Materials Letters 106 (2013) 97–99

Contents lists available at SciVerse ScienceDirect

Materials Letters

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

Cold gas spray titanium coatings onto a biocompatible polymer

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ARTICLE INFO

Article history:
Received 21 February 2013
Accepted 30 April 2013
Available online 10 May 2013

Keywords:
Cold Gas Spray
Coating
Titanium
Polymer
Implant

ABSTRACT

Titanium particles were deposited onto Polyetheretherketone substrates using Cold Gas Spray technology and a factorial number of experiments were designed in order to study different spraying conditions. The starting powder and the obtained coatings were characterized with the aim of linking the results with the coating process. By means of micro-Raman analysis, it was observed that the polymer was not degraded during the process in spite of the conditions of the nitrogen gas stream. X-Ray Diffraction analysis also confirms that the composition of the metallic particles was not affected. The results show that it is possible to coat biocompatible polymer implants with titanium leading to thick, homogeneous and well-adhered coatings.

1. Introduction

Polyetheretherketone (PEEK) polymer is known to be bioinert in hard and soft tissues when present as a bulk implant. Although it is not a bioactive material, direct bone contact has been previously reported [1]. In order to enhance the application of PEEK implants assuring a long-lasting life of the material, an improvement of its bioactivity is imperative. Therefore, processes able to coat the polymeric bulk without modifying its composition and boosting its performance are becoming required for carrying out the scaling-up of this product.

Cold Gas Spray (CGS) is a technique for developing coatings by means of accelerating powder particles towards a substrate using a gas stream. These layers are built-up due to the plastic deformation of the particles at the impact. Mainly, CGS attractiveness is based in its direct manufacturing and the possibility of coating large areas in brief periods of time combined with the low temperatures involved, which avoid the thermal degradation of the particle/substrate system. CGS has been widely used for fabricating coatings onto metallic substrates. Nevertheless, it is also feasible to develop metallic layers onto polymer substrates. R. Lupoi et al. studied the deposition of Co, Al and Sn powders on polyamide 6, polystyrene, polypropylene and polycarbonate-ABS blend [2]. Copper particles led to an excessive stress that predominantly eroded the polymer. Aluminum, due to its low specific weight, did not bring any considerable damage to the surface; however it was not possible to reach enough velocity for bonding the particles with the equipment that have been used in these experiments. On the other hand, tin coatings were successfully produced. Better results were obtained by Zhou et al. when spraying Al/Cu on the surface of carbon fiber-reinforced polymer matrix composite (PMC) for its use in the aerospace industry [3]. It was observed that the substrates softened to a minimal degree when exposed to the process gas, which enabled the Al particles to penetrate the polymer and form a mechanical bond. Later, Ganesan et al. effectively fabricated thick copper coatings (1000 μm) on polyvinyl chloride (PVC) polymeric substrate [4]. The results showed that the deposition efficiency was highly sensitive to the glass transition temperature of the substrate, irrespective of the process gas pressure. More recently, Jahedi et al. have dealt with the deposition of Cu particles on several polymers [5]. It was presented a very useful and complete study based in how the particles are mechanically embedded into the substrates depending on the spraying conditions and the nature of the polymer. Other authors have worked with the deposition of non-metallic powders on polymer substrates using CGS technology. Burlacov et al. deposited TiO_2 thin films on different types of thermoplastic polysulfone (PSU) [6]. The particles were mechanically fixed onto PSU and it was suggested that the polymeric material squeezed out of the surface after the particle impact, which would likely act as particle binder. Despite there is a lack of published data related to PEEK used in CGS technology, Sanpo et al. studied the antibacterial property of cold-sprayed HA-Ag/PEEK powders onto glass slides [7]. The study demonstrated the ability of depositing the composite powder and building-up the coating, which retained its inherent antibacterial property as clearly verified from the bacterial assays.

With the aim of enhancing the biocompatibility of PEEK implants, different CGS operation conditions of titanium powder on the polymer have been carried out. The scope of this study is based on the analysis of the selected spraying conditions and the characterization of the materials involved with the purpose of

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http://dx.doi.org/10.1016/j.matlet.2013.04.115

bringing certain criteria related to the interaction of Ti particles and PEEK substrates when operating with CGS systems.

2. Material and methods

A titanium powder obtained from a fused and crushed process was used as feedstock. The powder was quite angular and its particle size distribution was ranged between 20 and 90 μm. The CGS equipment used for obtaining the coatings was a KINETICS® 4000 (Cold Gas Technology, Ampfing, Germany), with a maximum operating pressure of 40 bar, temperature of 800 °C and it operated with nitrogen as the propellant gas. In addition, KINETICS® 4000 had the possibility of using a pre-chamber of 120 mm in length connected to the nozzle of the gun where powders are heated up for a longer time. The powder and the cross-section area of the samples were observed by Scanning Electron Microscopy, SEM (ProX Phenom). The particle size distribution was measured by laser diffraction and the substrate composition was determined by micro-Raman (Labram HR800, Horiba) with the purpose of determining if the polymer had been degraded during the spraying process. The phase composition of the powder and coatings was analyzed by a X'Pert PRO MPD diffractometer (PANalytical).

3. Results and discussion

A factorial design of experiments 2^2 was developed in order to determine the influence of temperature, pressure and the stand-off distance of the samples. Table 1 compiles the nomenclature and the distinct conditions of each spraying. The values are given in ratios of pressure (P)/stand-off distance (d) and temperature (T)/stand-off distance (d). The quality of the coatings differed sharply depending on the spraying conditions. In the case of the samples C295, C298 and C300 it was not possible to form the coating. The particles were mechanically embedded into the softened plastic substrate without the possibility of building-up the titanium layers. However, in the case of the sample C297, the coating was properly obtained showing a homogeneous thickness and a well-adhered structure free of cracks.

Table 1
Nomenclature of the obtained samples for the factorial design of experiments and its corresponding ratios.

		P/d [bar/mm]	
		1,5–2	2–2,5
T/d [°C/mm]	20–35	C297	C300
	30–35	C298	C295

In Fig. 1a and b it is possible to observe the cross-section area of the most significant coatings. Caused by the polymer softening because of the nitrogen stream, those samples sprayed with more energetic conditions led to a certain amount of titanium particles anchored into the PEEK substrate but without building-up the coating. This may be caused since the polymer cannot provide enough hardness in these spraying conditions for easing the plastic deformation of the particles at the impact. Previous to this experiments it was studied the variation of the gun velocity, which alters the period of time that the substrate is in contact with the gas stream. Thus, spraying with rapid gun velocities may not greatly affect the polymer. In any case, it was not observed the formation of the coating when comparing the distinct stand-off distances of those conditions with higher pressures (C295 and C300). On the other hand, reducing these variables would avoid the softening of the polymer, which leads to an increase in the plastic deformation of the titanium particles at the impact. Therefore, the sample C297 that was obtained by the lower-energetic spraying conditions was satisfactorily adhered to the substrate reaching thicknesses above 1000 μm. It is also possible to observe that the superior part of the coating has certain porosity, whereas closer to PEEK the coating is denser. This is caused by the peening effect of the impacting particles in CGS. Nevertheless, when using higher temperatures and maintaining fixed this pressure, it was not possible to achieve the same thickness.

The top surface areas of both the C297 sample and the PEEK substrate are presented in Fig. 1c and d. The polymer shows a flattened surface with no irregularities. On the other hand, the CGS coating provides great roughnesses to the top layer as the last particles that reached the substrate were not so drastically deformed. This can also be checked when observing its cross-section area in Fig. 1a. Anyhow, to achieve a rough biocompatible surface is a key-point for the final application of the material because this texture enhances the biocompatibility of the implant [8].

Raman spectroscopy was used in order to determine if the PEEK localized at the area closer to the first adhered particles was affected in some way by the heat of the gas stream or by the heat of the particles (Fig. 2). Other authors have reported the PEEK Raman band as a function of its plastic deformation. It was found a shift of the peaks during the tensile deformation [9]. Although is referenced in literature and also checked in this study that the polymer PEEK typically produces a spectra dominated by fluorescence [10], this was solved using Raman radiation with a wavelength of 1060 nm. The comparison of both spectra shows no differences, which suggests that the polymer was not severely affected in the coating process. Fig. 3 was carried out on the top

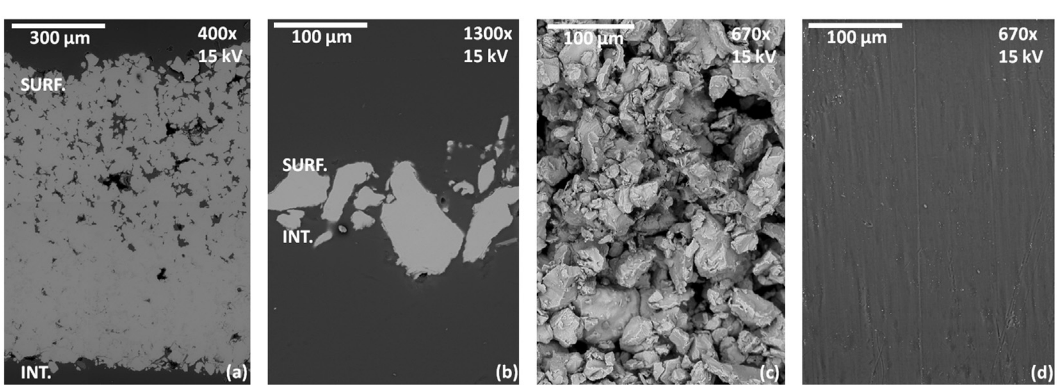

Fig. 1. SEM micrographs. Cross-section area of the samples: (a) C297 and (b) C295. Top surface area of the samples: (c) C295 and (d) PEEK polymer. Surface of the coating and interface are also detailed in samples C297 and C295 (1(a) and (b)).

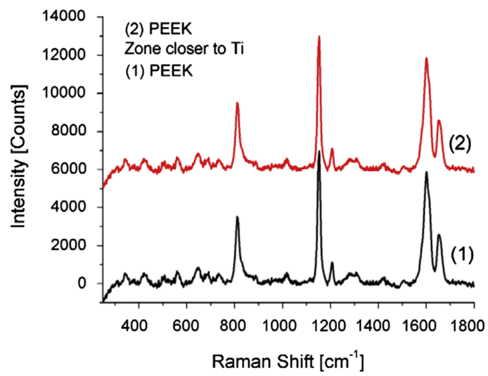

Fig. 2. Raman spectra obtained from PEEK (bulk) and a zone of PEEK substrate close to the Ti particles at the substrate boundary (CGS sample).

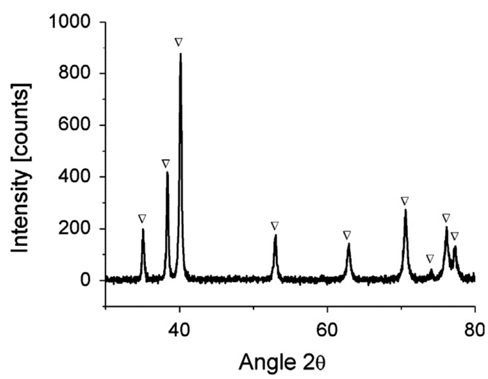

Fig. 3. XRD pattern of the sample C297.

surface of the coating and it was found that its composition consists in crystalline metallic Ti without presence of other species/undesired phases [11].

4. Conclusions

Thick, homogeneous and well-adhered titanium coatings were deposited on Polyetheretherketone (PEEK) polymer by Cold Gas Spray. From the proposed factorial design of experiments, it is concluded that the heat supplied by the gas stream softens the substrate. This fact critically influences the deposition of the metallic particles and the formation of the coating. However, it is possible to reach a balance between thermal softening of the polymer material and plastic deformation of the titanium particles at the impact in order to build-up the coating. It was not observed a shift in the Raman spectrum of the PEEK bulk compared to a PEEK area closer to the first adhered particles, which suggests that the starting polymer has not been degraded. Furthermore, composition of the metallic powder was not affected.

Acknowledgments

The authors wish to thank the Generalitat de Catalunya for the financial support for this Research Project 2009 SGR 00390.

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