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Characterization of thermally oxidized titanium based coating

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ABSTRACT

Purpose: Aim of the study is to improve the bioactivity of CoCr alloy upon covering the surface with titanium based coating.

Design/methodology/approach: CoCr alloy was coated by cold spraying of powder mixture having a composition of 92 wt.%Ti + 8 wt.%Al. Coated samples were thermally oxidized at 600°C for 60 hours. Characterization of the coating was made by X-Ray diffraction analyses, microstructural surveys, cross-section and surface SEM elemental mapping analyses, roughness and hardness measurements.

Findings: Results showed that sequential application of cold spray and thermal oxidation processes provided the multi-layered coating consisting of an inner titanium based layer and an outer oxide layer consisted of TiO_2 and Al_2O_3. Thermal oxidation also caused the remarkable increasing in the surface hardness as compared to the as-cold sprayed state.

Practical implications: Modifying the surface of CoCr metallic implants for long term success.

Originality/value: Producing a multilayer coating on the surface of the CoCr alloy for biomedical application by sequential application of cold spray and thermal oxidation processes is the orginality of the study.

Keywords: Thermal oxidation; Titanium; Cold spray; Microstructural characterization; Hardness

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MATERIALS

1. Introduction

CoCr alloys are used in manufacturing of load bearing implants because of their superior mechanical properties and wear resistance [1-4] Despite their superior properties, service life of the implants made of these materials is limited to 10-12 years. Development of localized corrosion, micro-wear and dissolution of their surfaces in the human body affect their performance and may lead to early failure of the implant. For these reasons, fabricating more stable and bioactive coatings on CoCr alloy surfaces is one of the current topics [2,5].

Titanium is one of the biocompatible materials in metallic biomaterials. The oxide film on titanium's surface shows bioactive character and it has adequate corrosion resistance in body environment. But the oxide film, which is present at titanium's surface natively, have poor mechanical properties and it can be easily removed under fretting and sliding wear conditions [6-8]. Many techniques are being used in producing mechanically and chemically more stable and thicker oxide layer on the surface of titanium and its alloys, such as thermal oxidation [6], micro arc oxidation [9], and anodic oxidation [10]. Thermal oxidation is mostly applied at temperatures above 200°C under normal atmospheric conditions.

Cold spray technique is a relatively new technique used for the surface modification of metals, composites and polymers [11]. In this process plastic deformation of sprayed powders as they impact on the surface of the substrate provides coating formation [12-14]. During the coating process, temperature does not reach the melting point of particles due to low process temperature. Therefore, oxide free coating can be obtained by this technique especially for easily oxidize metals such as copper and titanium.

In the scope of this study, CoCr alloy was coated with titanium based powder mixture via cold spray technique. Then titanium coated samples were thermally oxidized at 600°C for 60 hours to obtain thick, well adherent and mechanically stable oxide film [15]. Fabricated titanium based multi-layered coating on CoCr alloy characterized with X-Ray diffraction analyses, microstructural surveys, cross section and surface elemental mapping analyses, hardness and roughness measurements.

2. Material and method

In the current study multi-layered titanium based coating was produced on the surface of CoCr alloy via cold spray technique followed by thermal oxidation. The feedstock was prepared a mixture of titanium (Alfa Aesar, <44μm, 99.5 % purity) and aluminium (Alfa Aesar, <44μm, 99.5% purity) powders with a composition of 92 wt.%Ti + 8 wt.%Al. For the cold spray technique, RUSONIC Model K-201 coating equipment were used and the process parameters could be seen in Table 1. Afterwards, surfaces of the coatings were ground up to #2500 SiC abrasive paper and polished with the silica solution prior to thermal oxidation. Thermal oxidation process conducted in electrical resistant furnace (Nabertherm) at 600°C for 60 hours under the light of previous experimental studies [6] and samples were cooled down inside the furnace.

Microstructural characterizations were performed by scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectrometer and X-Ray diffraction (XRD) analysis. Phase analysis was carried out by using GBC MMA X-ray diffractometer with in 2θ range from 20° to 80° using Cu-Kα radiation, before and after thermal oxidation from the surfaces of the coatings. Moreover, obtained XRD patterns were compared with JCPDS (Joint Committee on Powder Diffraction Standards) patterns and new formed phases were settled. Microscopic examinations were executed with Philips SFEG SEM. In that respect, SEM images were used for determining the coating and oxide layer thicknesses, mapping and energy dispersive X-ray (EDX) analysis utilized to find out elemental distribution on cross section and surface. Surface roughness, cross-sectional and oxide layer hardness measurements are made by using Dektak 6M profilometer, Wilson micro hardness tester under indentation load of 25 gr and CSM depth sensing micro-nano hardness tester under indentation load of 10 gr, respectively.

Table 1.
Process parameters for the coating

Coating Speed	1 mm/s
# Pass	2
Distance Between Pass	2 mm
Process Gas	Air
Gas Pressure	6 Bar

3. Results and discussion

XRD patterns of the titanium based coatings before and after oxidation are given in Figure 1. Before oxidation of the coated samples only the peaks of α-Ti and Al phases were detected. After thermal oxidation done at 600°C for 60 hours, peaks of rutile (TiO_2) (pdf number: 01-076-0318) and corundum (pdf number: 01-077-2135) phases were detected on the XRD pattern of the oxidised titanium based coating. After thermal oxidation, peaks of α-Ti phase also appeared on the XRD pattern. This was basically due to the penetration of X-ray beneath the oxide layer through the inner titanium based layer. Based on the analysis of XRD pattern, oxide layer formed on the titanium based coating mainly consists of TiO_2 and minor amount of Al_2O_3.

SEM images taken from the cross-section of the coated samples before and after thermal oxidation were illustrated in Figures 2 and 3, respectively. As shown in Figure 2, a uniform, dense and crack free titanium based coating with the thickness of 720 μm has successfully deposited on the

CoCr substrate. Additionally, SEM examination revealed that the coating bonded well with the substrate and no evidence of discontinuity was detected along the interface. However some porosity in the coating arising from the nature of the employed cold spray process was determined by SEM examination. The porosity content in the titanium based coating determined by using of Clemex image analyser software was calculated as 5%.

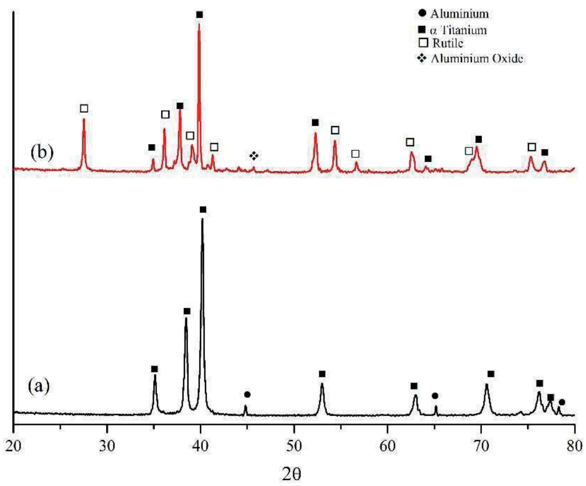

Fig. 1. XRD patterns of the samples (a) before and (b) after oxidation

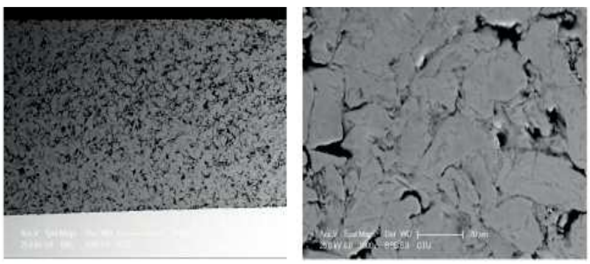

Fig. 2. SEM images of the coating before the thermal oxidation process

Thermal oxidation of the titanium based coating on the CoCr substrate (Fig. 3) provide two layered coating on the substrate along with changing of the microstructure and the porosity content of the coating. According to the XRD analysis and SEM examination, the coating consisted of the outer oxide layer mainly rutile (TiO_2) and an inner titanium based layer. Cross-sectional SEM examinations also revealed that oxide layer on the surface is approximately 3 µm. The oxide layer is almost crack-free and well adherent to titanium based coating. After the thermal oxidation, the porosity content in the oxidised titanium based coating was calculated to be increased to the 40%.

Fig. 3. SEM images of the coating after the thermal oxidation process

SEM elemental mapping analyses performed on the cross-section of the coated samples before and after oxidation are shown in Figures 4 and 5, respectively. Aluminium was generally well distributed in the titanium matrix as illustrated in Figure 4. In addition to this, minor amount of oxygen content was also detected in the as sprayed state after SEM elemental mapping analyses. In the case of thermal oxidation performed at 600°C for 60 hours in air, the cross-sectional SEM elemental mapping analysis (Fig. 5) showed that higher oxygen content was detected throughout the coating, as expected. However, oxygen especially concentrated at the outermost surface and penetrated throughout the coating as a result of porosity content. In the light of this observation, during the thermal oxidation, oxygen not only reacts with Ti and Al to from the oxide layer but also diffuses into the titanium in the coating. In addition to this, some of the aluminium in the titanium based coating partially diffused into the titanium particle because of higher aluminium diffusion efficiency and left Kirkendall type pores in the coating, which markedly increased the porosity of the titanium based coating to 40% [16,17]. Figure 6 shows SEM mapping analyses performed onto the surface of the oxidised sample. All constituents in the coating were detected on the oxide layer. This analysis revealed that oxidation firstly occurred on the surface of the coating and inhibited the diffusion of aluminium into the titanium, so that the oxide on the surface of the coating was mainly rutile (TiO_2) with minor Al_2O_3. These results are in good agreement with the results of the XRD analyses (Fig. 1).

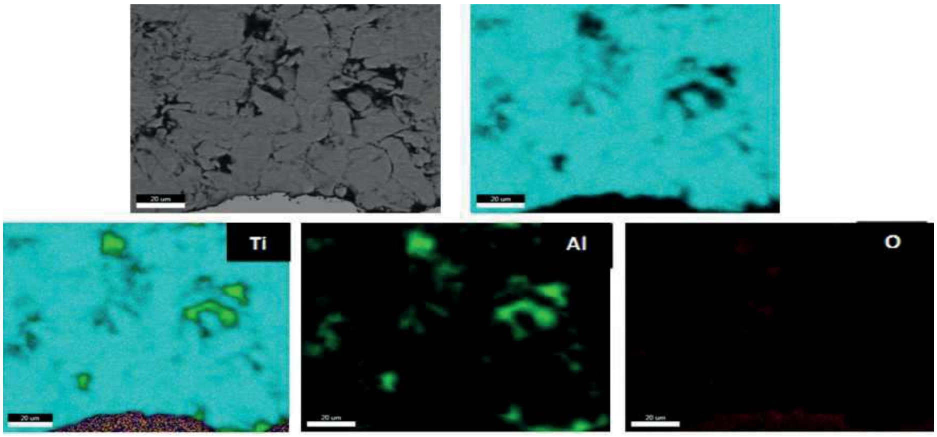

Fig. 4. Cross sectional SEM elemental mapping analysis before the thermal oxidation

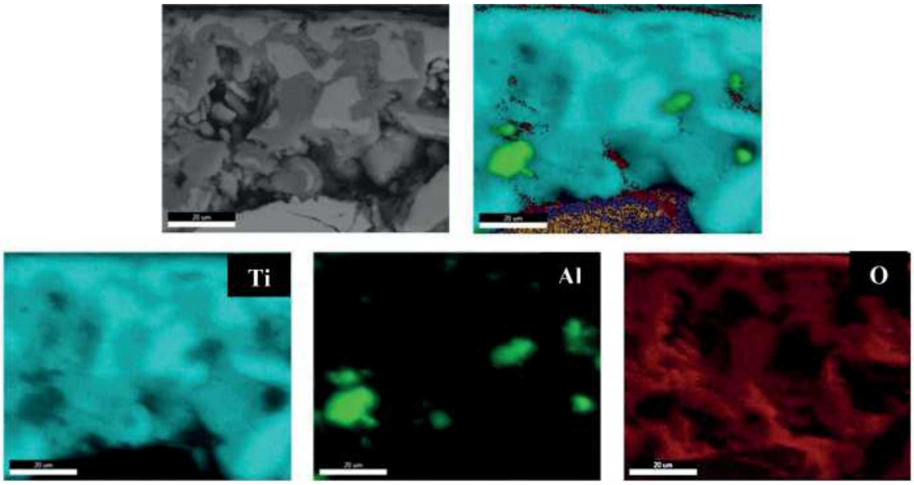

Fig. 5. Cross sectional SEM elemental mapping analysis after the thermal oxidation

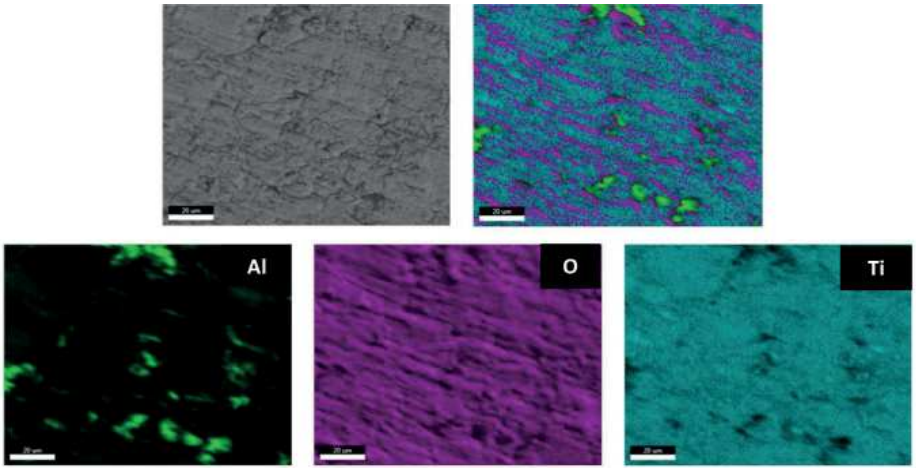

Fig. 6. Surface SEM elemental mapping analysis after the thermal oxidation

Surface roughness and hardness measurement results of the coatings are listed in Table 2. As can be seen in Table 2, the applied oxidation process in this study considerably affects the surface roughness of the coating (Fig. 7). The average surface roughness of the coating before the oxidation process was 0.10 µm. After the thermal oxidation, the average surface roughness of the oxidised coating increased up to 0.64 µm and was at least 5 times higher than those of the unoxidised samples. This increment increment in the surface roughness of the oxidized titanium based coating is ascribed to the growth mechanism of oxide layer during thermal oxidation, which is consistent with the results of the studies in literature [6,18,19]. On the other hand, increasing of the surface roughness improves the interactions of the material with its surrounding tissues and favourable effect of this condition to the bio-activity of materials was also reported [20].

Table 2.
Roughness and hardness values of coating before and after oxidation

Analysis	Before thermal oxidation	After thermal oxidation
Roughness, Ra	0.10	0.64
Hardness of coating, $HV_{0.025}$	114 ± 20	392 ± 89
Hardness of oxide layer, $HV_{0.010}$	-	848 ± 232

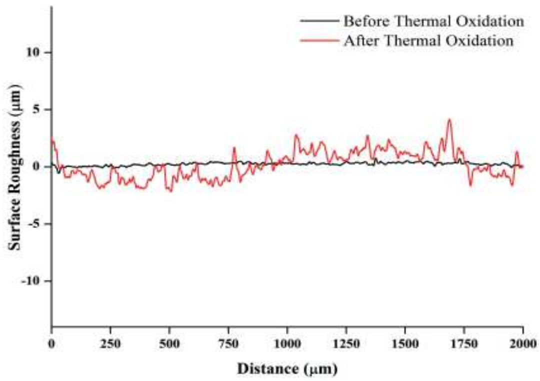

Fig. 7. Roughness profiles before and after thermal oxidation

Hardness values of the titanium based coating and oxide layer were given in Table 2. Thermal oxidation caused the remarkable increment in surface hardness of titanium based coating. Average surface hardness of the oxide layer was determined as 848 ± 232 $HV_{0.01}$, which is lower than the reported values [8]. The possible reasons of this relatively low hardness value obtained in this study could be the surface roughness of the oxide layer and contribution of the substrate due to penetration of the indenter (at load of 10g.) to a depth exceeding 10% of the oxide layer thickness. Furthermore roughening of the surface (Ra ≅ 0.65 µm) during growth of the a oxide layer during thermal oxidation imposed a large scatter in the average surface hardness value. The hardness of the inner titanium based layer between the outer oxide layer and substrate was measured as 392 ± 89 $HV_{0.025}$, which is at least three times higher than that of the as sprayed state. This can be attributed to solid solution hardening owing to the diffusion of both oxygen and aluminium to titanium matrix during thermal oxidation process.

4. Conclusions

Titanium based powder mixture (composition of 92 wt.%Ti + 8 wt.%Al) were successfully deposited onto the surface of CoCr alloy by cold spray process. Thermal oxidation carried out at 600°C for 60 hours in air produced multi-layered coating comprising an inner titanium (titanium matrix composite) layer and an outer oxide layer (mainly rutile) on the surface of CoCr alloy. Additionally, thermal oxidation caused a considerable increment in surface hardness and surface roughness of the titanium based coating on the CoCr alloy.

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