Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 252 (2006) 8557–8564
applied surface science
www.elsevier.com/locate/apsusc

CO_2 laser gas assisted nitriding of Ti–6Al–4V alloy

B.S. Yilbas [a,*], C. Karatas [b], Uslan [c], O. Keles [c], I.Y. Usta [c], M. Ahsan [a]

[a] *KFUPM, Dhahran, Saudi Arabia*
[b] *Hacettepe University, Ankara, Turkey*
[c] *Gazi University, Ankara, Turkey*

Received 12 June 2005; received in revised form 19 November 2005; accepted 25 November 2005
Available online 12 July 2006

Abstract

Laser gas assisted nitriding of Ti–6Al–4V alloy is carried out and nitride compounds formed and their concentration in the surface vicinity are examined. SEM, XRD and XPS are accommodated to examine the nitride layer characteristics. Microhardness across the nitride layer is measured. Temperature field and nitrogen distribution due to laser irradiation pulse is predicted. It is found that the nitride layer appears like golden color; however, it becomes dark gold color once the laser power irradiation is increased. The δ-TiN and ε-TiN are dominant phases in the surface vicinity. The needle like dendrite structure replace with the feathery like structure in the surface region due to high nitrogen concentration. No porous or microcracks are observed in the nitrided layer, except at high power irradiation, in this case, elongated cracks are observed in the surface region where the nitrogen concentration is considerably high.

Keywords: Laser; Nitriding; Ti–6Al–4V; Microstructure; Phases

1. Introduction

Titanium alloys are widely used in industries, particularly in aerospace industry due to their high toughness to mass ratio. In some industrial applications, the tribological properties of the alloy surface become important; in such cases, the alloy surface is subjected to wear. Therefore, the use of the alloy in such situations becomes limited due to the poor tribological properties of the surface. Moreover, many techniques are available to improve the surface properties of the alloy; however, the effectiveness including process time, precession, and process cost limit the applicability of these techniques. Laser gas assisted nitriding is one of the effective techniques to improve the surface properties of the alloy. In this case, nitrogen, as assisting gas, is used off-axis or co-axially with the laser beam during the laser processing of the surface. Moreover, laser processing parameters such as laser output power setting, pulsing frequency, spot diameter of the beam at the workpiece surface, transverse speed of either workpiece or laser beam, assisting gas pressure, and purity of the gas have significant effect on the nitriding process. However, most of the processing parameters are associated with the laser pulse power intensity at the workpiece surface; consequently, investigation into laser gas assisted nitriding process and the influence of laser pulse intensity on the quality of the nitrided surface becomes essential.

Considerable research studies were carried out to examine the laser gas assisted nitriding process [1–16]. Nitrogen content in the surface region can be uniformly distributed during laser gas assisted processing [1] and increasing nitrogen content in the melt layer improves the surface hardness of the substrate material [2]. This, in turn, improves significantly the wear properties of the surface, particularly addition of helium minimizes the oxidation reactions in the melt pool during laser irradiation of the surface [3,4]. Moreover, the rapid solidification after laser processing modifies the microstructure in the surface region influencing the hardness at the surface [5,6]. Once the nitrogen flow into the melt zone is reduced, dentrites and needles like structures form, which lower the hardness at the surface [7]. In the case of high nitrogen flow, feathery like structure forms in the surface vicinity of the substrate material and shallow layer of columnar TiN dentrites orienting perpendicular to the surface are resulted [8]. To improve the surface properties, preheating of the surface is suggested by Hu and Baker [9] and via this process the crack formation at the surface is minimized. Nitrogen depth profile is

* Corresponding author. Tel.: +966 3860 4481; fax: +966 3860 2949.
E-mail address: bsyilbas@kfupm.edu.sa (B.S. Yilbas).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2005.11.076

influenced by nitrogen mass flow rate, laser pulse energy and pulse profile [11–13]. Moreover, laser assisted processing can also be used to eliminate the mechanical short comes after plasma nitriding process. In this case, the white layer formed at the workpiece surface after the nitriding process can be mixed with the underlying nitride precipitates through laser melting [14]. Introducing the laser assisted duplex treatment at the surface improves the wear properties of the surface via improved adhesion of the TiN coating at the laser gas assisting nitrided surface [15,16].

Laser nitriding process was examined previously for nanosecond pulses in which case depth of nitride zone is limited to couple of micrometers for a single pulse irradiation [16]. However, laser nitride layer of the order of tens of micrometers is required for the practical applications. This requires modification of laser pulses with longer pulse lengths and high repetition rates. Consequently, in the present study, laser gas assisted nitriding process is considered and CO_2 laser delivering pulses within 2000 Hz is accommodated to secure the sufficient depth of nitride layer in the region below the workpiece surface. The diffusion equations for heat and species transfer are solved analytically and temperature as well as nitrogen concentration distributions in the region irradiated by a laser beam are predicted. To identify the nitride compounds, concentration, and microstructure SEM, XRD and XPS are carried out in the region subjected to the laser gas assisted processing.

2. Mathematical modelling

In order to be able to obtain an analytical solution to the problem, various factors are omitted and/or considered to be negligible in the present study. These factors include:

1. It is assumed that the thermionic emission is negligible; therefore, it is omitted.
2. No plasma is formed, i.e. the interaction between the laser beam and the charged particles is neglected.
3. All other processes, apart from the electromagnetic interaction with free electrons, affecting the absorption process are neglected, i.e. the absorption process is governed by the Beer–Lambert law.
4. Nucleation and liquid expulsion from the irradiated spot are omitted.
5. Beam focusing effects (spherical aberration) due to lens and plasma are assumed to be negligible.
6. The contribution of formation enthalpy of TiN in the melt zone is omitted due to relatively smaller energy input [17], because of the TiN formation, as compared to laser energy in the melt zone.

In addition, radiation losses from the irradiated surface are assumed to be negligible. Ready [18] estimated these losses as being between 6 and 10 orders lower than the incident energy. The steady state analysis of the heating process is carried out previously [19] provided valuable information on the behavior of the temperature at the surface during the laser irradiation pulse. However, the assumption of steady state behavior is limiting and it is, therefore, desirable to obtain an analytical solution to the unsteady heating problem. In this regard, the Fourier equation governing the unsteady heating can be written as

$$k\frac{\partial^2 T}{\partial x^2} + \rho C_p V_m \frac{\partial T}{\partial x} + I_0 \delta \exp(-\delta x) = \frac{\partial}{\partial t}(\rho C_p T) \quad (1)$$

where k, ρ, C_p, V_m, I_0, and δ are thermal conductivity, density, specific heat recession velocity of the surface, laser power intensity, and absorption coefficient of the substrate material, respectively.

Initially, it is assumed that the workpiece is at a uniform temperature. In order to simplify the mathematical arrangements it is further assumed that the workpiece is initially at 0 °C, i.e. $T(x, 0) = 0$ °C. Two boundary conditions are required to solve Eq. (1). It is, therefore, considered that at the surface the heat flux is equal to the rate of melt, i.e. at $x = 0{:}\partial T/\partial x_{|x=0} = \rho V_m L/k$, where V_m is the recession velocity of the surface due to melting and L is the latent heat of melting. The recession velocity of the surface is [19]:

$$V_m = \frac{I_1}{\rho[C_p T_s + L]} \quad (2)$$

where T_s is surface temperature and the power intensity at the surface is $I_1 = I_0(1 - r_f)$, r_f being the surface reflectivity. Moreover, it is also assumed that at a depth of infinity from the surface, the substrate material is at 0 °C, which is in equilibrium with the initial condition. In a such situation, heat diffusion cannot change the temperature from the initial condition at a depth of infinity below the surface, i.e. and at $x = \infty{:}T(\infty, t) = 0$ °C.

It is evident from Eqs. (1) and (2) that the problem is non-linear, since the velocity V_m is changing with time. Consequently, a complete solution to the heat transfer equation is extremely difficult, but a quasi-steady solution is feasible. The solution of Eqs. (1) and (2) with the appropriate boundary conditions can be obtained using a Laplace transformation. The mathematical arguments of the Laplace transformation are not given here due to lengthy arguments but are referred to in Ref. [20]. The solution of heat transfer equation yields:

$$\begin{aligned} T(x,t) = {} & \frac{I_0\delta\sqrt{\alpha}}{2\rho C_p(\alpha\delta - V)} \\ & \times \left(4\sqrt{t}\,\mathrm{ierfc}\left[\frac{x}{2\sqrt{(\alpha t)}} + b\sqrt{t}\right] + \frac{3b^2 + c^2}{2b(b^2 - c^2)}\right. \\ & \times \mathrm{erfc}\left[\frac{x}{2\sqrt{\alpha t}} + b\sqrt{t}\right] + \frac{1}{2b}\exp\left(\frac{-2bx}{\sqrt{\alpha}}\right) \\ & \times \mathrm{erfc}\left[\frac{x}{2\sqrt{\alpha t}} - b\sqrt{t}\right] + \frac{1}{b - c} \\ & \times \exp\{-[\delta x + (b^2 - c^2)t]\}\mathrm{erfc}\left\{-\left[\frac{x}{2\sqrt{\alpha t}} + c\sqrt{t}\right]\right\} \\ & - \frac{1}{b + c}\exp\left[-\frac{x}{\sqrt{\alpha}}(b + c) + (b^2 - c^2)t\right] \\ & \left.\times \mathrm{erfc}\left[\frac{x}{2\sqrt{\alpha t}} - c\sqrt{t}\right] - \frac{2}{b - c}\exp(-\delta x)\right) \end{aligned}$$