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Substrate preheating and structural properties of power plasma sprayed hydroxyapatite coatings

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Abstract

The aim of the present study was to investigate the influence of substrate preheating on the structural properties of hydroxyapatite coatings (HACs) deposited by using the high power (52 kW) laminar plasma jet. The deposition experiments were performed within the 20–200 °C temperature range at different stand-off distances. The structural properties in the thickness direction and at the surface of the HACs were investigated by using the micro-Raman spectroscopy, scanning electron microscopy coupled with energy dispersive spectrometry, and X-ray powder diffractometry. The deposition without the preheating of the substrate produced HACs with crystallinity gradient in the thickness direction. At the stand-off distance of 80 mm, the preheating of the substrate at 200 °C practically eliminated the crystallinity gradient. At distances from the coating/substrate interface shorter than ~100 μm, the increase of crystallinity with the preheating of the substrate was dominantly attributed to the recrystallization of hydroxyl-rich ACP into HA. At longer distances and higher initial substrate temperatures (> 100 °C), the crystallinity changes were negligible, whereas the recrystallization of hydroxyl-deficient ACP into oxyapatite (OA) was also possible. The X-ray diffractometry indicated the deposition conditions under which a minimum residual stress was achieved. The results of the present study strongly suggested the relation between the ACP→HA recrystallization process and the bonding strength of the HACs.

Keywords: Hydroxyapatite coatings; Plasma spraying; Substrate preheating; Structural properties; Micro-Raman spectroscopy

1. Introduction

Typical as-plasma-sprayed HACs exhibit structural and chemical gradients in thickness direction [1–5]. The structural gradient extends from an amorphous base to a crystalline surface. Considering the application of HACs as medical implants, the presence of such crystallinity gradient is unfavorable. The crystalline surface promotes poor initial bone fixation and the ACP base imparts low structural integrity of HACs [6]. The latter is of particular importance because the presence of the ACP phase has been held responsible for deterioration of the HAC's bonding strength [7]. The appearance of the amorphous layer at the interface explains the decrease of the adhesive strength mainly due to the brittles nature of the amorphous layer and the presence of many micro-cracks inside the layer due to the thermal stress and residual coating stresses arising from the high solidification rate [7]. As a result of a decreased adhesive strength due to the presence of the interfacial ACP layer, the damage of the implant may be reached during the implantation period when the bone/HAC bonding strength exceeds the HAC/substrate bonding strength [6]. In addition, the HACs that

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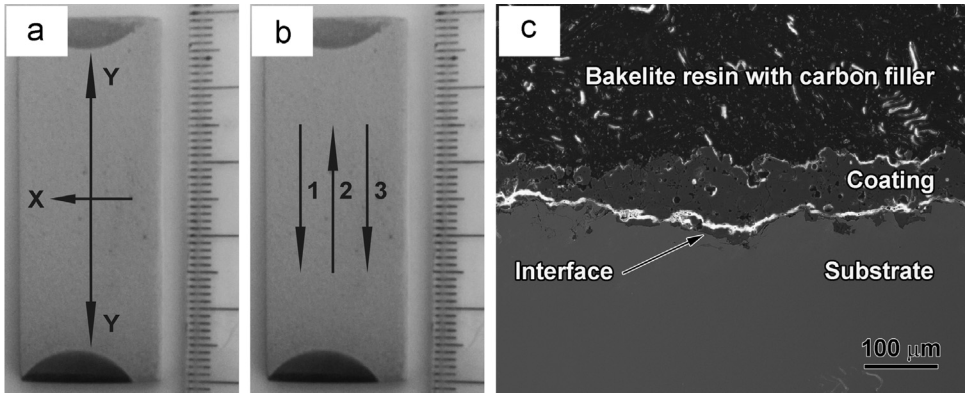

Fig. 1. Typical appearance of HACs deposited on steel substrate by using the PJ-100 installation. *X* and *Y* arrows designate the disk rotation and plasma deposition direction, respectively (a); 1, 2, or 3 designate the number of deposition run, whereas arrows indicate the direction for each deposition run (b); the SEM cross-sectional image of HAC deposited by single deposition run at stand-off distance of 80 mm without preheating of substrate (c).

contain the highly soluble ACP phase are prone to the excessive dissolution, which may have a great effect on the long-term reliability of the implants [6]. The excessive dissolution of the ACP phase and other highly soluble calcium phosphate phases may result in the formation of micro-voids between the HA splats [8]. As a result of coating disintegration and fragmentation, these HA particles may incorporate into the surrounding bone or potentially stimulate an inflammatory reaction with localized bone loss [8].

The post-deposition heat treatment may eliminate the presence of crystallinity gradient and the presence of the ACP phase in the coating/substrate interface region [3]. However, the post-deposition heat treatment lowers the dissolution of the HACs due to the formation of crystalline HA [9,10], which may adversely affect their osseointegration [11,12]. In addition, an improper heat treatment may deteriorate the bonding strength of the HACs [13,14].

Besides the post-deposition heat treatment, the preheating of the substrate considerably affects the bonding strength of the HACs [7,15–17]. Morks and Kobayashi [7], Vilotijević et al. [15], and Li et al. [16] have shown that the preheating of the substrate increases the bonding strength of the HACs. However, other opinions, such as in the study of Chou and Chang [17], can also be found. Morks and Kobayashi have attributed the increase in the bonding strength to (i) enhanced crystallinity at the coating/substrate interface, i.e. the absence of the brittle ACP layer and micro-cracks inside the layer due to the thermal and residual coating's stresses and (ii) improved wetting between the substrate and the first coating lamellae. On the other hand, Vilotijević et al., Li et al., and Chou and Chang have related changes in the bonding strength to changes in the residual stress of HACs with the preheating of the substrate.

Previous post-deposition heat treatment experiments of Yang et al. [14] on as-plasma-sprayed HACs have shown a relation between the recrystallization of ACP and the bonding strength of the HACs. Recently, Saber-Samandari et al. [18,19] have performed micro-Raman spectroscopy, scanning and transmission electron microscopy measurements on thermally produced HA splats (not coatings) to investigate the effects of substrate preheating. They have found that the preheating of the substrate (i) promotes early ACP→HA recrystallization, which has been detected in the flame-sprayed HA splats, and (ii) improves wetting for the flame-sprayed, plasma-sprayed, and high-velocity oxy-fuel HA splats. These results agree well with the conclusions of Morks and Kobayashi [7]. Tong et al. [1] have also proposed that the preheating of the substrate may raise the adhesion of the HACs but they have not explicitly related this phenomenon to the recrystallization of ACP.

The aim of this study was to investigate the effects of substrate preheating on the structural properties of the HACs in the thickness direction and the surface region. In addition, the structural changes observed in this study were correlated with the results from the bonding strength measurements of Vilotijević et al. [15] performed on the same type of the HACs. The deposition of the HACs was performed with a high power (52 kW) laminar plasma jet. Specific properties of this plasma jet are its unusually long plume (70 mm; i.e. twice the plume length of the conventional plasma gun), high radial and axial plasma temperature homogeneity, as well as the laminar plasma flow along 2/3 of its length from the anode nozzle exit [15].

2. Materials and methods

2.1. Substrate material and feedstock powder

The substrate material was an implantation grade biomedical stainless steel AISI 316 LVM. The steel was cut in plates with the dimensions of 25 mm × 50 mm × 3 mm. The steel plates were sand-blasted with 2 mm Al_2O_3 particles and cleaned in ultrasonic bath prior to the deposition process. After sand-blasting, the surface roughness of the steel plates was determined to be 5.00 ± 0.28 µm (according to Perthen Perthometer).

The commercially available HA powder with the mean particle size of 90 ± 15 µm (Capital 90, Plasma Biotal, UK) was used for the deposition of HACs. The chemical and phase composition of the HA powder was confirmed by using the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry, micro-Raman spectroscopy (MRS) and X-ray powder diffractometry (XRD). The data on the granulation of the HA powder were obtained from the manufacturer's data sheet.