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Publisher's version / Version de l'éditeur:

TMS Annual Meeting, 1, pp. 569-576, 2011

LASER CLADDING OF FUNCTIONAL COATINGS FOR BIOMEDICAL APPLICATIONS

Shaodong Wang and Lijue Xue

National Research Council of Canada, Industrial Materials Institute
800 Collip Circle, London, Ontario, Canada N6G 4X8

Keywords: Laser cladding, Coating, Medical implants, Ti foam, Ti-6Al-4V alloy

Abstract

Surface coating can be used to enhance and/or optimize the functionalities of medical implants and devices. Laser cladding, a material additive technology, has a potential to apply various functional coatings on the metallic materials for biomedical applications. Two laser clad coatings have been investigated for potential medical implant applications: (1) Ti-6Al-4V alloy coating laser-clad on porous titanium foams; and (2) Composite coating of Ti-6Al-4V combined with CoCrMo alloy laser-clad on solid Ti-6Al-4V substrates. The microstructure of the laser-clad coating was examined by optical microscope (OM) and scanning electron microscope (SEM). Microhardness was measured in the laser-clad coating. Sliding wear testing was particularly performed to evaluate the wear resistance of (Ti-6Al-4V + CoCrMo) composite coating using pin-on-disc wear testing. Initial results show that laser-clad Ti-6Al-4V coating on porous titanium foams is dense and crack-free. The addition of a small amount of CoCrMo alloy will significantly increase the wear resistance of the Ti-6Al-4V composite coating.

Introduction

Titanium and Ti-6Al-4V alloy have excellent biocompatibility, especially when directly contact with tissue or bone. Also titanium and its alloys have high corrosion resistance, low elasticity modulus and high specific strength which make them suitable to be used as biomaterials [1]. But the inferior wear resistance causes it difficult for some applications, such as bone screws or joints, since the poor wear properties make it tends to seize when in sliding contact with itself and other metals [2].

Furthermore, porous titanium shows better compatibility of stiffness with bone tissue comparing to solid material. Porous structure also allows ingrowth of bone tissue which creates good bonding between the implant and bone [3-4]. But for some applications which require relatively high strength, especially high surface strength, porous titanium foam with a dense surface coating will have more advantages. There are technical challenges that need to be addressed to deposit dense Ti-6Al-4V coatings with metallurgical bonding to the porous Ti substrates.

On the other hand, biomedical CoCrMo alloys show excellent wear resistance, high stiffness, high corrosion resistance and good bio-chemical inertness [5-6]. The combination of CoCrMo alloy coating with light-weight Ti-6Al-4V base will create superior bio-components (such as knee implants, metal-to-metal hip joints and dental prosthetics) which possess superior wear and corrosion resistant surface with desired bulk mechanical properties.

The challenge of depositing CoCrMo alloys on Ti-6Al-4V substrates by laser cladding is metallurgical incompatibility of the two materials, which results in cracking. Cracks formed in the laser-clad coatings are presumably caused by two effects: (a) interaction between the two materials at high temperature can lead to the formation of various intermetallic compounds that are naturally very brittle; (b) the mismatch in the thermal-mechanical properties between the two materials leads to excessive residual stresses in the coatings and results in subsequent cracking.

The current study investigated laser cladding of dense Ti-6Al-4V coating onto porous Ti foam and examined the microstructure and microhardness of the laser-clad Ti-6Al-4V layer. The study also evaluated the influence of the CoCrMo alloy content in the coating matrix (CoCrMo alloy + Ti-6Al-4V) on mechanical properties of the laser-clad coating, including microhardness and slide wear resistance. The purpose of this work is to obtain the preliminary information about the laser-clad coating of Ti-6Al-4V, with the addition of CoCrMo alloy, for potential biomedical applications.

Experimental Procedure

Experimental Set-Up

Laser cladding was carried out by using a 500 W pulsed Nd:YAG laser (LASAG) of 1.064 μm wavelength along with a processing head with a focal length of 115 mm, which was connected through a 600 μm diameter optical fiber. Argon was used as powder carrying gas as well as shielding gas. Porous titanium substrates were prepared by NRC-IMI (Boucherville) using the patented technology [7]. Ti-6Al-4V alloy powder as a feedstock was used for laser cladding on the surface of porous titanium rods and discs. A special laser cladding procedure was developed to ensure that deposited Ti-6Al-4V coating is dense with metallurgical bonding to the Ti foam. Ti-6Al-4V alloy flat substrates were also used to investigate the influence of the CoCrMo alloy content in the laser-clad Ti-6Al-4V coating matrix. Premixed Ti-6Al-4V powders with varying percentages of Co-Cr-Mo content were laser clad on Ti-6Al-4V substrates. Characteristics of powders for laser cladding were listed in Table 1.

Table 1 Characteristics of powders for laser cladding

Powders	Composition (wt%)	Particle Size	Density (kg/m^3)	Melting Temperature (°C)
Ti-6Al-4V alloy	Ti: Balance Al: 5.5 – 6.76 V: 3.5 – 4.5	-325 mesh (< 44 μm)	4.42	1604~1660
Co-Cr-Mo alloy	Co: Balance Cr: 26 – 30 Mo: 5.0 – 7.0	-325 mesh (< 44 μm)	8.28	1260~1265

Sample Characterization

Microstructure examination of the cross-section of laser-clad coating was conducted by optical microscope and SEM/EDX after mechanical polishing. Vickers microhardness measurements were performed on the Buehler MICROMET II microhardness tester with a load of 100 g on the laser-clad layer after fine grinding and polishing. A pin-on-disk-type (Falex ISC) tribometer was used for wear testing under dry-sliding conditions. To allow wear tests, a pad of coating with dimension of 25.4 mm × 25.4 mm (1" × 1") was laser clad on Ti-6Al-4V substrates. The laser-clad coating was fine ground to obtain a flat surface and cleaned with acetone before wear tests. The pin-on-disc wear tests were carried out under a dry and uncontrolled atmosphere. Wear resistance was characterized by using the volume loss of the specimen and by observing the wear scars. The volume loss was calculated from the weight loss and coating density, which can be estimated using the law of mixture between the CoCrMo alloy and Ti-6Al-4V alloy. The mass loss of Cr-steel balls was not measured.

Results and Discussion

Laser Cladding of Ti-6Al-4V coating on Porous Titanium Rods and discs

Figure 1 shows the samples of porous titanium rods and disc laser-clad with Ti-6Al-4V alloy coating. The coating can be machined (ground) to a desired surface finish. The laser-clad coating is 1 ~ 2 mm in theckness.

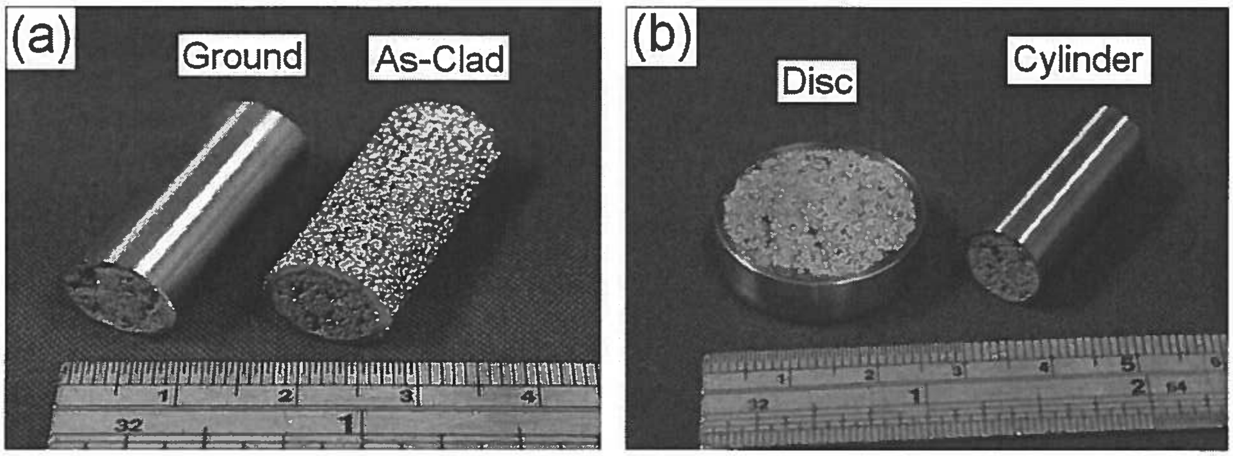

Figure 1 a) Examples of Ti-6Al-4V laser-clad Ti foam specimens before and after machining; and b) different shapes of specimens.

Figure 2 shows the cross-section of a Ti-6Al-4V laser-clad Ti foam rod by SEM. Just adjacent to the Ti foam core, there is a transition layer. When laser cladding, the laser heat source melted a thin layer of the outmost surface of the Ti foam rod as well as Ti-6Al-4V powder blown in the molten pool. The melted metal soaked a small layer into the Ti foam through the porous structure to form this transition layer. Pores are existent in this layer. Outside this transition layer, there is a solid laser-clad layer of Ti-6Al-4V with on cracks and porosities. Laser cladding creates a metallurgical bonding between the Ti foam and clad layer.

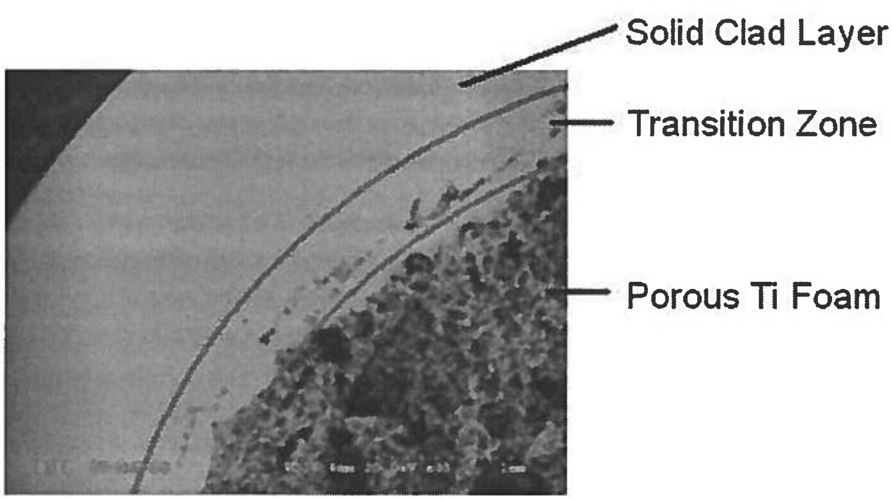

Figure 2 SEM photo for cross-section of laser-clad Ti-6Al-4V layer on porous Ti foam core.

The hardness profile of the laser-clad layer along the depth was plotted in Figure 3. The Vickers hardness in the laser clad Ti-6Al-4V layer is quite uniform at the average value of 314 $Hv_{0.1}$, which is slightly lower than wrought Ti-6Al-4V in annealed condition (354 HV converted from 36 HRC [8]). The hardness in the transition zone has a large variation due to the existence of pores.

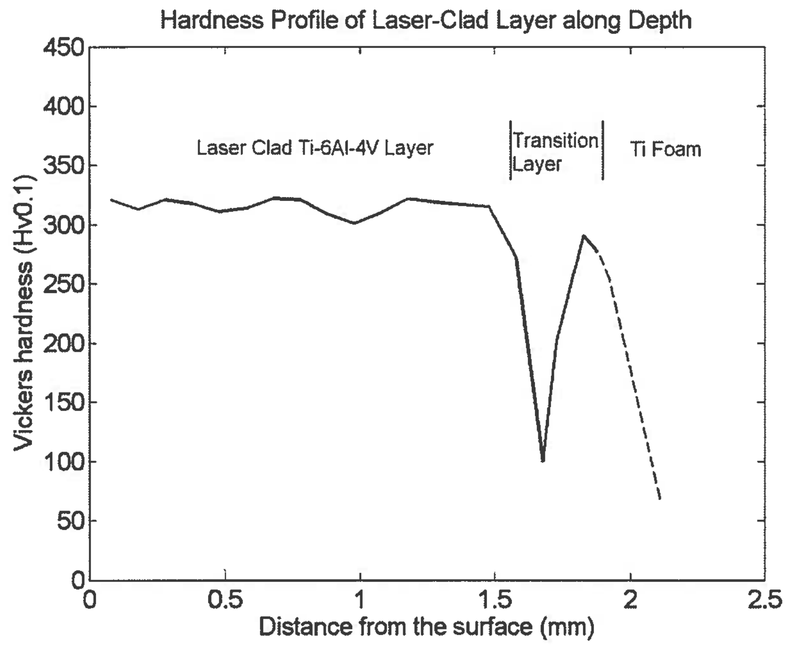

Figure 3 Hardness profile of laser clad Ti-6Al-4V layer on Ti foam along depth.

<u>Laser Clad of Pre-Mixed Powder Mixture (Ti-6Al-4V + CoCrMo) on Ti-6Al-4V Plate</u>

Three different ratios of Ti-6Al-4V and CoCrMo alloy powders in wt% were mixed, as shown in Table 2.

Table 2 Contents of Ti-6Al-4V and CoCrMo alloy powder mixtures

Specimen	CoCrMo (wt%)	Ti-6Al-4V (wt%)
A	10	90
B	17	83
C	25	75

Since laser-clad samples with powder mixture of 25 wt% CoCrMo alloy showed sever cracking when directly deposited onto Ti-6Al-4V substrate, specimen C was prepared by depositing powder mixture of 10 wt% CoCrMo alloy first as a buffer layer, then depositing powder mixture with 25 wt% CoCrMo alloy. But still, specimen C (CoCrMo alloy at 25 wt%) showed that cracks existed in the coatings. So, the wear tests were only conducted on specimens A and B.

<u>Microstructure:</u> The laser-clad layers were free of pores and showed a good metallurgical bonding to the substrate (Figures 4a & 4b) for specimens A and B. It was also noticed that some micro-cracks existed in the coatings of specimens A and B. Further investigation (Figure 5) showed that some micro-cracks form in the region where Co and Cr elements are rich. It implies that hard but brittle intermetallic compounds may form in this region, and cause cracking. It will require further

detailed investigation in the future to reveal what will be the effects of these micro-cracks on the potential medical applications.

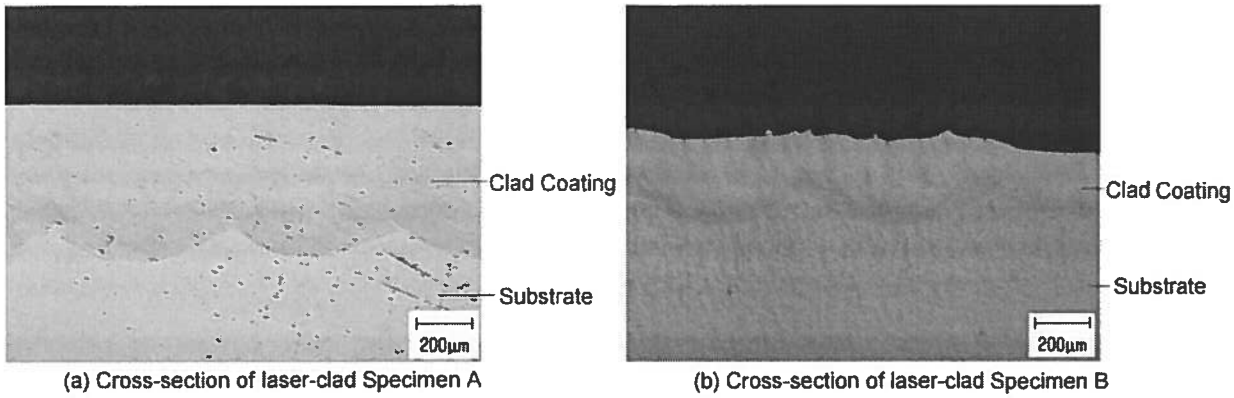

Figure 4 Optical micrographs of the cross-section of the laser-clad coatings: (a) specimen A; and (b) specimen B.

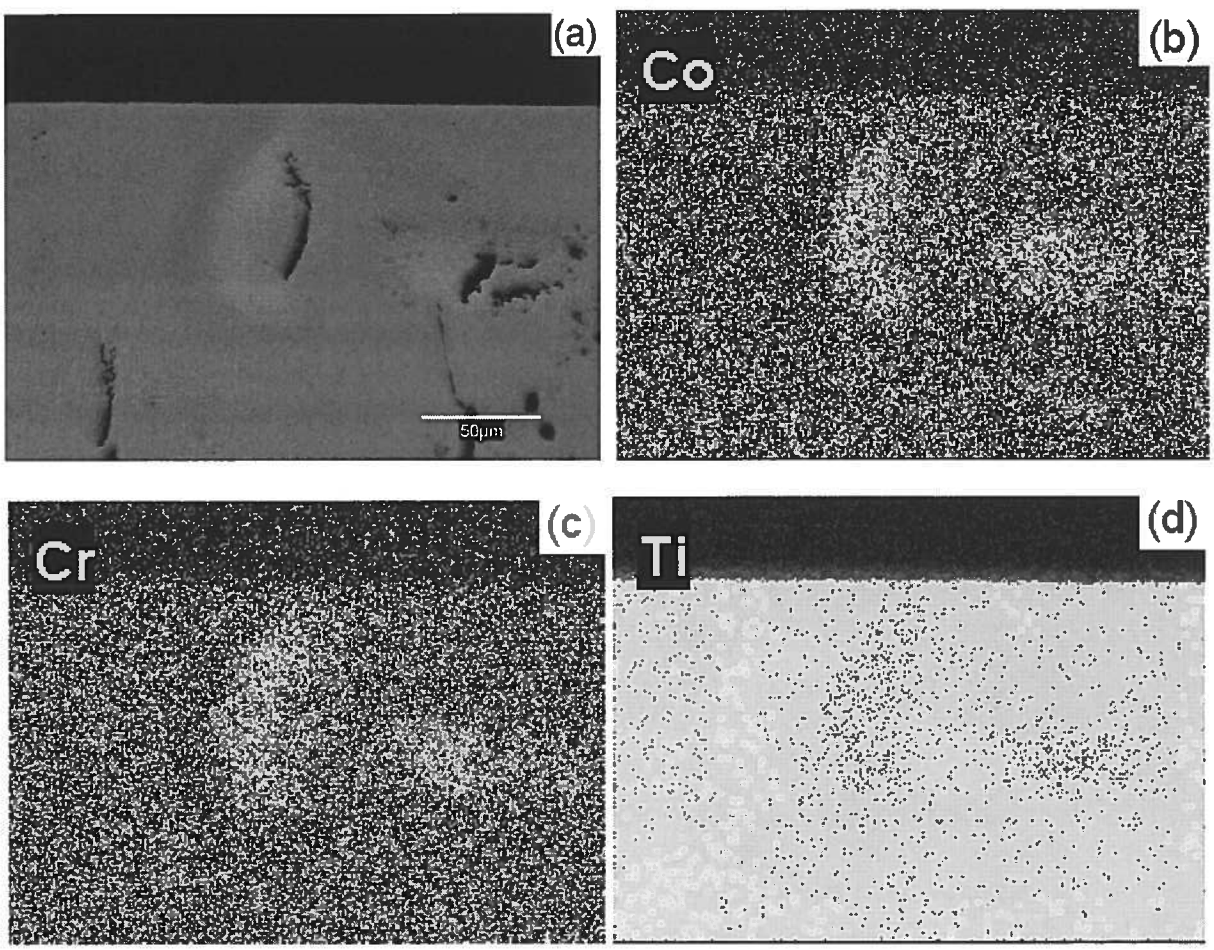

Figure 5 SEM/EDX images on the micro-cracks in the laser clad coating (specimen A): (a) SEM image for the investigated area; (b) EDX analysis for Co element distribution; (c) EDX analysis for Cr element distribution; (d) EDX analysis for Ti element distribution.

<u>Microhardness:</u> Results of Vickers hardness measurement (100 g load and 15 second duration) of the coatings are listed in Table 3. The hardness of Ti-6Al-4V substrate was also measured and

listed as a reference. Results show that the hardness of the coatings increased with the increase of CoCrMo alloy content in the powder mixtures.

Table 3 Microhardness of substrate and laser clad coatings

Specimen	Hardness (Hv0.1)
Ti-6Al-4V Substrate	316
A (90 wt% Ti-6Al-4V + 10 wt% Co-Cr)	347
B (83 wt% Ti-6Al-4V + 17 wt% Co-Cr)	419
C (75 wt% Ti-6Al-4V + 25 wt% Co-Cr)	486

<u>Pin-on-disc Wear Testing:</u> Dry sliding wear tests were conducted using a Falex ISC pin-on-disk tribometer by sliding 12.7 mm (1/2") diameter AISI 52100 Cr-steel balls (HRC 62-63) against the surface of the testing samples under a normal load of 3.5 N at a linear sliding speed of 0.2 m/s, for a total sliding distance of 1500 m. The wear track radius was 10 mm (The wear track radius of 14 mm was also used for Ti-6Al-4V substrate). The wear scars of the wear tests are displayed in Figure 6.

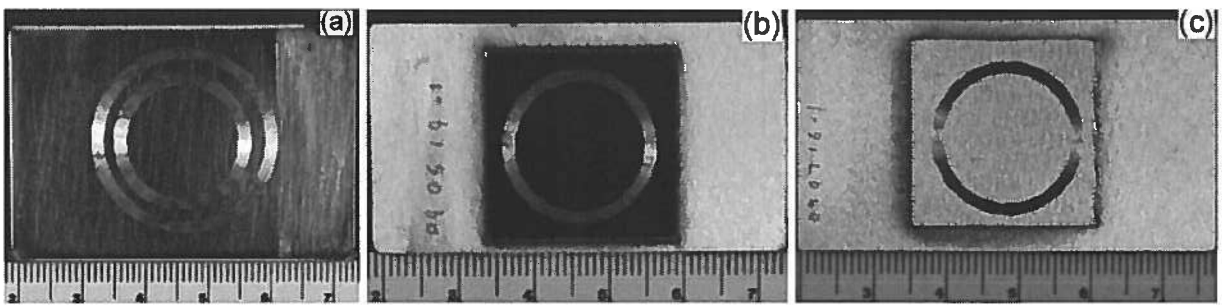

Figure 6 Worn surface after pin-on-disk sliding wear tests: (a) Ti-6Al-4V substrate (two wear tracks at 10 mm and 14 mm of radius, respectively); (b) specimen A (wear track at 10 mm of radius); (c) specimen B (wear track at 10 mm of radius).

Weight loss (ΔW) of the wear test samples was measured using a precision balance, with an accuracy of ±0.1 mg. Volume loss (ΔV) was obtained by the following equation:

$$\Delta V = \frac{\Delta W}{D} \qquad (1)$$

where D is the density of the laser clad coatings. Since the coating is a mixture of two powders, the law of mixture was used to estimate the coating density.

Using wear loss of Ti-6Al-4V substrate as a reference, relative wear resistance, R, of the coatings was calculated by dividing wear (volume loss) of Ti-6Al-4V, ΔV_{Ti}, by wear of the coating, $\Delta V_{coating}$:

$$R = \frac{\Delta V_{Ti}}{\Delta V_{coating}} \qquad (2)$$

The relative wear resistance of laser-clad coatings produced using powder mixture of Ti-6Al-4V and CoCrMo alloy under dry sliding wear conditions against a Cr-steel ball is shown in Figure 7.

Both specimen A and specimen B exhibited better resistance than the Ti-6Al-4V substrate. Results showed that even with 10 wt% of CoCrMo alloy in the coating (specimen A), the wear resistance was more than doubled comparing to Ti-6Al-4V substrate, under the given sliding conditions. The increase amount of CoCrMo alloy in the coating furthermore increases the wear resistance (specimen B). At this moment, we don't know whether the improvements in hardness and wear resistance through the addition of 10 – 17 wt% of CoCrMo alloy will be good enough for the medical application or higher concentration of CoCrMo will still be required.

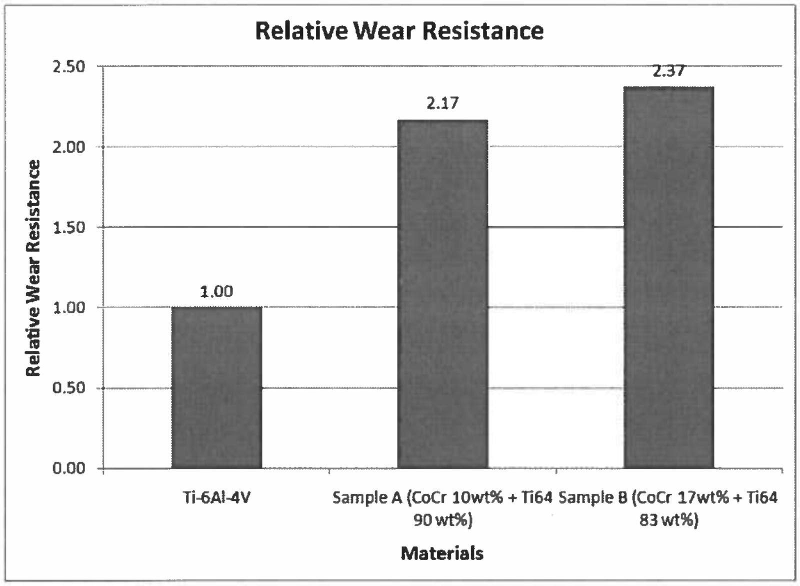

Figure 7 Relative wear resistance of laser clad coatings being investigated under dry sliding wear conditions against a Cr-steel ball at a total sliding distance of 1500m.

Further investigation of wear scar was conducted by using SEM observation. Figure 8 showed the SEM images of sliding wear scars. For Ti-6Al-4V substrate, the scratching marks are quite uniform (Figure 8a). For laser-clad Ti-6Al-4V coating with addition of CoCrMo alloy (specimens A & B), some scratches were deeper than others (Figures 8b & 8c), which may be attributed to the existence of CoCr rich regions where the hardness is relatively high. These regions will provide more resistance to abrasive wear.

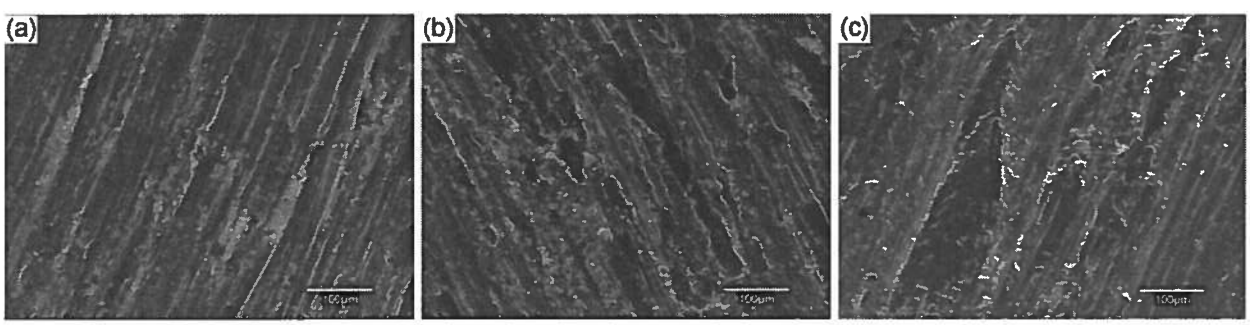

Figure 8 SEM micrographs showing the characteristic morphology of the wear scar of (a) Ti-6Al-4V substrate; (b) specimen A; (c) specimen B.

Summary

- Ti-6Al-4V alloy coating about 1-2 mm thick was successfully deposited on porous Ti foam using a specially developed laser cladding procedure. The clad Ti-6Al-4V coating was dense and crack-free with metallurgical bonding to the Ti foam.
- Pre-mixed Ti-6Al-4V powders with different percentages of CoCrMo alloy were laser-clad on solid Ti-6Al-4V substrates. The hardness of the clad Ti-6Al-4V coating was improved with the increased amount of CoCrMo content.
- Preliminary pin-on-disc sliding wear testing results showed that the addition of the CoCrMo alloy in the laser-clad Ti-6Al-4V coating significantly increases its wear resistance. Even with 10 wt% of CoCrMo alloy addition in the coating, the wear resistance was doubled as compared to Ti-6Al-4V substrate under the wear test condition used in this study.

Acknowledgements

The authors would like to thank Dr. Louis-Philippe Lefebvre from NRC-IMI (Boucherville) for providing the porous Ti foam rods and discs, Mr. Gary Wabersich from NRC-IMI (London) for preparing the laser-clad samples for tests, and Mr. Michael Meinert from NRC-IMI (London) for performing the SEM examination.

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