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Diffusion of carbon and nitrogen in TC4 titanium alloy plasma electrolytic saturation

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ABSTRACT

The study aims at deriving an equation for the temperature field of the specimen- vapour-gaseous envelope (VGE) – electrolyte three-phase system, followed by the calculation of the temperature distribution expression. The diffusion mechanism of carbon and nitrogen, in light of the theory of molecular diffusion, and the mechanism behind the plasma electrolytic saturation, is also discussed. In the PES process, the diffusion of carbon and nitrogen is affected by the strengthening voltage and processing time, which in turn affects the thickness and element distribution of the diffusion layer. Carbon, of which the diffusion depth ranges from 0.5 μm to 2.5 μm, is mainly distributed into the outermost layer. While the nitrogen is able to distribute throughout the diffusion layer as indicated by its several tens microns of diffusion depth. Further, the influence of process parameters on the diffusion of atoms during the strengthening process is verified experimentally.

1. Introduction

Titanium and its alloys are widely used in various scientific fields such as aerospace, machinery manufacturing, and biomedicine due to their light weight, high specific strength and good corrosion resistance [1,2]. Nevertheless, insufficient stiffness, poor wear-resistance properties and considerably high friction coefficient restrict the proper development of Titanium alloy [3]. Studies show that the surface hardness and wear resistance of titanium alloys can be elevated by gas nitriding [4], ion beam modification [5], plasma electrolytic oxidation (PEO) [6], Surface Nanocrystallization (SNC) [7] as well as Plasma Electrolytic Saturation (PES) [8]. Among the various techniques, the PES is a new development because of its simple processing equipment, less processing time, lower treatment temperature [9].

In the process of PES, the workpiece served as the anode, and a graphite served as the cathode are placed in the electrolyte that is composed of organic solution and electrolyte. When a certain voltage is applied between the two electrodes, a vapour-gaseous envelope (VGE) will be generated on the electrode surface [10]. Discharge occurs on workpiece surface along with the breakdown of VGE when the voltage exceeds a certain threshold, such a phenomenon is called Plasma electrolysis [11]. The plasma generated by gas electrolysis contains a large amount of carbon and nitrogen atoms and ions with high-energy. These high-energy particles continuously bombard the surface of the workpiece. In the end, the carbonitride diffusion layer is formed on the surface of the specimen by a synthesis of thermochemical treatment, electrochemical treatment and plasma treatment [12]. The surface hardness of the treated specimen has doubled. Friction and wear properties have also been improved [13]. According to previous research, the outermost diffusion layer is the brightest, and gradually darken inward. The thickness of the diffusion layer is 2 μm approximately, and the formation of Ti (C, N) is mainly due to the diffusion of carbon and nitrogen into the titanium lattice [14]. The diffusion of carbon and nitrogen is influenced by temperature, time and diffusion coefficient. Belkin [15] suggested that the temperature field is closely related to the processing voltage. Loo, F. [16] and Yilbas, B.S. [17] respectively investigated the diffusion of carbon and nitrogen in titanium at different temperatures.

However, fewer studies on the diffusion mechanism of carbon and nitrogen during the PES of titanium alloys have been reported. In this work, the influence of processing parameters on the element distribution in Ti (C, N) diffusion layer will be investigated. Also, the formation mechanism of the diffusion layer will be explained from the viewpoint of diffusion providing a theoretical basis for the further development of this technology.

2. Diffusion mechanism

2.1. Model

The specimen – VGE – electrolyte three-phase system is established according to the experimental conditions (Fig. 1). The

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specimen material used is conventionally rolled TC4 titanium alloy. TC4 bars are placed vertically, radial for the abscissa. The radius of the specimen is 2.5 mm. The VGE thickness is δ. The heat generated during the strengthening process is conducted to the VGE in the first place and then transferred to the specimen in the form of steady-state heat conduction, resulting in a stable temperature throughout the model. Because of the flow of the electrolyte and the VGE [18], and the complexity of heat transferring process [19], it was difficult to consider the influence of all factors. Therefore, the following idealized assumptions were made for the sake of convenience in modeling, without impeding the reliability of the results:

i. Keep the VGE thickness uniform;
ii. When the steady state is reached, the liquid level remains essentially unchanged;
iii. During the calculation of the temperature field of the VGE, the curvature of the VGE is neglected and calculated as a situation of one-dimensional large-plane steady-state thermal conductivity;
iv. The electrolyte temperature is considered uniform, thus the conductivity is stable.

2.2. Temperature distribution

The temperature is a key factor that directly affects the strengthening effect. Because the intense discharge effect keeps the specimen at a higher temperature during the strengthening process. However, the specimen's surface temperature measurement is extremely difficult when the strengthening process occurs in the liquid environment accompanied with intense reaction. In this paper, the principle of energy transfer is used to derive the temperature distribution of the whole system, which provides the basis for the later analysis. In the whole system, the heat transfer is divided into two processes: firstly, the heat transfer process between the electrolyte and the VGE and secondly, the heat transfer process between the VGE and the specimen. This is explained below.

Firstly, heat transfer between the electrolyte and the VGE is calculated as follows. The variation in VGE temperature is directly affected by the input energy. The energy conversion in the strengthening process is mainly from the electrical energy to the heat energy. Therefore, the temperature distribution in the VGE is related to the strengthening voltage. When the input energy and heat loss are equal, the system is in a dynamic balance. At this point, the temperature of the electrolyte reaches saturation temperature, and the heat transfer between the VGE and the electrolyte is steady-state heat conduction.

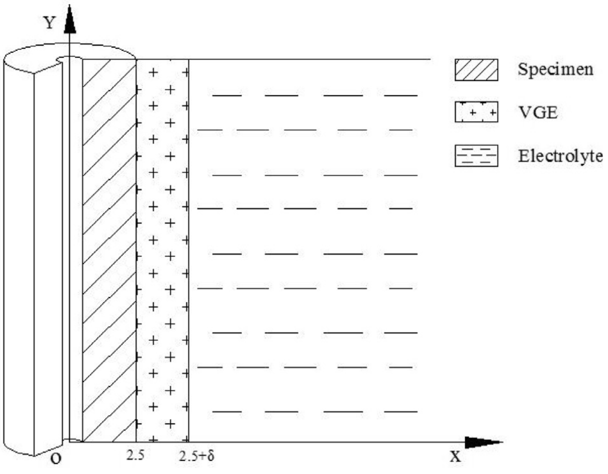

Fig. 1. Specimen-VGE-electrolyte three-phase system.

Differential equation of heat conduction is given by

$$\lambda \frac{d^2T}{d(x-2.5)^2} + W = 0 \tag{1}$$

The boundary conditions are

$$\begin{cases} T(x=\delta+2.5) = T \\ -\lambda \frac{dT}{dx}(x=2.5) = -q_c \\ -\lambda \frac{dT}{dx}(x=\delta+2.5) = -q_l \end{cases} \tag{2}$$

Here q_c denotes Specimen-VGE heat flux density, and q_l denotes VGE-electrolyte heat flux density [20].

The temperature distribution of the VGE is

$$T(x) = -\frac{W}{2\lambda_v}(x-2.5)^2 + \frac{q_c}{\lambda_v}(x-2.5) + T_s + \frac{W\delta^2}{2\lambda_v} - \frac{q_c\delta}{\lambda_v}(x \geqslant 2.5) \tag{3}$$

The specimen and VGE junction temperature is

$$T(x=2.5) = T_s + \frac{W\delta^2}{2\lambda_v} - \frac{q_c\delta}{\lambda_v} \tag{4}$$

VGE thickness is

$$\delta = \frac{\chi U^2}{q_l + q_c} \tag{5}$$

Internal heat source is

$$W = \frac{\chi U^2}{\delta^2} \tag{6}$$

Here χ is VGE conductivity [21].

Secondly, the heat transfer between the VGE and the specimen is analyzed as follows. The heat transfer between the specimen and the VGE is the non-steady convection heat transfer in theory. But the specimen temperature increases swiftly and achieves the balance in less than 1 s due to the great convective heat transfer coefficient of about 3000–15000 W/(m^2·°C) [22], in this working condition. Thus, the process is similar to one-dimensional steady-state heat conduction. Once the steady state is reached, the energy absorbed by the specimen equals the heat loss. At the same time, the temperature distribution in the specimen remains stable. Under the influence of the heat dissipation effect at the end of the specimen, the temperature alters along the radii direction. The sample temperature distribution is calculated as follows:

Differential equation of heat conduction is

$$\frac{d^2T}{dx^2} + \frac{1}{x}\frac{dT}{dx} = 0 \tag{7}$$

The boundary conditions are

$$\begin{cases} -\lambda_s \frac{dT}{dx}(x=2.5) = -q_c \\ T(x=2.5) = T(x=2.5) \end{cases} \tag{8}$$

The specimen temperature distribution is

$$T(x) = \frac{2.5 \times 10^{-3} q_c}{\lambda_s}(\ln x - \ln 2.5) + T(x=2.5) \tag{9}$$

Substituting Eq. (4) into Eq. (9) gives the final expression of the specimen temperature distribution as follows

$$T(x) = \frac{2.5 \times 10^{-3} q_c}{\lambda_s}(\ln\ x - \ln\ 2.5) + T_s + \frac{W\delta^2}{2\lambda_v} - \frac{q_c\delta}{\lambda_v} \tag{10}$$