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Plasma spraying of biologically derived hydroxyapatite on implantable materials

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Plasma spraying of hydroxyapatite (HA) coatings on human implants is considered to provide a promising means of enhancing their biocompatibility and improving tissue growth. This paper briefly describes a method of extracting HA powder from a biological source, namely human teeth. The physical and chemical characteristics of the derived powder are studied and the suitability of this powder for plasma spraying applications is ascertained. The deposited coatings are found to retain the chemistry characteristic of the apatite. Typical results of metallographic and scanning electron microscopy (SEM) studies and hardness measurements on the sprayed HA coatings are presented.

1. Introduction

Hydroxyapatite (HA), which is a material similar to the major constituent in human bones and teeth, is one of the best known biocompatible materials. Devices manufactured from HA material are, therefore, potentially least susceptible to rejection by the body. As such, a majority of the efforts aimed at achieving truly biocompatible surfaces for human implants have involved the use of the above mineral. While techniques to form bulk HA devices are available [1], the use of these bulk ceramics is severely limited by their insufficient strength to serve as structural *in vivo* replacements for load bearing implants employed in orthopaedics and dentistry [2]. Of late, surface modification using HA coatings has been found to provide a most promising means of combining the strength, ductility and ease of fabrication of metallic implants with the increased biocompatibility and tissue growth afforded by HA [3, 4].

Ideally, it is required that the deposited HA coatings retain the structure and chemistry characteristic of the apatite. Furthermore, the deposited layer should be well adhered to the metallic implant and the interfacial shear strength should be adequately high, unlike the brittle nature of bulk HA devices. In this respect, it is pertinent to mention that HA is known to form a direct interfacial bond with bone [5, 6] shortly after implantation. Several methods have been tried in recent years to deposit HA layers [7–9] and thermal spraying, particularly plasma spraying, is generally preferred [10]. In fact, plasma sprayed HA coatings on titanium and titanium alloy orthopaedic and dental implants are already being clinically used [11, 12]. While the mechanism of bone bonding to plasma sprayed HA coatings remains a matter of speculation, it has been established that the interfacial tensile bond strength for the HA-coated implants is significantly greater than that for the uncoated substrate [13].

In view of the potential applications of hydroxyapatite as a raw material for the fabrication of human implant devices, numerous studies have been devoted to the synthetic preparation of HA powder by a variety of methods [14, 15]. However, it is possible that the likelihood of rejection of an implant by the human body can be further reduced by the use of a biologically extracted HA powder. Furthermore, such extraction is also feasible due to the fact that both bone material and tooth enamel have high HA contents of 65–70% and 95–98%, respectively [4].

The present paper deals with an effort concerning plasma spraying of a HA powder biologically derived from human teeth. The method employed for powder extraction is briefly outlined and the determined characteristics of the said powder are presented. The suitability of the above powder for plasma spraying is also evaluated. Biocompatibility studies of the deposited coatings and appropriate animal studies using the HA-coated implants are currently in progress and their results will be presented in a subsequent paper.

2. Experimental Procedure

2.1. Preparation of hydroxyapatite powder

In order to prepare the hydroxyapatite powder, human teeth samples were collected from local hospitals. These were first washed thoroughly with soap water and subsequently with alcohol. The samples were then deproteinized by distillation with an alkali

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for 8–10 h. After deproteinization, the samples were first washed with water, then sintered at 650 °C, and finally ground to size.

2.2. Plasma spraying of HA powder

In order to ascertain the suitability of the biologically derived HA powder for plasma spraying applications, a METCO 7MB plasma spray system (METCO Inc., USA) was used. Ti–6Al–4V alloy sheets of 5.1 mm thickness and rods of 4.5 mm diameter were employed as substrates. It may be mentioned that HA is reported to react with Ti and its oxides at high temperatures to create a chemical bond between the coating and the substrate [7] and plasma spraying can initiate such a reaction. The spray parameters employed for coating deposition are indicated in Table I.

2.3. Characterization of prepared powder and sprayed coatings

The morphology of the prepared HA powder and the surface topography of its plasma sprayed coatings were observed using a scanning electron microscope (International Scientific Instruments, USA; Model ISI 100A). Both the powder and coating specimens were carbon-coated prior to observation under scanning electron microscopy (SEM) to avoid charging. X-ray diffraction (XRD) investigation (SIEMENS, Germany; Horizontal Diffractometer Model) of the powder and coating was also carried out for phase confirmation. The chemical composition of the prepared HA powder was determined using wet chemical techniques, while its thermal behaviour was ascertained using a standard thermal analyser (Shimadzu Co., Japan; Model DT-40). The metallographic evaluation of coatings was done using an optical microscope (Leitz, Germany; Metalloplan Model) and their hardness was measured using a digital universal hardness tester (Eseway, USA; Model ESE, Type DVSBM).

3. Results and discussion

3.1. Powder characterization

The suitability of any given powder for spraying applications is primarily governed by its physical properties. In general, any material that can be melted without decomposing can be sprayed. In this respect, plasma spraying happens to be a particularly advantageous means of coating deposition owing to the very high temperatures (in excess of 10 000 K) available in the plasma flame to facilitate particle melting. The coating quality is also largely dependent upon the powder characteristics. Properties such as chemical composition, particle shape, particle size distribution and other powder-related parameters are important considerations in achieving optimum results as these significantly influence particle melting characteristics during coating as well as the performance of the deposited layer.

TABLE I Plasma spray parameters used for coating deposition

Pressure (psi)	
Primary gas (Ar)	100
Secondary gas (H_2)	50
Flow rate ($ft^3\ hr^{-1}$)	
Primary gas (Ar)	80
Secondary gas (H_2)	15
Carrier gas (Ar)	37
Arc current (A)	700
Powder feed rate ($lb\ hr^{-1}$)	6.2
Spray distance (inch)	2.5

3.1.1. Powder morphology and flowability

A typical SEM photograph illustrating the shape and size characteristics of the HA powder derived from the human teeth is shown in Fig. 1. The figure reveals the powder to be much coarser than the commercially available spray-grade ceramic powders, which are typically constituted of particles less than 100 μm in size. It is also observed that the powder has a wide particle size range and irregular particle shapes, both being rather typical of any powder eventually comminuted by the grinding method. Presumably, the latter is responsible for the non-flowability of the powder during the Hall Flow test performed during this study. It should, however, be mentioned here that a free-flowing powder is not a prerequisite for spraying applications—as was done in the present case, an air/electronic vibrator can be employed to make such powders flow during spraying.

3.1.2. Chemical analysis

A wet chemical analysis of a sample of the biologically derived HA powder was carried out to determine its chemical composition. The analysis revealed the powder composition (in wt %) to be Ca = 44.0, P = 17.4 and O = 35.9 with some loss of volatiles on ignition. The above values correspond to almost a 17% excess

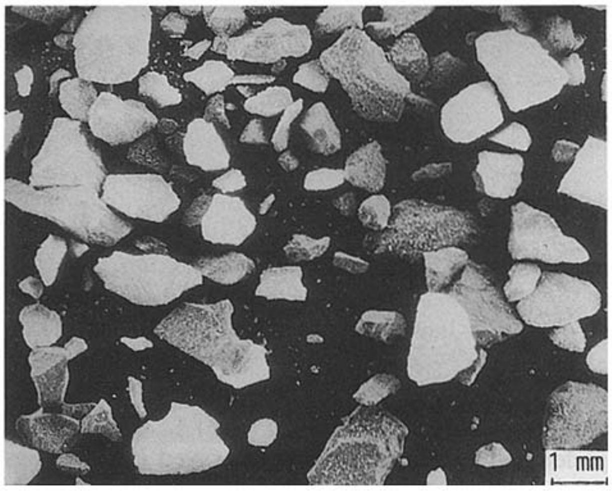

Figure 1 SEM photograph showing the typical morphology of the extracted hydroxyapatite powder.

of calcium as compared with the theoretical Ca/P ratio determined from the stoichiometry of pure hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. This can be attributed to the presence of other calcium-containing salts, or of other calcium–phosphorous compounds which are relatively more calcium-rich in comparison to the apatite.

3.1.3. X-Ray diffraction analysis

An XRD investigation of the HA powder was also done for the purpose of phase confirmation. The XRD pattern obtained using FeK_α radiation is illustrated in Fig. 2a and all the major peaks therein were found to very closely match the standard XRD pattern for hydroxyapatite [16]. Apart from the peaks characteristic of HA, the XRD pattern also exhibited a few other minor unidentified peaks as shown in the summary of XRD data provided in Table II. The unidentified peaks presumably originate from the other calcium-containing compound(s) mentioned above which lead to a super-stoichiometric Ca/P ratio.

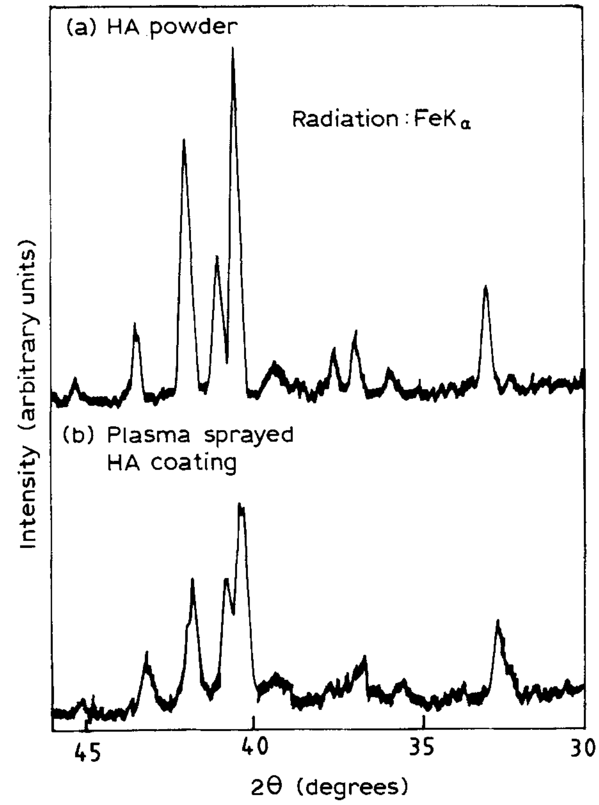

Figure 2 XRD patterns, using FeK_α radiation (a) starting HA powder; and (b) plasma-sprayed HA coating.

The lattice constants of the HA powder were also calculated from the X-ray data. Using the plane spacing formula for the hexagonal unit cell and simultaneously solving the equations resulting for the two highest angle peaks yields the lattice constants values a = 0.9408 nm and c = 0.6888 nm as compared to a = 0.9432 nm and c = 0.6881 nm which are considered standard for HA [16].

3.1.4. Thermogravimetric analysis

A thermal analysis was done to study the thermal behaviour of HA crystals in the temperature range 0–1000 °C. The temperature profile of the crystals was predominantly linear over the temperature range, except in the incubation zone up to 100 °C. The crystals were very stable in this zone. Following a slightly exothermic behaviour initially, an endothermic behaviour was observed up to 1000 °C. The weight loss in this range due to evaporation of any residual matter was found to be about 10%.

3.2. Characterization of sprayed HA coatings

The coatings, generated by plasma deposition of the biologically derived HA powder using the spray parameters indicated in Table I, were extensively evaluated. The studies on the coatings included observation of their typical microstructure and surface topography, and XRD analysis to compare the phase composition of the sprayed coatings and the prepared HA powder. Hardness measurements on the coated and bare substrates were also made.

TABLE II Summary of X-ray diffraction analysis

	Powder		Coating		HA Card (JCPDS No. 24-33)	
	d (nm)	I/I_0 (%)	*d* (nm)	I/I_0 (%)	*d* (nm)	I/I_0 (%)
Matching peaks	0.3420	33	0.3451	43	0.3440	42
	0.3068	20	0.3084	26	0.3087	14
	0.2805	100	0.2811	100	0.2817	100
	0.2778	44	0.2785	64	0.2779	43
	0.2715	76	0.2715	64	0.2723	55
	0.2625	24	0.2631	29	0.2631	24
	0.2258	28	0.2262	16	0.2265	20
	0.1943	28	0.1949	32	0.1945	24
	0.1841	29	0.1846	34	0.1841	26
Unidentified peaks	0.4046	13	0.4075	21	–	–
	0.3868	10	0.3868	22	–	–
	0.3013	15	0.3036	16	–	–
	0.2880	13	0.2880	18	–	–

Results of each of these tests are briefly discussed below. However, before proceeding, it is apt to mention here that a high plasma arc current of 700 A had to be used during spraying as attempts to apply coatings at lower arc currents of 500 and 600 A were unsuccessful, presumably due to poor deposition efficiency resulting from inadequate melting of the powder in the plasma flame. This is attributed to a very coarse particle size of the starting HA powder. As the extent of particle melting is substantially improved by decreasing the particle size [17], it is possible that lower arc currents can be used for coating generation if a fine HA powder is employed for spraying.

3.2.1. Metallographic evaluation

Test specimens of coatings generated by plasma spraying of the HA powder were mounted and their cross-sections were observed under an optical microscope. The bonding appeared good with no discernible discontinuities between the substrate and the deposited layer. A typical microstructure of the plasma-sprayed HA layer is shown in Fig. 3. The figure also shows the HA coating thickness to be around 75–100 μm.

3.2.2. X-Ray diffraction analysis

X-ray diffraction analysis of the coatings was conducted to compare the phase composition of the sprayed HA deposit with that of the prepared powder. The XRD pattern for the HA coating obtained using FeK_α radiation is depicted in Fig. 2b. The pattern summarized in Table II, on comparison with the data card for HA [16], reveals that the coating retains the chemistry characteristic of the apatite. The crystallographic structure is seen to remain virtually unaltered, except that some line broadening is observed.

3.2.3. Surface Morphology

The as-sprayed HA coatings were observed under SEM to study the surface topography of the deposited layer. Fig. 4 shows a photomicrograph illustrating the typical surface topography of HA coatings in the as-sprayed condition. The figure reveals a microporous coating surface which is often desirable for human implant applications. In the case of HA, it has been reported that mechanical interdigitation on a micrometre to submicrometre level may significantly contribute to bone-to-HA attachment and a microtextured coating surface is necessary for this purpose [13]. It is also relevant to mention here that the porosity in the deposited HA layer can potentially be controlled by manipulating the spray variables.

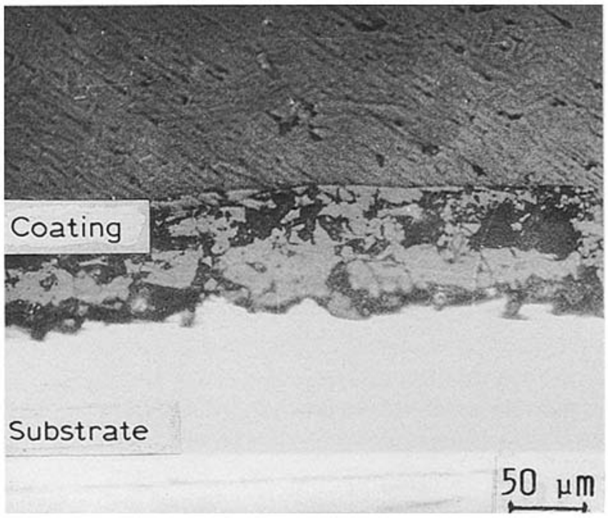

Figure 3 Typical microstructure of the plasma-sprayed HA layer.

3.2.4. Hardness measurements

The hardness values of both the HA-coated and bare Ti-alloy flats were measured. The results are shown in Table III and these indicate that there is no significant difference between the uncoated and coated samples. This is probably due to the very thin layer of the applied coating (approximately 75–100 μm).

4. Conclusions

This paper deals with the formation of HA coatings by plasma spraying of a powder derived from a biological source. The method used to extract the powder from human teeth is briefly described. Characterization of the above powder revealed that it was predominantly constituted of HA. Although the deposition rate of this powder was unsatisfactory at low arc currents due to its rather coarse particle size, plasma spraying employing an arc current of 700 A was found to present no difficulty. An XRD investigation of the

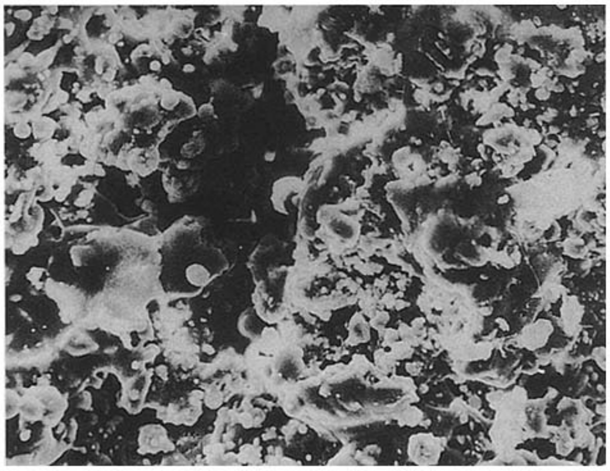

Figure 4 Typical surface topography of the plasma-sprayed HA coating 1 cm = 20 μm.

TABLE III Comparison of hardness values of bare and coated substrates

Hardness	Bare substrate	HA-coated substrate
Rockwell superficial (30 T)	54.6	55.2
Vickers	78.3	79.8

coating showed that it retained the chemistry and structure characteristic of the apatite during spraying.

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