Surface & Coatings Technology 297 (2016) 34–42

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Surface stiffness gradient in Ti parts obtained by laser surface alloying with Cu and Nb

João B. Fogagnolo [a,*], Adilson V. Rodrigues [a], Edwin Sallica-Leva [a], Milton S.F. Lima [b], Rubens Caram [a]

[a] University of Campinas, School of Mechanical Engineering, Rua Mendeleiev 200, 13083-860 Campinas, SP, Brazil
[b] Instituto de Estudos Avançados, São José dos Campos, SP, Brazil

ARTICLE INFO

Article history:
Received 12 January 2016
Revised 9 April 2016
Accepted in revised form 11 April 2016
Available online 17 April 2016

Keywords:
Graded materials
Ti–Nb alloys
Ti–Cu alloys
Surface engineering

ABSTRACT

Titanium alloy components with a stiffness gradient have attracted technological interest for biomedical and structural applications. A stiffness gradient can be achieved by generating a chemical gradient or through localized phase transformation. The laser surface alloying technique can be used to fabricate parts with stiffness and hardness gradients by introducing a compositional gradient at the surface of the component. In this work, the surface of commercially pure titanium was modified by laser surface alloying, employing Nb or Cu as alloying elements. Single laser tracks were obtained using different heat inputs. The fusion zone of the laser tracks was characterized by scanning electron microscopy, X-ray diffraction and nanoindentation. The alloying content in the fusion zone decreased in response to increasing heat input. Independently of the heat input, the fusion zone of the Cu-alloyed laser tracks contained α phase dendrites, Ti_2Cu, α/α′ phase lamellae, and the α-Ti + Ti_2Cu eutectoid constituent. At a low heat input, the higher Nb content introduced on the modified surface sufficed to metastabilize the α″ and β phases, while α′ was predominantly present in the laser tracks produced at higher heat inputs. All the laser tracks presented significantly increased hardness, while the change in Young's modulus was dependent on the added alloying element and the processing parameters. The Young's modulus of the Nb-alloyed laser track obtained at 200 W was 30% lower than that of the substrate, while all the other conditions produced a stiffer surface region. Hence, a harder but less rigid coating can be obtained by this route.

1. Introduction

The possibility of manufacturing components with graded properties is extremely important in engineering. Steels are classic examples of components with a hardness gradient. The carburizing process is a very well-known example of surface hardening of steels that produces parts with a harder surface and a more ductile core, which is highly advantageous for components subjected to mechanical strain and surface friction. This route requires a compositional gradient (higher carbon content close to the component's surface) in order to produce a part with a hardness gradient. On the other hand, parts with a hardness gradient can also be obtained without a compositional gradient. It is widely known that different phases with distinct properties can be formed in steels, depending on the cooling rate and carbon content. The decomposition of austenite, for example, allows one to obtain a part with a harder surface (with martensitic phase) and a ductile core (with ferrite-pearlite microstructure). Like hardness gradients in steel, Ti and its alloys also allow for the manufacture of mechanical components with stiffness gradients. Similar to the aforementioned examples, stiffness gradients can be obtained in parts with or without a compositional gradient. The concept of components with a stiffness gradient was initially proposed for biomechanical purposes, such as subjecting distinct portions of the bone to different levels of stress [1] or even to reduce the contact stress in total hip joint replacement [2]. Moreover, osteoblast differentiation seems to be affected by the stiffness of biomaterial [3]. The use of components with a porosity gradient was initially tested [4] with a view to manufacturing metallic components with a stiffness gradient.

Full-density Ti parts with compositional gradients, and hence, with stiffness gradients, have been reported in earlier works. For example, using laser engineered net shaping (LENS), Nag et al. [5] described a component made of Ti—Ta alloy whose Young's modulus was a function of the Ta content. However, their purpose was to analyze a wide range of alloy compositions using smaller quantities of material. The study of routes to manufacture components made of titanium alloy with stiffness gradients, from the standpoint of their intended functionality, started later. One of the first papers with this new focus was published by Zhao et al. [6]. The work of these authors involved Ti—30Zr alloys with varied contents of Cr and Mo. The alloys were solubilized at 1123 K for one hour and then rapidly cooled in an ice-water mixture, enabling the complete stabilization of β phase at room temperature.

---

* Corresponding author.
E-mail address: fogagnolo@fem.unicamp.br (J.B. Fogagnolo).

http://dx.doi.org/10.1016/j.surfcoat.2016.04.025
0257-8972/

Strain-induced precipitation of α' phase was therefore used to increase hardening and Young's modulus, resulting in parts with a stiffness gradient obtained by localized deformation. The deformed region became stiffer while the non-deformed region remained more flexible. Subsequently, Zhao et al. [7] reported increases in hardness and Young's modulus by means of ω phase precipitation. The researchers of the same group also proposed an application for components with a stiffness gradient [8]. They argued that a high Young's modulus is desirable in some orthopedic implants in order to decrease their adverse elastic recovery and facilitate their implantation during surgery when manually bent inside the patient's body for *in-situ* spinal rod contouring. However, orthopedic implants must also have a low Young's modulus in order to decrease undesirable stress shielding and thereby reduce the phenomenon of bone resorption. These two conflicting requirements may be partly attained in stiffness-graded Ti components. This concept, which the authors call “self-adjustment of Young's modulus,” enables elastic recovery after bending to decrease in the course of surgery, by deformation-induced phase transformation in the bent region, allowing the rest of the orthopedic implant to retain a low Young's modulus.

Hanada et al. [9] took advantage of the effect of texture on the Young's modulus [10], which is quite pronounced in Ti alloys with α'' and β phases due to the anisotropy of the modulus of elasticity in different crystal directions of these phases, to expand the possibilities of obtaining stiffness-graded Ti components. They proposed a hip prosthesis stem whose stiffness and hardness in the neck are greater than in the rod region. They used Ti–33.6Nb–4Sn alloy and the processing route included cold rolling, cold swaging, cold die-forging and machining, resulting in a structure composed of stress-induced α'' martensite with $\langle 010\rangle$texture and β phase with $\langle 101\rangle$texture, with a Young's modulus of approximately 40 GPa. A heat treatment applied in the neck region promoted $\alpha'' \rightarrow \beta$ reverse transformation and α phase precipitation, increasing the hardness and stiffness without affecting the properties of the distal portions of the stem.

Simultaneously, Lopes et al. [11] reported a similar stiffness-graded hip prosthetic stem heat-treated to promote α phase precipitation in metastable β phase, thus enhancing Young's modulus and hardness in the neck region. These authors worked on Ti–30Nb–2Sn alloy (in mass%); α phase precipitation was promoted by a localized heat treatment at 400 °C in the neck region of the hip prosthesis stem. They reported that the Young's modulus and hardness were 110 GPa and 420 HV, respectively, in the neck region, and 65 GPa and 220 HV in the stem region.

As mentioned earlier, the first reports on stiffness-graded Ti parts were based on phase transformation, without a chemical gradient. In fact, the literature on stiffness-graded Ti components with chemical gradients is rather scanty. Kralya et al. [12] investigated the effect of plasma nitriding on the fatigue strength of VT22 titanium alloy and stated that they used an intermediate molybdenum layer, thereby preventing the decrease in fatigue resistance that normally occurs with harder coatings. They attributed this result to the lower stiffness of the intermediate layer. Based on this result, in a previous paper [13] we suggested that the fatigue strength of Ti components could be improved by the presence of a less rigid coating. This less rigid coating would presumably decrease the component's surface stresses, thereby hypothetically delaying the onset of fatigue cracking. The processing route selected to fabricate components with a less rigid surface layer was laser surface alloying with preplaced powders. Using this route, a sufficient amount of a β-stabilizer element such as Nb was introduced on the surface layer to stabilize the less rigid phases such as α'' and β phases. In the present work, aiming to obtain a less rigid surface on Ti substrate, we have extended the analysis of the processing parameters, comparing two distinct β-stabilizer elements: a β-isomorphous (Nb) and a β-eutectoid (Cu) element. Hardness and Young's modulus were determined by nanoindentation and are discussed in terms of the alloying content, which was controlled by the heat input.

2. Experimental procedure

We used sheets of commercially pure titanium grade 2 as substrate and Nb (supplied by CBMM, Brazil, 99.9% purity) and Cu (supplied by Citra Metalúrgica, Brazil, 99.7% purity) powder as alloying material. The powder was mixed with acetone to form a slurry, which then was applied on the substrate. After the acetone dried, a thin uniform layer of Nb or Cu powder was left on the substrate. Fig. 1 shows (a) the Nb powder preplaced on the titanium sheet prior to laser treatment, and (b) a perpendicular view showing the thickness of the preplaced powder layer. Note that this method enabled us to place a practically homogenous layer of powder about 200 μm thick on the surface of the Ti sheet.

Linear laser tracks were produced on the material's surface using an ytterbium fiber laser operating at a wavelength of 1.07 μm, with an approximation of the Gaussian beam distribution mode. The spot diameter of the beam was 1.6 mm at the material's surface. A protective flux of 30 l/min argon (99.999 purity, O_2, CO_2, $CO < 1$ ppm, $H_2O < 2$ ppm, $N_2 < 3$ ppm, total hydrogen content <0.5 ppm) was used in the melting region to inhibit oxidation. An x–y table with computer numerical control was used to move the samples at a constant speed of 10 mm/s under the laser beam. The laser power was set at 200, 300 or 400 W. For comparative purposes, linear laser tracks were produced on the material's surface with no preplaced powders, which are hereinafter referred to as unalloyed laser tracks.

The microstructure and chemical composition obtained in the fusion zone of the laser tracks was characterized by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS). The backscattered electron mode was employed to enable chemical contrast in the SEM. The phases on the surface of the sheet were identified by X-ray diffraction (XRD). To remove the elevation of the fusion zone relative to the sheet's surface and obtain a planar surface, which was necessary to perform the XRD analysis, the sheets were first sandpapered and polished. Nanoindentation was performed to determine the hardness and Young's modulus of the substrate and the fusion zone of the laser tracks, using a nanoindentation tester NHT from CSM Instruments with a previously calibrated Berkovich diamond tip. All the indentations were programmed to reach a depth of 2000 nm under controlled displacement. The measurements were taken at a distance of 100 μm from the surface and then at intervals of 200 μm down to the substrate.

3. Results and discussion

Fig. 2 illustrates the effect of heat input on the laser tracks, showing a cross section of the fusion zone of the laser tracks using different laser power densities, recorded by SEM in backscattered electron mode (BSE). Table 1 summarizes the width, depth and the cross-sectional area of the fusion zone, measured in the transverse direction, and the resulting depth/width ratio. Note that the surface of all the fusion zones is elevated relative to that of the sheet. This elevation can be attributed to the presence of pores and, to a lesser extent, to the undercut located parallel to the junction of the fusion zone and substrate surfaces. Evidently, the addition of alloying material increased the elevation of the fusion zone of the alloyed laser tracks. Besides that, a pronounced crack is visible in the laser track alloyed with Cu using 200 W of laser power.

As expected, an increase in laser power resulted in wider and deeper laser tracks, and therefore, a larger cross-sectional area. Since the displacement speed of the laser beam and the laser beam diameter were kept constant, higher laser power represents higher input energy, which can melt a larger amount of material, thus increasing the volume of the fusion zone.

The depth/width ratio, or aspect ratio, is useful to characterize the fusion zone produced by the straight displacement of a laser beam on a metallic surface. Thus, depending on the aspect ratio, the formation of the fusion zone can be classified as conduction or keyhole mode,