitting lines, values of exponent n and rate constant K_p can be obtained, and results are shown in Table 3. n value of all specimens treated at designated temperatures is near 2.0. This finding indicates that similar to most thermodiffusion in metal and alloys [29−31], thermodiffusion of nitriding on TZ20 alloy at 500 °C, 575 °C, and 650 °C also obeys the parabolic law. According to Equation (1), K_p value describes relative thermodiffusion rate. Thus, based on K_p values in Table 3, sharply increasing thermodiffusion rate of nitriding on TZ20 alloy as temperature increased from 500 °C to 650 °C was easily obtained.

For thermodiffusion in metals and alloys, the rate constant K_p can be expressed using the Arrhenius law:

$$K_p = A e^{-\frac{E}{RT}}, \tag{2}$$

where A corresponds to a constant for a certain alloy, E represents the activation energy, R is a gas constant, 8.314 J/(mol·K), and T stands for absolute temperature. Equation (2) can also be transformed into ln-linear form:

$$\ln K_p = \ln A - \frac{E}{RT}, \tag{3}$$

Table 3 shows ln K_p at test temperatures obtained from fitting lines in Fig. 1(b). Fig. 2 presents ln K_p values based on results in Table 3 at various test temperatures and the fitting line. According to Equation (3) and Fig. 2, ln A and E/R can be determined easily, with values reaching 13.2 and 2.24 × 10^4, respectively. Thus, activation energy E approximated 186 kJ/mol. This value is lower than