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Diffusion treatment of Ni–B coatings by induction heating to harden the surface of Ti–6Al–4V alloy

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ABSTRACT

Electroless nickel–boron coatings on Ti–6Al–4V alloy were obtained by immersion in nickel chloride aqueous solutions with sodium borohydride. The diffusion treatments were carried out by induction heating using a superficial magnetic field intensity (current in the coil) that allows to achieve a surface temperature of 1020 °C in 100 s.

The effect of induction heating on microstructure and mechanical properties of the Ni–B coated samples were evaluated by SEM, energy dispersive X-ray spectroscope (EDS), wavelength-dispersive spectrometry (WDS), glow discharge optical spectrometer (GDOS) and microhardness testing and the results were compared with those obtained previously by heat treatments in oven at 800 °C for 40 h.

Surface hardness higher than 900 HV_{100} and depth of hardening thicker than 300 μm were achieved by diffusion of the Ni–B layer carried out by induction heating.

1. Introduction

Titanium and its alloys are extensively used in the aeronautic industry thanks to their excellent properties. The use of these alloys under severe wear and frictional conditions are highly restricted because of their poor wear resistance. Various surface modification processes were carried out to improve the hardness and wear resistance of these alloys [1–9]. Recently, a method based on the Ni–B electroless plating followed by diffusion heat treatment was proposed by the authors [10]. The deposition of a Ni–B amorphous layer on the Ti–6Al–4V surface was obtained by immersion of the alloy in a $NiCl_2$ aqueous solution added with either dimethylamine borane (DMAB) or $NaBH_4$ as reducing agents. The following heat treatment in inert atmosphere led to a surface hardness up to 1000 HV_{100} which was related to the diffusion of nickel and boron into the substrate [11]. However, in previous works it was demonstrated that higher surface hardening was obtained after a diffusion process in oven at 800 °C for 40 h.

The aim of this work is to reduce the time to obtain a surface hardened layer on Ti6Al4V titanium alloy, by a diffusion treatment of Ni and B. This can be achieved by carrying out the diffusion treatment at a temperature above the beta transus temperature. In fact, at this temperature, general in the range from 990 °C to 1010 °C for Ti–6Al–4V, titanium undergoes an allotropic transformation from a hexagonal close-packed structure (α) to a body centred cubic (β) phase, in which diffusion is considerably higher. As heating process, the choice fell on the induction heating since it is a very versatile technique. It has been successfully used in several heat treatment processes because it can produce high power densities which allow short interaction times to reach the required temperature. This gives tight control of the heating 'pattern' with the pattern following the applied magnetic field quite closely and allows reduced thermal distortion and damage. The induced current flow within the part is most intense on the surface, and decays rapidly below the surface. So the outside will heat more quickly than the inside. One of the most common applications is induction hardening of steel parts. The induction hardening process is a localised heating which produces a surface hardening of an area that needs wear-resistance, while retaining the toughness of the original structure as needed elsewhere. The depth of induction hardened patterns can be controlled through the choice of induction-frequency, power-density and interaction time. This usually means that the process can be accomplished in a relatively short time and with high efficiency because energy is only applied where necessary. Moreover, the ability to heat treat in-line, as opposed to batch processing, with high productivity and a clean environment is an obvious benefit of induction heat treatment.

2. Experimental

Specimens of Ti–6Al–4V were obtained from a 18 mm diameter billet and mechanically polished using standard metallographic procedures. The length of the samples was 100 mm. The surface of the specimens was degreased with alcohol and

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Table 1
Composition of the electroless bath.

Compound	Concentration
Nickel chloride	20 g l^{-1}
Sodium hydroxide	90 g l^{-1}
Sodium borohydride	1 g l^{-1}
Tallium nitrate	0.11 g l^{-1}
Ethylendiamine	100 ml l^{-1}
Temperature	90–95 °C
pH	>12

air dried, then activated by chemical etching in a 6% HF aqueous solution for about 1 min at room temperature. After chemical etching, the specimens were rinsed with deionised water and immersed in the Ni–B electroless solution.

The chemical composition of the electroless solution is reported in Table 1. Electroless Ni–B deposits of 20 μm were obtained after 1 h of immersion.

Diffusion heat treatments of the plated specimens were carried out by induction heating in air, followed by cooling in air. The coil was constituted by six spires of a copper tube 10 mm × 10 mm × 1 mm for a total length of 55 mm and cooled with water. The inductor has been supplied by a frequency converter with the following specifications: frequency 450 kHz, rated power 100 kW.

By a proper choice of superficial magnetic field intensity (current in the coil) and frequency it is possible to concentrate the power density only in the region to be treated. For this specific case, the choice of frequency is related also to the frequency converters available at the Electrical Engineering Department (University of Padua). Among the different power generators a frequency of 450 kHz has been chosen in order to reach a very small penetration depth of the electromagnetic wave. The current influences the time of the process, the surface temperature, and the penetration of the heating. The purpose was to find the value of the current that makes it possible to heat uniformly the surface at a higher temperature than the beta-transus temperature, leaving the core of the substrate at a lower temperature than beta-transus temperature, in order to avoid the growth of the previous β grains.

In order to evaluate the main parameters of the heating process, a numerical simulation with a Flux2D has been performed [12,13], using the electromagnetic characteristics of the Ti–6Al–4V alloy and NiB coating summarized in Table 2. This software, based on the Finite Element Method, was able to predict the time necessary to reach the treatment temperature and the radial and axial temperature distribution in the workpiece (since the inductor-piece has a twofold symmetry, the Flux2d software considers only one quadrant of the existing four in which the total geometry can be divided in), with a good agreement with the experimental results.

Flux2D simulations were realised with the frequency value of 450 kHz and with values of the current in the coil ranging between 50 A and 500 A.

The specimen concentration profiles were obtained by a LECO GDS 750 A glow discharge optical spectrometer (GDOS) with an anode surface area of 4 mm^2 at 700 V with a current of 20 mA. In order to determine the profile concentration of elements in the NiB coating, the planar surface of the Ti6Al4V billet (the base of the cylinder) was analysed after immersion in the NiB electroless solution for 1 h. Since the base of the cylinder samples was external to the spires during induction heating, and since it is not possible to realise GDOS measurements on a curved surface, it was necessary to cut a 1 mm slice from the surface (along the axial direction), and then encapsulate it in conductive resin leaving the planar surface exposed, in order to determine the profile concentration of the elements inside the reaction layer after the heat treatment. Subsequently, this sample was thinned until reaching the zone of diffusion. Like this, it was possible to perform the GDOS analysis of the reaction layer starting from the inner side.

The coating morphology and alloys microstructure were characterised by optical microscopy, and by a Cambridge Stereoscan 440 SEM equipped with a Philips PV9800 energy dispersive X-ray spectroscope (EDS) and a ThermoFisher MAXray parallel beam spectrometer (PBS). The PBS combines the resolving properties of wavelength-dispersive spectrometry (WDS) with the sensitivity of a large area energy-dispersive detector for low voltage/low beam current applications [14]. The analysis with PBS–WDS, that allows the detection of light elements as boron, was performed to determine the eventually presence of borides, using a MoB4C145 diffractor, under an accelerating voltage of 10 kV and a probe current of 10 nA.

The microhardness profiles were obtained by a Leitz-Werlag microhardness tester with 100 g weight.

Table 2
Properties of Ti–6Al–4V alloy and Ni–B coating.

Property	Ti–6Al–4V	Ni–B
Electrical resistivity [μΩ cm]	168	89
Permeability	1	1
Thermal conductivity 20–100 °C [W (m K)$^{-1}$]	5.8	82
Specific heat at 50 °C [J (kg K)$^{-1}$]	610	527
Density [g cm^{-3}]	4.42	8.25

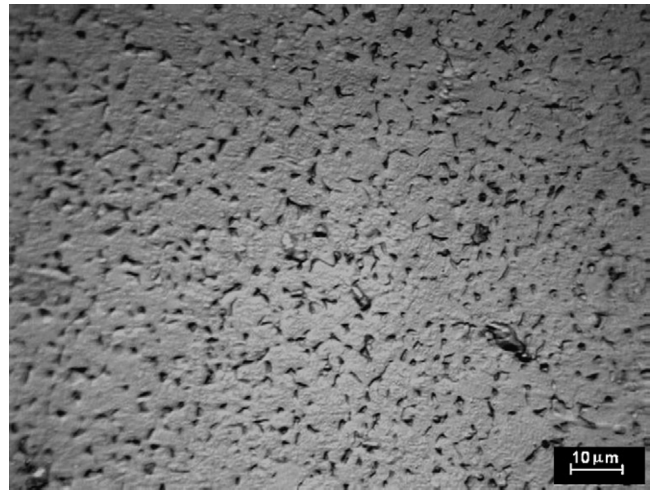

Fig. 1. Microstructure of the as-received Ti–6Al–4V alloy.

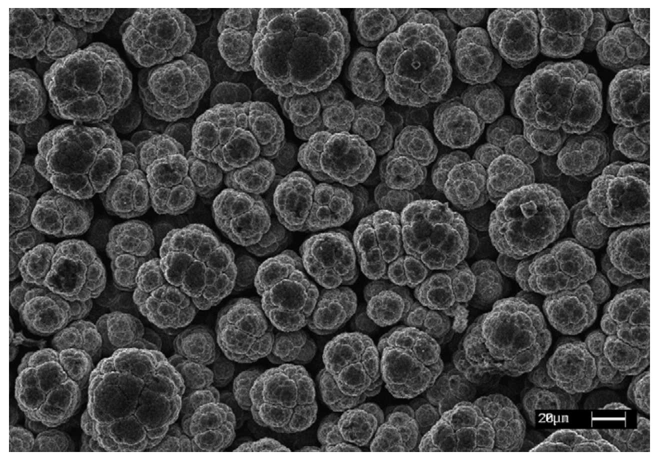

Fig. 2. SEM image of surface of Ni–B coated sample.

3. Results and discussion

The microstructure of the as-received Ti–6Al–4V alloy was constituted of equiaxed α phase with a small amount of intergranular β phase (Fig. 1).

The deposition process produced an amorphous, uniform and dense Ni–B coating without porosity and cracks, exhibiting a cauliflower-like structure (Fig. 2) [10,11]. The coating thickness was about 20 μm as confirmed by the GDOS concentration profiles

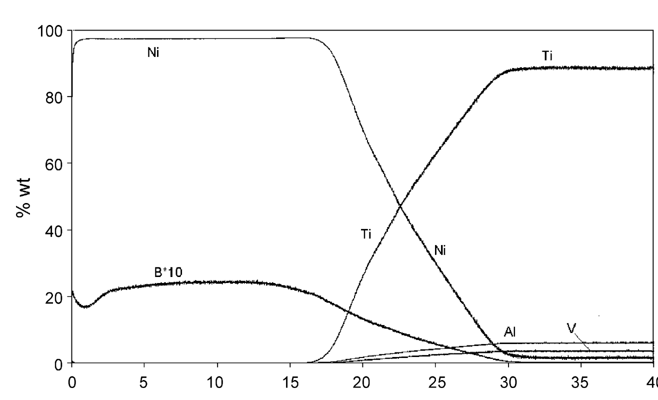

Fig. 3. GDOS profile of Ni–B coated sample.