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HAp–ZrO_2 composite coatings prepared by plasma spraying for biomedical applications

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Abstract

Applicational properties of HAp–ZrO_2 composite coatings prepared on a titanium alloy substrate using plasma spraying method and analogous HAp coatings are compared. Results of the studies indicate that there is a strong dependence of the phase composition, thickness, porosity and adhesion to the substrate of the obtained coatings on the characteristics of the starting powders used for their preparation.

Keywords: B. Composites; D. Apatite; D. ZrO_2; Coatings

1. Introduction

Both, hydroxyapatite (HAp) and zirconia (ZrO_2) are well-known and valuable implant materials. However, the interest in their composites which could combine the unique biocompatibility and bioactivity of HAp ceramics with very good mechanical properties of the materials based on partially stabilized zirconia has started quite recently [1,2].

Preparation of a two-phase HAp−ZrO_2 composite material gives rise to some questions, which have not been fully clarified in previous studies. In particular, these questions concern the influence of ZrO_2 on phase stability of HAp [3]. Thermal behaviour of HAp in the presence of ZrO_2 as the admixture depends on a number of factors which may, but not necessarily have to, cause its degradation. This problem is of crucial importance from both scientific and applicational points of view since HAp degradation results in changes in its physico-chemical properties. This determines the behaviour of an implant material in a living system by altering its solubility, biocompatibility and resorbability. On the other hand, calcium contained in HAp can interact with ZrO_2 which can result in its transformation from tetragonal into cubic form. This process makes it impossible to reinforce the composite material by the transformation which is a unique toughening mechanism inherent to ZrO_2 ceramics. Degradation of hydroxyapatite in HAp–ZrO_2 composites may be avoided or limited during hot isostatic pressing (HIP) [4].

Most of the studies which have been carried out in recent years dealt with the preparation of HAp–ZrO_2 composites in the form of dense sinters [5,6]. Only a few reports described the HAp–ZrO_2 composite coatings obtained on other materials [7]. Therefore the studies aimed at evaluation of phase composition, homogeneity, porosity and adhesion to metallic substrate of HAp–ZrO_2 composite layers prepared by plasma spraying seemed to be worthwhile. They have been carried out in the present work in which the coatings of pure HAp have constituted the reference material.

2. Materials and methods

HAp used for plasma spraying was prepared by the wet method using CaO and H_3PO_4 as starting materials [8]. The precipitate was washed with distilled water and dried at 110 °C. Then the precipitate was calcined at 800 °C for 3 h

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and attrition milled for 2 h in ethanol. X-ray diffraction analysis confirmed that the material obtained was a pure HAp phase with BET surface area of 25.7 ± 0.2 m^2/g and mean particle size D_{BET} = 74 nm. Studies of the powder morphology carried out by transmission electron microscopy (TEM) showed that it was composed of isometric, agglomerated crystallites (Fig. 1).

HAp powder used for preparation of the coating by plasma spraying was granulated and fractionated using sieves of 0.090–0.250 mm mesh. The following grain fractions were obtained:

0.090/0.125 [mm]—denoted as the ‘‘fine’’ fraction
0.125/0.200 [mm]—denoted as the ‘‘medium’’ fraction
0.200/0.250 [mm]—denoted as the ‘‘coarse’’ fraction

After fractionation the granules were heated at 1250 °C with 2 h soaking time.

The HAp matrix in the composite coatings was reinforced with ZrO_2 powder partially stabilized with CaO. The powder which was a solid solution of 6 mol% CaO in ZrO_2 (CaO–ZrO_2) was prepared by precipitation of hydrated zirconia. Zirconyl chloride $ZrOCl_2$ and $CaCO_3$ were used as precursors. Precipitation was carried out using aqueous ammonia solution and ammonium carbonate. The precipitate obtained was washed with distilled water and after drying calcined at 650 °C for 1 h. Crystalline CaO–ZrO_2 powder was ground in a attritor mill in ethanol for 3 h. BET surface area of this powder was equal to 62.2 ± 0.2 m^2/g, whereas the particle size calculated from surface area measurements was equal to D_{BET} = 16 nm. Powder morphology is shown in Fig. 2. CaO–ZrO_2 powder contained 36 vol% of tetragonal crystallites and 64 vol% of monoclinic ones.

The content of CaO–ZrO_2 reinforcing phase in the HAp matrix was equal to 20 wt.%. The starting HAp/CaO–ZrO_2 composite powders were prepared by mixing the appropriate amounts of both powders in a attritor mill in ethanol for 0.5 h. Similarly to pure HAp, before the spraying process the sets of composite powders were granulated and fractionated using sieves of 0.090–0.250 mm mesh. The following fractions were obtained:

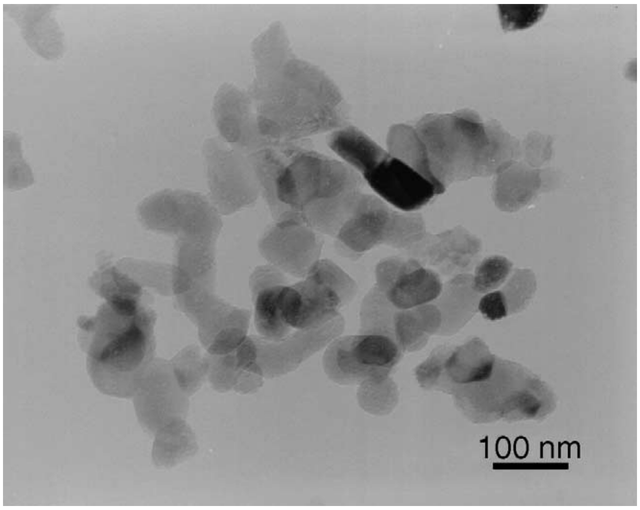

Fig. 1. TEM micrograph of pure HAp phase.

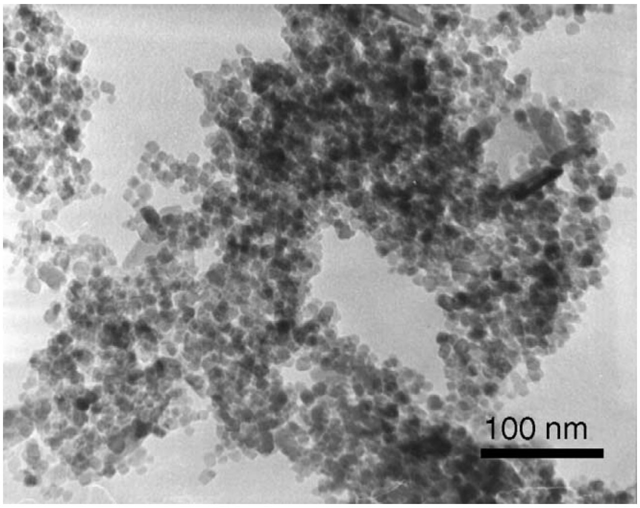

Fig. 2. TEM micrograph of 6 mol% CaO–ZrO_2 powder.

0.090/0.125 [mm]—denoted as ‘‘fine’’ fraction
0.125/0.250 [mm]—denoted as ‘‘coarse’’ fraction

The granules were calcined at 1250 °C with 2 h soaking time.

Plasma HAp/CaO–ZrO_2 and HAp coatings were prepared on a metallic substrate made of titanium alloy WT3-1. Parameters of plasma spraying process for all granulated powders were the same. The rate of introduction of the powders into a plasma stream was equal to ca. 10 m/s. Gaseous argon and hydrogen (5–6%) was used to generate plasma. Optimal spraying distance was equal to 10/15 cm (maintained within ±0.5 cm), whereas the electric power in the plasma stream was equal to U = 50 V and I = 400 A. Before the spraying process the metal substrate was subjected to abrasive as well as ultrasonic treatments.

Thickness, porosity of all ceramic layers prepared as well as their adhesion to the metallic substrate were examined. The adhesion was investigated according to ISO 13779-4 standard using a HECKERT FPZ100 equipment for mechanical adhesive test. Microstructure was examined on a scanning electron microscope (SEM) Jeol 5400. Phase composition of the obtained coatings was established by X-ray diffraction investigations (XRD 7 Rich. Seifert & Co. diffractometer).

3. Results and discussion

Porosity of the plasma sprayed HAp/CaO–ZrO_2 composite as well as hydroxyapatite coatings was determined based on their photographic images obtained in a binary

Table 1
Porosity of the coatings obtained by plasma spraying

Coating	Porosity in the cross-section [%]	Porosity on the surface [%]
HAp "coarse fraction"	19	19
HAp "medium fraction"	7	11
HAp "fine fraction"	6	7
HAp/CaO–ZrO_2 "coarse fraction"	27	18
HAp/CaO–ZrO_2 "fine fraction"	23	34

Table 2
Thickness of the coatings obtained by plasma spraying

Coating	Coating thickness [μm]
HAp "coarse fraction"	236
HAp "medium fraction"	184
HAp "fine fraction"	160
HAp/CaO–ZrO_2 "coarse fraction"	241
HAp/CaO–ZrO_2 "fine fraction"	207

mode (Table 1). It was found that the prepared ceramic layers differed in thickness and porosity in spite of similar conditions of the spraying method. Since parameters of the coating process were similar the differences in the obtained layers must have resulted from various characteristics of the starting powders.

Results of thickness measurements are collected in Table 2. A distinct correlation between porosity and thickness of the coatings can be noticed: thicker coatings ($\geq$200 μm) showed higher porosity, whereas the proportion of pores in thinner ones was lower. The layers obtained from "fine" and "medium" fractions of pure HAp exhibited the lowest porosity, both on the surface and in the cross-section. Porosity of the coatings prepared using "fine" HAp/CaO–ZrO_2 composite fraction was approximately four times higher than that of the coatings prepared from "fine" HAp granules.

These findings were confirmed by microscopic studies (Fig. 3). All the ceramic layers studied showed high development of surface, but on the surface of composite coatings distinct cracks, open pores as well as the clusters of extremely fine ZrO_2 inclusions were visible (Fig. 3a). HAp coatings were more compact with significantly lower number of pores (Fig. 3b).

Adhesion to the substrate is one of the most important mechanical properties of ceramic covering materials for metallic implants. In Table 3 the results of measurements of the adhesion of the obtained coatings to the alloy substrate are presented. It can be clearly seen that the coatings prepared from pure HAp phase showed much better adhesion than those made of composite material. Poorer adhesion in this case may be due to their higher porosity and thickness. Lower porosity on the surface and in the cross-section leads to better adhesion of the HAp coatings. Our studies confirmed that as the thickness of the layer increases its adhesion to the metallic surface decreases for both composite and pure HAp coatings [9].

Fig. 4 shows the XRD diffraction patterns corresponding to the HAp/CaO–ZrO_2 composite as well as HAp coatings. Since the phase composition of composite coatings prepared from "fine" and "coarse" granulated powders were similar, only one diffraction pattern is shown in Fig. 4.

XRD spectrum of the composite coating is significantly different from those of the corresponding HAp ones. Changes in the intensities of the reflections originating from HAp as well as the peaks indicating a partial HAp decomposition and the reaction between ZrO_2 and CaO are visible in this spectrum. XRD analysis shows that such phases as HAp, α-TCP, TTCP present due to HAp thermal decomposition, co-exist in the coating with $CaZrO_3$ which appeared as a result of the reaction between CaO and ZrO_2. Additionally, a distinct reflection at $2\Theta = 30.200^\circ$ indicating the presence of zirconia can be seen in the spectrum. However, determination of its polymorphic form present in the system is difficult. Two peaks corresponding to cubic and tetragonal forms appear at very close 2Θ values giving a characteristic doublet visible as one big reflection in the XRD pattern. It can be supposed, however, that cubic ZrO_2 prevails in the system. This is most probably the reason for lowering of adhesion of the composite coatings to the substrate.

$CaZrO_3$ is the next phase clearly distinguishable in the XRD pattern. Its presence proves that the reaction between

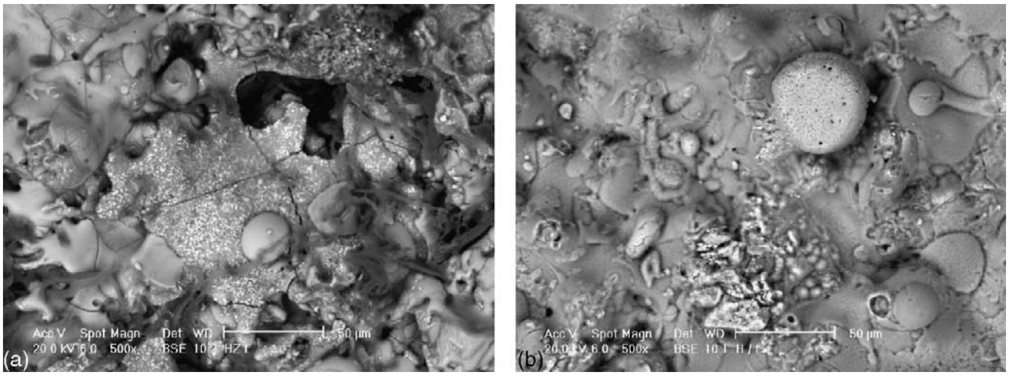

Fig. 3. SEM micrographs of plasma-sprayed coatings: (a) HAp/CaO–ZrO_2 composite coating; (b) HAp coating.

Table 3
Results of the studies of the coatings adhesion to metallic substrate

Coating [MPa]	Breaking stress
HAp "coarse fraction"	47.06 ± 4.21
HAp "medium fraction"	30.60 ± 3.04
HAp "fine fraction"	26.89 ± 3.01
HAp/CaO–ZrO_2 "coarse fraction"	11.77 ± 1.94
HAp/CaO–ZrO_2 "fine fraction"	15.20 ± 2.22

ZrO_2 and CaO resulting from HAp thermal decomposition has occurred in the system. Since the coatings described in the work were reinforced with ZrO_2 partially stabilized with calcium oxide, CaO excess in the system can result in the transformation of tetragonal ZrO_2 to the cubic one as well as to the formation of $CaZrO_3$. Thus, HAp thermal decomposition is necessary for the formation of $CaZrO_3$. On the other hand, plasma-sprayed layers prepared from similar fraction of pure HAp did not show any sign of thermal decomposition. Hence, it is clear that HAp is partially decomposed in the presence of ZrO_2 in HAp-based composites.

X-ray diffraction patterns of pure HAp coatings indicate that the grain size of the granulated powders used in the plasma spraying process influences significantly not only the thickness (Table 2) but also the composition and crystallinity degree of the ceramic layer. HAp coatings obtained using the "medium" and "coarse" fractions show higher degree of crystallinity than those prepared using the "fine" fraction of the granulated powder. HAp coating obtained from the "fine" fraction was the thinnest one prepared in the studies (160 μm) and it was highly amorphous (Fig. 4).

Phase composition of the prepared coatings is influenced by the behaviour of HAp granules at high temperatures of plasma spraying process. Only in the case of layers prepared from the "fine" fraction of pure HAp, the formation of TTCP and CaO (characteristic reflection corresponding to this phase at $2\theta = 37.450^\circ$) was observed. This phenomenon can be explained based on the fact known from the literature that CaO as well as TTCP can be formed in non-equilibrium conditions, such as sudden temperature changes [10]. These are the conditions of plasma spraying process. Hence, the appearance of CaO in the coating obtained from fine HAp particles which melt to the highest degree in plasma is fully justified. CaO appearing in the system results from thermal decomposition of thermodynamically unstable TTCP. Apart from a distinct reflection originating from the only crystalline phase in the system, i.e. CaO it is possible to distinguish a number of diffuse peaks in the XRD pattern of the coating. The most probable interpretation of the reflections corresponding to the HAp decomposition products is presented in the XRD pattern shown in Fig. 4. It is important to note, however, that such analysis is not easy due to low crystallinity degree of the material studied as well as the peak overlapping which result in high diffusion of the spectrum.

In the case of HAp coatings obtained using "medium" and "coarse" fractions of granulated particles no signs of HAp thermal decomposition during plasma spraying process were observed. If such degradation did occur then it stopped in its initial step leading to the formation of OHAp and OAp. The peaks corresponding to these phases overlap and therefore they cannot be distinguished in the XRD diffraction studies. Our results confirm the literature reports according to which the intensity of the HAp decomposition in the plasma flame depends on the process parameters [11]. Absence of the degradation products observed in our studies can be rationalized by the specific properties of the starting material used in the coating preparation, particularly the proper choice of the powder grain size. In the plasma spraying process the material is introduced into the flame of plasma of extremely high temperature at which fine grains are melted significantly faster than the larger ones. Thus, as has been shown, the temperature influences the phase composition of the coating prepared from fine particles to a

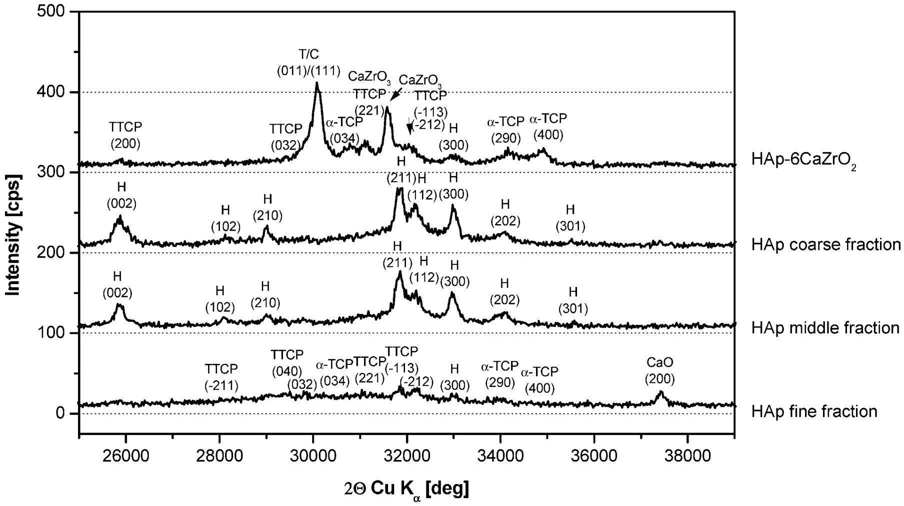

Fig. 4. X-ray diffraction patterns of HAp and HAp/CaO–ZrO_2 coatings obtained by plasma spraying (H, hydroxyapatite; T, tetragonal ZrO_2; C, cubic ZrO_2).

higher extent. Larger grains are melted only on their surface. During cooling calcium phosphates resulting from decomposition react with water and thus are again transformed into the form thermodynamically stable under normal conditions, i.e. hydroxyapatite [9].

4. Conclusions

The studies carried out on HAp/CaO–ZrO_2 composite as well as HAp coatings prepared by plasma spraying on metallic substrate have shown that under similar conditions of the coating process thickness, porosity, crystallinity and microstructure depend on the composition and size of the granulated powders used. Composite coatings exhibit significantly higher porosity both in the cross-section and on their surface. Lower porosity of the coatings prepared from pure HAp leads to their better adhesion to the metallic substrate than that of the HAp/CaO–ZrO_2 coatings. Apart from HAp and ZrO_2 the composite coatings also contain αTCP, TTCP and $CaZrO_3$.

HAp coating prepared using ‘‘fine’’ fraction of granulated powders shows the presence of such phases as TTCP, TCP and CaO. This proves a complete degradation of HAp during the plasma spraying process. These phases do not occur in the HAp layers prepared using fractions of ‘‘medium’’ and ‘‘coarse’’ granules, i.e. HAp degradation does not take place in these coatings.

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