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In situ laser deposition of NiTi intermetallics for corrosion improvement of Ti−6Al−4V alloy

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Abstract: NiTi intermetallic coatings were fabricated on the surface of Ti−6Al−4V alloy by melting Ni and Ti powders using laser metal deposition (LMD) process. The effects of NiTi reinforcement content on the microstructure, hardness and corrosion properties of the coatings were examined. The results show that the deposited coatings are characterized by NiTi, $NiTi_2$ and $NiTi_3$ intermetallic phases. An appreciable increase in corrosion resistance is obtained for all the coatings, and Ti55Ni45 coating shows the highest corrosion resistance; while coatings Ti50Ni50 and Ti45Ni55 follow in that succession. The reinforcement materials are proven to be corrosion resistant in the tested environment, and the effect of Ti is more dominant.

Key words: Ti−6Al−4V alloy; NiTi intermetallic; laser metal deposition; corrosion behaviour

1 Introduction

Ti−6Al−4V alloy is considered a capable structural material for aerospace, biomedical and petrochemical industries due to the combination of outstanding high specific strength, biocompatibility and good corrosion resistance [1]. However, due to the potential difference of the $\alpha+\beta$ phase of the alloy, galvanic interaction increases and acts as preferential sites for corrosion. Furthermore, the vanadium oxide that forms on the surface is insoluble in aqueous solution. Hence, the deterioration in the corrosion behaviour of Ti−6Al−4V alloy is evident [2]. As a result, their applications are restricted in severe corrosive environments.

Numerous studies with the purpose of improving the surface properties of Ti−6Al−4V alloy have been undertaken with different degrees of success. Researchers agree that changing the nature of the surface by using different surface engineering techniques is the best solution to overcome the limitation of titanium alloys [3,4]. Laser processing techniques have been found to be free from these shortcomings and can be used to enhance the surface properties of ferrous and non-ferrous metal surfaces [5−9]. As a flexible process, laser surface technique is used in the fabrication of different coatings for improving the surface properties and the repair of the worn parts [10]. Among the laser surface coating methods, laser deposition is the preferred method because of the novel microstructures and phases that can be formed due to rapid cooling and solidification rates associated with the processing technique [11]. Coatings generally have such microstructures that cannot be easily obtained by conventional techniques. One of the advantages of laser surface coating is that quite a number of metallic powders can be used to form intermetallic compounds exhibiting excellent wear resistance, good corrosion and oxidation resistance properties.

NiTi coatings have been a subject of great interest and have been widely exploited for a range of applications including aerospace, biomedical engineering and micro electrochemical system due to the above mentioned advantageous properties [12−16]. Many metals including stainless steel, aluminium and copper surfaces have been coated with NiTi to enhance their mechanical properties and corrosion resistance using laser deposition techniques, plasma transfer arc (PTA), plasma welding, plasma spray coating and sputtering process, all with different degrees of successes [17−20].

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Among the wide research conducted in surface modification of Ti−6Al−4V, the focus has been on the microstructural evolution, improved hardness and wear resistance, with little on improving corrosion resistance. According to the available information in the open literature, there is no research on laser deposition of NiTi on Ti−6Al−4V alloy. In this work, mechanically alloyed Ni and Ti elemental powders were used to form in situ NiTi intermetallic — thin surface coatings on the Ti−6Al−4V substrate. The laser metal deposition technique was employed to melt powders of different compositions: Ti50Ni50, Ti45Ni55 and Ti55Ni45. The microstructure, phase composition, microhardness and corrosion properties of the coatings were investigated.

2 Experimental

2.1 Materials

The materials used in the experiment are elemental Ni and Ti powders with the particle size fraction within the range from 45 to 63 μm. Prior to milling, the powders were weighed and mixed together to give nominal compositions of Ti55Ni45, Ti50Ni50 and Ti45Ni55 (mass fraction, %). The initially mixed powders were mechanically alloyed in a planetary ball mill by subjecting the particles to repeated welding, fracturing and re-welding from the collision of the particles and the grinding medium. The milling was performed for 2 h to allow the powders to reach a steady state where homogeneous NiTi powder was produced. The ball to powder ratio was kept uniform at 10:1 and the rotation speed was 300 r/min.

2.2 Laser surface coating

The cold rolled Ti−6Al−4V plate with dimensions of 72 mm × 72 mm × 5 mm was used as the substrate for depositing the coatings. The plates were sandblasted and cleaned with acetone prior to the laser coating process. Table 1 shows the laser experimental processing parameters of the coating deposition. The free flowing NiTi pre-alloyed was fed through a three-way nozzle with argon shielding gas stream. The argon gas flow rate was 5 L/min. The CW 4.4 kW Rofin Sinar Nd: YAG laser operated with 1.064 μm in wavelength was used to deposit the coatings. The beam spot on the target was 2 mm in diameter. The scanning speed, laser power and the powder flow rate were kept constant.

2.3 Microhardness analysis

The Vickers hardness of polished specimens was determined using a Matsuzawa Seiko Vickers microhardness tester (model MHT−1) with a Vickers diamond indenter. An indenting load of 100 g, a spacing of 50 μm and a dwell time of 10 s were used for each hardness indent action. Indentations were made across the deposited layer in three areas from the top of a clad into the substrate. The Vickers hardness was calculated using the equation:

$$H_{\mathrm{HV}} = 1.854\frac{F}{S} \tag{1}$$

where F is the applied load (kg) and S is the area of the indentation (mm^2).

2.4 Corrosion analysis

The electrochemical corrosion test was conducted using potentiodynamic polarisation technique equipped with potentiostat Autolab type 3 according to ASTM G3−89 and ASTM 5−94 standards in 3.5% NaCl solution. A three-electrode arrangement, with an electrode containing Ag/AgCl 3 mol/L KCl as the reference electrode (SCE) was used. The electrochemical corrosion behaviour of the samples was investigated using linear polarization. The analysis was carried out at a scan rate of 0.111 m/s, a start potential of −1.5 V and a stop potential of +1.5 V for a duration of 1 h.

2.5 Characterization of materials

The metallographic samples were sectioned with a Corundum L205 cut-off wheel using a Struers Discotom−2 cutting machine. After sectioning, the specimens were hot-mounted in clear thermosetting Bakelite resin. The specimens were then ground and polished to a 0.04 μm (OP-S suspension) surface finish with a Struers TegraForce−5 auto/manual polisher and etched in Kroll reagent by immersing the samples for approximately 10 s. The microstructure was characterized on an Olympus BX51M optical microscope and a Jeol JSM 6510 scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was conducted using the Rigaku/Dmax 2200 PC automatic X-ray diffractometer with Cu target K_{α} radiation for phase identification.

Table 1 Laser experimental processing parameters for coating deposition

Composition	Laser power/W	Beam spot diameter/mm	Scanning speed/ (mm·s^{-1})	Powder feed rate/ (g·min^{-1})	Carrier and shield gas	Gas flow rate/ (L·min^{-1})
Ti45Ni55 Ti50Ni50 Ti55Ni45	800	2	8	3	Argon	5