Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 2017–2022
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

An evaluation of plasma-sprayed coatings based on Al_2O_3 and Al_2O_3–13 wt.% TiO_2 with bond coat on pure titanium substrate

Şenol Yılmaz *

Sakarya University, Engineering Faculty, Department of Metallurgical and Material Engineering, 54187 Esentepe Campus, Sakarya, Turkey

Received 15 March 2008; received in revised form 25 October 2008; accepted 9 November 2008
Available online 11 December 2008

Abstract

In this study, the effects of bond coat on the properties of Al_2O_3 and Al_2O_3–13 wt.% TiO_2 coatings, which is plasma sprayed onto a commercial pure titanium substrate with and without Ni–5 wt.% Al (METCO 450 NS) as bond coating layer were investigated in terms of microhardness, bonding strength and surface roughness. Optical and scanning electron microscopy (SEM) examinations revealed that there is a uniform coating layer with no spalling and delamination. However, there is a little amount of porosity. The results indicated that the application of bond coat layer in the plasma spraying of Al_2O_3 and Al_2O_3–13 wt.% TiO_2 on pure titanium substrate has increased the hardness and bonding strength of coatings. While the adhesive bonding is dominant without bond coat, the cohesive bonding is dominant with the application of the bond coating layer. It has been observed that percentage of cohesion strength was about three times higher than that of adhesion strength.

Keywords: B. Porosity; C. Mechanical properties; D. Al_2O_3; E. Biomedical applications

1. Introduction

Ceramic materials with high hardness and high resistance to thermal and corrosive conditions and relatively low densities offer many advantages over metallic and polymeric materials [1,2]. Oxide ceramics such as alumina, zirconia, titania, chromia, silica and yttria have been used widely as surface coating materials to improve wear, erosion, cavitation, fretting and corrosion resistance [1] and to provide lubrication and thermal insulation [3]. They are especially useful in applications where wear and corrosion resistances are required simultaneously. Thermal spraying techniques represent a group of widely used processes for the production of various overplayed protective coatings to improve the surface characteristics of materials. Plasma spraying is a widely used method among the thermal spray processes [1,4–7].

It is well known that one of the main concerns when using plasma-spray techniques is the determination of the coating to substrate adhesion [8]. The main mechanism of the coating–substrate adhesion in conventional plasma spraying is mechanical interlocking. The irregularities of a rough surface are filled with the spreading molten materials due to the impact pressure. The subsequent solidification leads to mechanical interlocking or 'keying' [9]. The mismatch between the thermal expansion coefficients of ceramic and metals leads to the development of excessive stresses at the interface, which is the main cause of problems in metal–ceramic joining. This is a common problem for depositing ceramic coating on metals [10]. To solve that problem is to use a metallic bond coat onto the substrate for better interface adherence of the coating [10,11]. Bond coatings are used widely in many industrial plasma-spray applications. They have specific functions; because the substrate and the main coating have different coefficient of thermal expansion, bond coating layer should be used to provide a good thermal expansion match between these two different layers. Bond coatings are always thinner than the main coatings [12,13].

Ti and Ti-based alloys are widely used in several fields of bone substitution due to their biocompatibility, high corrosion resistance and good mechanical properties [14,15]. These alloys possess some excellent properties, including low density, high strength, and corrosion resistance [16]. Many kinds of prosthetic implants have been developed for both orthopedic and dental applications. Ti and Ti-based alloys can be coated

* Tel.: +90 264 2955768; fax: +90 264 2955601.
E-mail addresses: symaz@sakarya.edu.tr, symaz68@gmail.com.

0272-8842/$34.00
doi:10.1016/j.ceramint.2008.11.017

using different methods, such as conventional enameling, sputtering techniques and plasma spray [14,15]. The as-obtained implants can offer several advantages, in terms of the high mechanical properties of the metallic substrate combined with coating. Moreover, a good protection of the substrate from corrosion and biological fluids is provided [14].

The aim of this study is to find out the effect of bond coat application on mechanical properties and microstructural characteristic of Al_2O_3 and Al_2O_3–13 wt.% TiO_2 coatings on titanium. Al_2O_3 and Al_2O_3–13 wt.% TiO_2 coatings increase corrosion, wear resistance and beneficial bioreactivity in biomedical applications. The coatings were characterized by X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM) and a Vickers microhardness tester. Bonding strength of coatings was tested using adhesion test ASTM C-633.

2. Experimental details

2.1. Substrate and coatings

The substrate used for the coatings was the commercial pure titanium with the dimensions of 20 mm in diameter and 10 mm in height. The composition (wt.%) of substrate was N: 0.02, C: 0.08, H: 0.007, Fe: 0.18, O: 0.15 and Ti as the balance. The substrates were prepared metallographically by polishing with 1000 grid emery paper at the final stage. The surface of Ti-substrates was grit-blasted to provide surface roughness for better adherence between the coating and metallic substrate with 35 grid Al_2O_3 under 0.2 MPa pressure and a flow rate of 2 kg min^{-1}. Grit blasting was realized at the 45° with 50 mm distance to the substrate surface (because sand particles can get away from the surface without impressing elastically and not turn back to the nozzle). The grid blasting machine is manual grit blasting equipment of Cetingil made with 8 mm WC nozzle. The resulting average roughness of the substrate surface (R_a) after grid blasting that measured Perthometer M4P surface roughness tester is between 3.8 and 4.8 μm.

This was followed by an ultrasonic cleaning in ethyl alcohol using acetone solvent for 15 min and dried. A distance of 100 mm was chosen between the gun and substrate during the deposition of the coating powders. Alumina (METCO 105 NS) and alumina–13 wt.% TiO_2 (METCO 130 SF) coatings were produced using an atmospheric plasma-spraying (APS) technique on titanium with and without bond coating. Ni–5 wt.% Al (METCO 450 NS) was used for the bond layer. The plasma-spraying parameters and the plasma-spray powder particle sizes are given in Tables 1 and 2. The torch nozzle used for coatings was METCO 3 MB with 6 mm alloyed Cu nozzle. The position of the injector relative to the nozzle exit was 90°. The injector is in the same axis with torch. Powder unit of injector was METCO 3 MP powder feed unit. The coating operations were performed in the room temperature.

In this study, the critical plasma-spray parameter (CPS) was approximately 1000, and is defined by [7,13,17]:

$$\mathrm{CPS} = \frac{\text{voltage} \times \text{current}}{\text{primary gas (Ar) flow rate}} \qquad (1)$$

Table 1
Plasma-spray coating parameters of Ni–5 wt.% Al bond layer, Al_2O_3 and Al_2O_3–13 wt.% TiO_2 ceramic coatings.

Parameters (units)	Ni–5 wt.% Al coating	Al_2O_3 coatings	Al_2O_3–13 wt.% TiO_2 ceramic coatings
Plasma gun	3 MB	3 MB	3 MB
Current (A)	500	500	500
Voltage (V)	64–70	75	70–75
Gas flow for Ar (l/min)	27	40	40
Gas flow for H_2 (l/min)	14	14	14
Spray distance (mm)	130	100	100
Powder feed rate (g/min)	34	39	39
Carrier gas flow (l/min)	3–6	2–6	2–6

Table 2
The plasma-spray powder particles size.

Plasma-spray powders	Particle size (μm)
Pure Al_2O_3	−20 + 5
Al_2O_3–13 wt.% TiO_2	−30 + 5
Ni–5 wt.% Al (bond coat)	−88 + 45

2.2. Characterization

XRD analysis was conducted with a RIGAKU D/MAX-2200/PC type difractometer with a Cu Kα radiation, which has a wavelength of 1.54059 Å to analyze phases present in the coatings, qualitatively. Optical microscope (Olympus BHM 313 U) and scanning electron microscopy (JEOL 6060 LV) were used to study the microstructure and morphology of the coatings. The hardness of coating layer and bond coat were measured on the polished cross-sections of the samples using a Vickers microhardness tester (FutureTech FM 700) with a load of 100 gf. Indenting time of the Vickers indenter was applied for 10 s. Bonding strength of coatings was tested using adhesion test ASTM C-633. The coating layer was glued on the pull rods using an epoxy adhesive which was cured for 24 h at room temperature. All tests were carried out by using a tensile machine under ambient conditions with a cross-head speed of 0.5 mm min^{-1} to determine bond strength. In addition, pull rods were also glued directly to each other and measured the strength of the epoxy. The bonding type of coatings and the percentage of adhesion and cohesion were calculated by the measurement of the separation percents of coating on surface using a planemeter.

3. Results and discussion

3.1. Microstructure

Figs. 1–3 show the microstructure of the Al_2O_3 and Al_2O_3–13 wt.% TiO_2 coatings produced by atmospheric plasma spray. In all the coatings, some pores and splat boundaries are observed. The ceramic layer and bond layer mainly display a lamellar structure, in which the lamellar of both the ceramic layer and bond coat layer are almost parallel to the substrate