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Microstructure and Corrosion Behavior of Laser Synthesized Cobalt Based Powder on Ti-6Al-4V

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Abstract. The corrosion behavior of titanium alloys when used for various dynamic offshore components has been a major concern of titanium drilling risers in deepwater energy extraction. A way of achieving specified requirement is the development of coatings suitable to protect the base material against corrosion. In this work, laser cladding technique which is known as a leading edge due to its distinctive properties and outcomes was used in synthesizing Co-based powder on titanium alloy. The processing parameters used were laser power of 900W; scan speed of 0.6 to 1.2 m/min; powder feed rate 1.0g/min; beam spot size 3mm; gas flow rate 1.2L/min. The effects of cobalt addition and laser parameters on corrosion behavior of laser clad Ti6Al4V coating in 0.5M sulfuric medium were investigated using linear potentiodynamic polarization. The changes in microstructure and corrosion behavior were analyzed using scanning electron microscopy (SEM) while the X-ray diffraction (XRD) indicates the intermetallics in the coatings. Results showed that the coatings displayed good metallurgical bonding with dendritic formations between the coatings and the substrate. The anodic current density increased with lower scan speed. However, the corrosion current densities of laser-clad samples were lower than Ti6Al4V alloy.

1. Introduction

Since titanium and its alloys became available in the mid-twentieth century, its level of use in offshore and petrochemical applications competes with about 80% of its usage in the aerospace industry [1]. The unique properties of titanium and its alloy such as low density, excellent combination of high specific strength ratio which is maintained at elevated temperature, low modulus of elasticity, good compatibility and good corrosion resistance, makes it a choice material in a wide range engineering application such as power generation, offshore and chemical industries [2, 3]. However, passive behavior of Ti6Al4V in sulphuric, and hydrochloric acids has been a prime concern by many investigators [4, 5]. Contu et al [11] explained that when titanium alloy is submerged in sulphuric acid during applications, it is covered by a thin film of TiH₂. According to Tiyyagura et al [6], hydride formation on the surface is usually not stable for lower over-potentials. In order to mitigate this challenge, there is a need to produce a surface that is deficient of such passive film layer [7]. Surface modification techniques such as laser cladding technique have been employed to fabricate coatings with advanced mechanical and corrosion properties in metal surface improvement [8]. Cobalt based alloys tend to be a less deleterious material used mostly as a supporting material with numerous



applications in the engineering field because of its excellent resistance to corrosion. Retorts and gas turbine engines or parts (vanes, blades, turbines and compressor discs) are few of the sections in heat treatment plants where cobalt-alloys are commonly utilized and these sections are exposed to long term alternation stresses at elevated temperatures, due to their exceptional strength at high temperatures and also, low susceptibility to sulfidation, nitriding and oxidation [9, 10]. Moreover, the addition of Ni [11] in laser cladding of Co is expected to produce complex phases of CoNi intermetallic with a wide range of superior and functional properties. In this study, a detailed investigation has been undertaken to identify the effect of cobalt based alloy and parameters of laser surface cladding on the microstructure, improvement in electro - chemical behavior of Ti - 6Al - 4V.

2. Experimental

2.1. Materials and coating preparation

In this study, Ti-6Al-4V plates were used as substrates (50 x 50 x 5 mm). The substrate were sandblasted by spraying them with SiO₂ grit sand and cleaned with acetone before exposure to laser beam to influence absorptivity of the laser beam radiation. LSC experiment was carried out using a continuous wave 4.4 kW RofinSinar Nd: YAG laser. The processing parameters used were laser power of 900W; scan speed of 0.6to1.2m/min; powder federate 1.0g/min; beam spot size 3mm; gas flow rate 1.2L/min. In the course of laser cladding process, the molten pool was protected by argon gas flowing at 3 L/min. This was done in order to prevent oxidation as Ti has high affinity for oxygen.

2.2. Microstructural characterization and corrosion measurement

The microstructures of the laser clad coatings were analyzed by SEM equipped with an (EDS) Energy Dispersive Spectroscopy (FE-SEM JSM-7600F) while the phases were examined using Philips PW1713 X-ray diffractometer (XRD) fitted with monochromatic CuK α radiation set at 40Kv and 20mA, while phase identification was done using Philips Analytical X'Pert High Scores software fitted with an in built (ICSD) database. The electrochemical behavior of thespecimen was studied 0.5 M H₂SO₄environment at room temperature using the potentiodynamic polarization method at scan rate of 2mV/S starting from -1.0 V (with respect to the OCP) toabout 1.2 V. Platinum rod was used as the counter electrode and a silver/silver chloride (3 MKCl) as the reference electrode (SSE). The electrochemical parameters were calculated by analyses of the Tafel region using the General Purpose Electrochemical Software (GPES) version 4.9.

3. Results and analyses

3.1. Microstructure and characterization of laser coatings

Figure 1 reveals the SEM image showing the morphologies of the coatings and distributions for 70Co-30Ni coating fabricated at different scan speeds. It is noted that all the coatings revealed good dense and strong metallurgical bonding. This is substantiated by the fact that coatings fabricated by laser cladding technique on titanium (Ti6Al4V) is supported by the action of higher heat input as stated by Tan et al [12]. Figure 1 (a) is characterized by larger grains while Figure. 1(b) is characterized by smaller grains which could be seen at top right of the coating. At Figure 1 (a) lower scan speed revealed grain growth with equiaxed structures. The rationale is that, at low laser scan speeds, the clad layer rests on a larger dilution zone, due to a prolonged energy input from the heat source to support inter-diffusion with migration of elemental atoms between the coating and the substrate [13]. The coating in Figure 1b was exposed to rapid heating and solidification owing to high scanning speed, therefore resulting in uneven heating rate which lead to transformation from equiaxed to dendritic microstructures structure. Unlike the equiaxed grains associated with coating deposited at lower scan speed, Figure 1b is characterized by a mixture of thin columnar grains and dendritic structures owing to increased solidification rate at higher scan speed [14]. Higher scan speed is characterized by increased cooling rate as a result of rapid heat transport from the melt pool leading to formation of larger band of dendritic structures. Literature has shown that rapid solidification of Co tends to grow as dendrites [15].

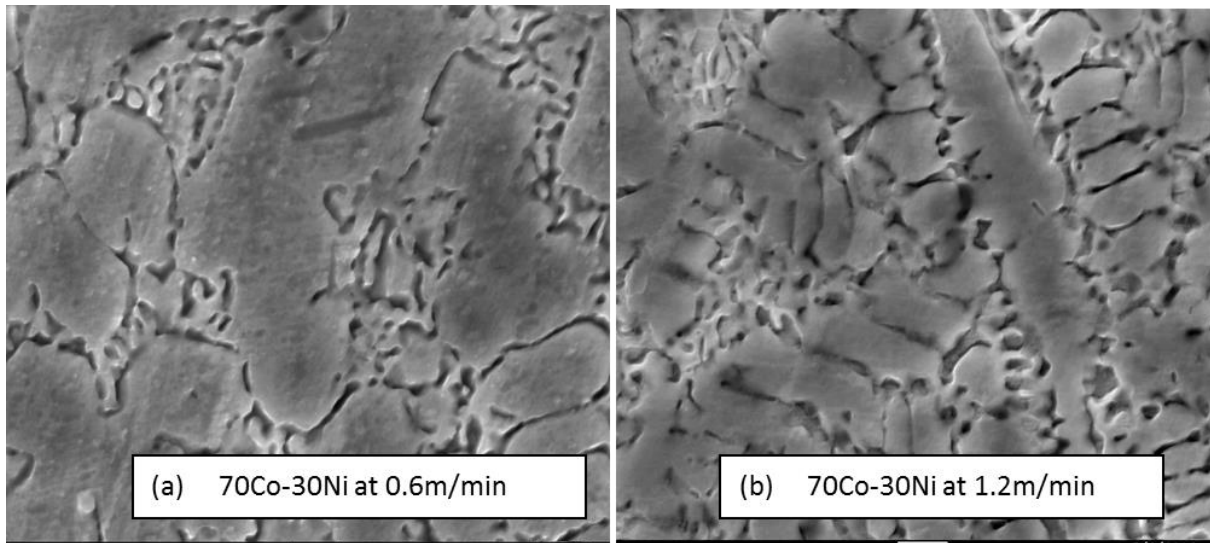


Figure 1: SEM showing microstructural evolution of 70Co-30Ni clad samples at (a) 0.6 m/min and (b) 1.2 m/min at 900 W.

3.2. Phase analysis

The XRD patterns displayed in Figure 2 clearly shows that the phases formed in these coatings differ significantly, as a result of varying laser parameters. At 0.6m/min scan speed the phases revealed Ti_2Ni , Co_3Ti , $Al_{13}Co_4$ while at 1.2 m/min, the XRD spectrum result revealed additional novel phases of $NiTi$ and Ni_3Ti . Intermetallic phases of Co_3Ti and $Al_{13}Co_4$ were identified as dominant phases in the spectrum. Weng et al [16] stated that high energy radiated by the laser beam lead to molten powders interactions with substrate, thereby yielding complex chemical reactions. Consequently, emanation of Ti and other alloying elements from the substrate at both scan speeds indicates sufficient energy intensity to encourage intense material diffusion and mixing between the substrate and the coating [14].

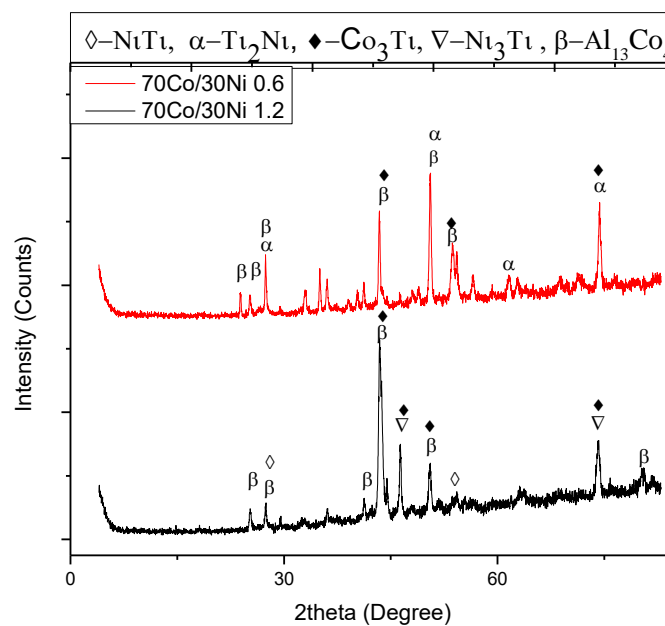


Figure 2: X-ray diffraction analysis of laser Clad 70Co-30Ni clad samples.

3.3. Corrosion behavior

Figure 3 illustrates the potentiodynamic polarization curves of 70Co/30Ni laser clad on Ti6Al4V substrate at scan speeds 0.6 and 1.2 m/min both at laser power of 900W. Electrochemical oxidation behaviors were investigated with the help of potentiodynamic polarization technique in 0.5M H₂SO₄. An increase in laser scan speed resulted in corrosion current density of the fabricated coatings declining from 0.0000473mA to 0.0000417mA, thus revealing the effect of laser speed on corrosion current by changing the grain size of 70Co-30Ni alloy. There is a slight passivation trend over the range of potentials for the substrate on the anodic branch. However, Ti6Al4V is known to form protective film on the alloy surface which turns to slow down/stop accelerated electrochemical surface deterioration [17]. The anti-corrosion of fabricated coatings may be linked to simultaneous effects of important factors, for instance chemical composition, phase structure, grain size and preferred orientation [18]. Non-uniform distribution of the Co-Ti reinforcement can be observed on the microstructure of this coating on both 0.6m/min and 1.2m/min samples. The grain boundaries show no sign of micro pores, no cracks and intermediate homogeneity of the fabricated is displayed. 70Co/30Ni at 0.6m/min is represented by Ti₂Ni, Al₁₃Co₄ and Co₃Ti phases as shown in Figure 2. Hence, improved corrosion properties are displayed by the fabricated coatings. This is due to the fact that Ni-Ti phase is nobler than Ti6Al4V [19]. High laser scan speed (1.2m/min) resulted in less potential value while low scan rate (0.6m/min) resulted in increased potential for coating. The 70Co-30Ni coating at 0.6 m/min displays a slight primary passivation potential while 1.2 m/min 70Co-30Ni fully shows passivation with a greater passivation area and a prolonged trans-passive region.

Table 1: Potentiodynamic polarization data of samples in 0.5M H₂SO₄

Laser parameters	E _{corr} , Calc (V)	E _{corr} , Obs (V)	i _{corr} (A/cm ²)	CR (mm/yr)	R _p (Ω.cm ²)
Control	-0.24539	-0.26757	0.00016067	1.3855	627.35
70Co/30Ni- 0.6 (900)	0.033378	-0.039468	4.73E-05	0.40819	1455
70Co/30Ni- 1.2 (900)	-0.18729	-0.22669	4.17E-05	0.36001	777.86

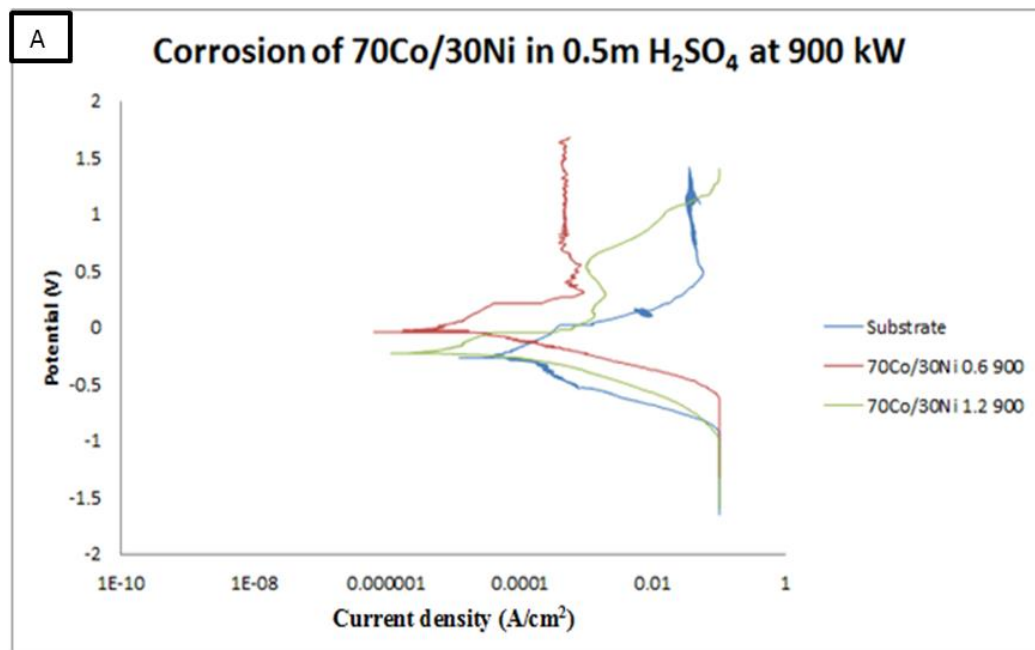


Figure 3: Potentiodynamic polarization curves of Ti6Al4V substrate and laser clad 70Co/30Ni at 0.6m/min and 1.2m/min.

4. Conclusion

Coatings produced a crack free, dense and strong metallurgical bond with significant effect on the microstructure and corrosion properties. The microstructural characteristic at lower scan speed shows larger grains with equiaxed structures while high scan speed is characterized by a mixture of thin columnar grains and dendritic structures owing to increased solidification rate. XRD analysis confirms the presence of novel phases such as Ti_2Ni , Co_3Ti , and $Al_{13}Co_4$. These intermetallic phases dispersed within the coating matrix could be responsible for the improved corrosion obtained. Laser clad coatings exhibited active-passive behavior in sulfuric environment. The anodic current density increased with lower scan speed. Likewise, the corrosion current densities of laser-clad samples were lower than Ti6Al4V alloy. In summary, cobalt is considered a more active element in improving the corrosion behavior of titanium in aggressive corrosive medium.

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