Applied Surface Science 258 (2012) 3871–3876

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Deposition of titanium nitride and hydroxyapatite-based biocompatible composite by reactive plasma spraying

Radu Alexandru Roşu [a,b], Viorel-Aurel Şerban [a], Alexandra Ioana Bucur [c,*], Uţu Dragoş [a]

[a] University "Politehnica" of Timişoara, Faculty of Mechanical Engineering, 1 Mihai Viteazul Blv., 300222 Timişoara, Romania
[b] National Research & Development Institute for Welding and Material Testing Timisoara, 30 Mihai Viteazul Blv., 300222 Timişoara, Romania
[c] National Institute for Research and Development in Electrochemistry and Condensed Matter Timisoara, Analysis and Characterization Dept, 1 P Andronescu Street, 300224 Timisoara, Romania

ARTICLE INFO

Article history:
Received 28 September 2011
Received in revised form
23 November 2011
Accepted 10 December 2011
Available online 19 December 2011

Keywords:
Reactive plasma spraying
Hydroxyapatite
Titanium nitride

ABSTRACT

Titanium nitride is a bioceramic material successfully used for covering medical implants due to the high hardness meaning good wear resistance. Hydroxyapatite is a bioactive ceramic that contributes to the restoration of bone tissue, which together with titanium nitride may contribute to obtaining a superior composite in terms of mechanical and bone tissue interaction matters.

The paper presents the experimental results in obtaining composite layers of titanium nitride and hydroxyapatite by reactive plasma spraying in ambient atmosphere. X-ray diffraction analysis shows that in both cases of powders mixtures used (10% HA + 90% Ti; 25% HA + 75% Ti), hydroxyapatite decomposition occurred; in variant 1 the decomposition is higher compared with the second variant. Microstructure of the deposited layers was investigated using scanning electron microscope, the surfaces presenting a lamellar morphology without defects such as cracks or microcracks. Surface roughness values obtained vary as function of the spraying distance, presenting higher values at lower thermal spraying distances.

1. Introduction

Titanium alloys have low density, good mechanical properties and a high level of biocompatibility, being used successfully for various implants and medical devices [1]. Among the titanium alloys, Ti6Al4V is the most used in medicine due to its good mechanical properties, despite some reservations about the releasing of Al and V ions under certain conditions, ions which may accumulate inside the tissues [2]. This can be improved by depositing materials with superior biocompatibility onto this type of alloys, which will act as a barrier to ion releasing phenomena [3].

During the recent years many studies were carried on about the development of composite coatings, thus combining the high mechanical characteristics of the metallic materials used in order to manufacture implants (strength, hardness) [4] with the high bioactivity properties of the ceramic materials, especially based on calcium phosphate(s), because of their structure which is similar to that of the human bone [5]. The purpose is to obtain the perfect biomaterial for applications that are subjected to loads bearing [6]. In the last years many researches are described, which present the manufacturing of such composite materials by various methods such as thermal spraying or powder metallurgy techniques [7,8].

Titanium nitride (TiN) is a biocompatible ceramic material which possesses high values for hardness and good wear and corrosion resistance properties in physiological environment [9,10]. Titanium nitride is used for orthopedic implants due to the high biocompatibility properties, for example to cover the femoral head of the hip joint in order to improve the wear resistance and fatigue [11]. By covering medical implants with titanium nitride, the biocompatibility of implants manufactured from various metallic alloys (cobalt–chromium, titanium alloys) is improved, increasing the wear and corrosion resistance and avoiding the allergic reactions which may occur when a metallic implant is introduced in the human body [12,13].

Titanium nitride can be deposited by PVD method (Physical Vapor Deposition) or CVD (Chemical Vapor Deposition), but at small layer thickness (<10 μm) [14]. Thicker layers of titanium nitride (TiN, Ti_2N and residual Ti) were obtained by reactive plasma spraying [15]. Lisong Xiao and collaborators have achieved coatings of titanium nitride layer by reactive plasma spraying in ambient atmosphere [16], X-ray diffraction analysis of the obtained layers showing that these are composed of TiN and small quantities of Ti_3O.

Hydroxyapatite is a ceramic material used successfully in orthopedics and dentistry due to the bioactive properties and its structure which is similar to that of the human bone mineral component, behaving as a reservoir of calcium, phosphorus, sodium and magnesium and ensuring the easy regeneration of the bone tissue

* Corresponding author. Tel.: +40 256494413; fax: +40 256204698.
E-mail address: alexandra.i.bucur@gmail.com (A.I. Bucur).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2011.12.049

[17]. Stoichiometric hydroxyapatite consists in 39.9% Ca, 18.5% P, 41.4% O and 0.2% H and the molar ratio Ca/P is 1.67. The molar ratio of hydroxyapatite in the human body is not stoichiometric (less than 1.67); it contains additional amounts of sodium, magnesium, carbonate, fluorine and chlorine ions, which are substitutes for Ca^{2+} and $PO_4{}^{3-}$ [18]. The mechanical characteristics of the hydroxyapatite are low, for this reason it cannot be used to bulk implants subjected to heavy loads [17,19], but it is used to cover the implants made of metallic materials such as titanium alloys, which can resist to this type of solicitations. Covering with hydroxyapatite layers leads to an easier acceptance of the implants by the surrounding tissue (biointegration), leading to rapid osseointegration of hip, knee or elbow prosthesis, or dental implants [20]. The most common ways of coating metallic implants with hydroxyapatite are thermal spraying [20], laser [21], and sol–gel [22].

Many studies are also focused in recent years on the manufacturing of coatings consisting in composites of metallic biocompatible materials and bioactive ceramic materials based on biodegradable calcium phosphates. The phenomenon of decomposition which occurs after the introduction of the implant in the body leads to releasing of elements for bone tissue restoration [23], thus the bone fixation is made directly by developing of the natural bone tissue in the microporosities resulted after the decomposition of the bioactive biodegradable materials, minimizing the implant failure and leading to superior osseointegration [24].

Another important element in the achievement of biocompatible coatings is the surface roughness obtained after the deposition, a rough surface leading to better fixation of the implant in bone tissue due to increased contact surface [25,26].

Despite that in the recent years many experimental research was done on the development of composite coatings of metallic materials and calcium phosphate based materials, until present no research about obtaining composite layers of titanium nitride and hydroxyapatite by reactive plasma thermal spraying in ambient atmosphere using mixed powders of titanium and hydroxyapatite was achieved.

2. Experimental procedure

2.1. Fabrication of the TiN–HA based biocompatible composites

Commercially pure titanium (α-Ti) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) powders were used as deposition materials, with average particle size ranging between 15 and 25 μm for titanium powder and between 10 and 20 μm for the hydroxyapatite. The powders were provided by Sigma–Aldrich Company. As substrate titanium alloy (Ti6Al4V) discs Ø 30 mm × 10 mm provided by Bibus Steel Company were used.

The powders were mixed by ball milling with agate balls with a HA/Ti ratio (wt%) in two variants:

variant 1: 10% HA + 90% Ti;
variant 2: 25% HA + 75% Ti.

The two mixtures were deposited by reactive plasma spraying method on to the titanium alloy substrate at 4 different spraying distances (80, 90, 100, 110 mm).

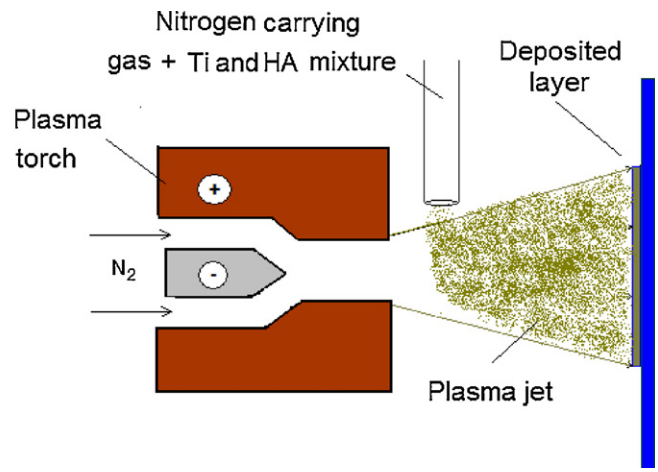

Fig. 1. Principle of composite coatings achievement from TiN and HA by reactive plasma spraying.

2.2. Thermal spraying equipment

Sulzer Metco plasma thermal spraying equipment was used for the deposition of the composite layers. As plasmagen and transport gas, nitrogen was used. In Fig. 1 there is the schematic representation of the composite coatings of TiN and HA achievement process, and the parameters used for depositions are presented in Table 1. Before spraying, the titanium samples were blasted with alumina with the average particle size of 1 mm at the pressure blast of 6×10^5 Pa and distance of 50–60 mm. After blasting, the samples were cleaned with ethylic alcohol.

Due to high temperatures, titanium powder melts in the nitrogen plasma jet and is driven directly to the substrate. Particles that reach the surface of the substrate in melted state adhere to the latter by specific mechanisms [20]. The reaction between the molten titanium particles, oxygen from air and nitrogen, leads to compounds such as nitrides and oxides of titanium (TiN, Ti_2N, TiO_2, Ti_3O) [14].

2.3. Characterization of surface morphology

Scanning electron microscope (SEM) Inspect S with Energy-dispersive X-ray spectroscopy (EDX) was used to characterize the surfaces morphology.

The phase composition of the deposited layers was investigated by X-ray diffraction (XRD) using a PANalytical X'Pert Pro MPD diffractometer. The working conditions were 45 kV and 30 mA, using copper radiation with the wavelength λ = 1.541 Å.

The microlayers thickness was determined using Easy Check F-N device and the surface roughness determination was made by use of the Surftest 201 (SJ-201) device from Mitutoyo.

3. Results and discussions

3.1. XRD characterization

Figs. 2 and 3 show the X-ray diffraction pattern of the coatings of titanium nitride and hydroxyapatite composites obtained by reactive plasma spraying in both variants: variant 1 (10% HA + 90%

Table 1
Parameters used for depositions of TiN and HA based biocompatible composites coatings.

Plasma current (A)	Plasma voltage (V)	Primary gas flow (l/min)	Carrier gas flow (l/min)	Powder feed rate (g/min)	Spraying distance (mm)	Cooling
500	60	40	10	15	80–110	Nitrogen