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Residual stress measurement in thermal sprayed hydroxyapatite coatings

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Hydroxyapatite coatings have been used for many years on dental and prosthetic implants to provide a biocompatible surface for long-term fixation of the implant to bone. In this study two thermal spraying processes, air plasma spraying (APS) and a high velocity oxy fuel process (CDS) have been employed to produce hydroxyapatite coatings. An X-ray diffraction technique (XRD) has been applied to measure the residual stresses in thermal sprayed hydroxyapatite coatings. It has been shown that such stresses are sensitive to spraying parameters and that the newer high velocity oxy fuel spraying process results in lower residual stresses than the conventional air plasma spraying process. Heat treatment of the coating has been shown to significantly reduce the residual stress in the coating.

1. Introduction

The crippling and painful disability produced by osteoarthritis is a problem on a worldwide scale; each year, in excess of 400 000 hip joints are replaced. For patients in the 65 + year age group there is a 90% success rate for a total hip replacement over a 10-year period but for those in the 16–24 year age group, who are generally more active than the elderly, it can be expected that a revision operation will have to be performed approximately three years after initial surgery. With an increasingly ageing population, the demand for surgery to replace the hip joint will go on rising. Therefore improvements to increase the life span of hip replacement joints, especially in younger patients, would significantly reduce the number of revision operations required and free surgeons to undertake more primary surgery [1].

Cementless fixation is concerned with the close contact of the bone to the implant surface. It is essentially dependent on bone being able to form around the implant and maintain the bond. This has led to the study of the interface between bone and either an inert porous surface which allows bony ingrowth, or a bioactive coating, such as hydroxyapatite, which promotes bony ingrowth [2].

The biocompatibility of several calcium phosphates has been studied using both *in vivo* [3–7] and *in vitro* [8–12] testing. The results indicate that hydroxyapatite (HA) is totally biocompatible; it promotes bone growth and direct apposition to bone has been reported. Crystalline hydroxyapatite has been reported to be the most stable form of calcium phosphate, with amorphous hydroxyapatite and β-tri-calcium phosphate being less stable and more readily resorbed by the body. The application of bioactive hydroxyapatite coatings to implants is attracting considerable interest, with emphasis on the use of plasma spraying to apply the coating.

Plasma spraying is a type of thermal spraying process, where the coating powder is heated near or above its melting temperature in a plasma gas stream which accelerates it towards the substrate, where on impact the particle is cooled rapidly due to the large surface area and the large temperature difference between the particle and the substrate [13]. Two thermal spraying techniques have been used in this study; an air plasma spraying process (APS) and a high velocity oxy fuel process known as CDS.

HA coatings combine the superior mechanical performance of the metal component with the excellent biological responses of hydroxyapatite, since monolithic hydroxyapatite itself has a low tensile strength and low resistance to fatigue failure. Plasma-sprayed hydroxyapatite coatings with their macroporous surfaces can significantly improve bone ingrowth. The stability at the coating/bone interface can also be strongly influenced by both the nature of the surface and the presence of phases which can be resorbed and therefore influence cell behaviour.

Residual stress in thermal-sprayed coatings is an inherent problem caused by the difference in thermal properties between the coating and substrate materials combined with the rapid cooling rate. The performance of the coating can be affected by the magnitude of the residual stress [14, 15]. A compressive residual stress would be beneficial for a hydroxyapatite coating as the crack resistance would be increased and spalling of the coating minimized. This study investigates the use of an X-ray diffraction technique to measure residual stress in hydroxyapatite sprayed coatings. The objectives were to examine a range of coatings produced using the two different

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spraying techniques and to compare the residual stresses in the coatings using X-ray diffraction.

2. Materials and methods

2.1. Materials

Two hydroxyapatite powders were used:

(1) with a nominal particle size of 5–25 μm, for use with the CDS process,
(ii) with a nominal particle size 40–150 μm, for use with the APS process.

The coatings were sprayed onto a 2 mm thick substrate of Ti–6Al–4V alloy.

2.2. Methods

2.2.1. Thermal spraying

The APS and CDS hydroxyapatite coatings were applied using commercial thermal spraying systems. Gas mixtures of argon/nitrogen and argon/helium were used for the APS process and a propane/oxygen mixture for the CDS process. The APS spraying parameters were varied to produce three coatings for each gas mixture with the aim of showing standard, over- and underheated coatings. The CDS spraying parameters were varied to produce two coatings which were standard and overheated.

A standard and an overheated APS coating were heat treated at 600, 700, 800 and 900 °C for 30 min in air, to determine the effect on residual stress.

2.2.2. X-ray diffraction (XRD) and residual stress measurement

The Philips PW 1730/10 4 kW X-ray generator, using Philips PC-APD diffraction software for data collection and analysis, was used to obtain the XRD patterns for all thermal sprayed coatings. The residual stress in a coating can be calculated from the accurately measured position of a relevant peak in the XRD pattern [16]. The shift of a peak corresponds to a change in the unit cell dimensions and this is usually caused by stress. Using the PC-APD software for analysing XRD patterns the position of a peak can be accurately measured. It is important to select an appropriate peak, with a reasonable relative intensity to the I_{100} hydroxyapatite peak and simple *hkl* indices, such as the 300 and 004 planes, which give the stress in the two major planes of the hydroxyapatite structure. Since the hydroxyapatite structure is hexagonal, $a = b \neq c$, the a and c lattice parameters can be calculated from the relationship

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h + hk + l}{a}\right) + \frac{l}{c}$$

using the 300 plane this simplifies to

$$a = \sqrt{12d^2} = 2\sqrt{3d}$$

and similarly for the 004 plane

$$c = \sqrt{16d^2} = 4d$$

where d is the plane spacing calculated from the XRD pattern using Bragg's law, which rearranges to

$$d = \frac{\lambda}{\sin\theta}$$

where λ is the wavelength of the incident beam and θ is the measured diffraction angle.

Once the lattice parameters have been determined for the powders and the coatings, the lattice strain can be worked out and by using a suitable modulus for hydroxyapatite the residual stress in the coating can be calculated. The two powders used for spraying the APS and CDS coatings acted as standards for the residual stress calculations. Optical microscope techniques have been used to measure the thickness of all the thermal sprayed coatings.

Residual stress through the thickness of the coating was examined by polishing back the surface of the sprayed coating in 30 μm steps. This was achieved by mounting the sample in acrylic resin and polishing with a water-based 0.03 μm alumina paste on a surface 1 texmet polishing cloth. The stock removal rate was monitored by measuring the dimension change of a Vickers hardness indent. In addition, the percentage crystallinity was calculated from the XRD patterns.

3. Results

The spraying parameters and coating nomenclature used, along with the coating thickness and deposition rate are listed in Table I. The residual stresses for the APS coatings were all tensile and are shown in Fig. 1. The effect of coating deposition rate on the percentage crystallinity of the APS coatings can be seen in Fig. 2. The effect of coating thickness on residual stress for the CDS coatings is shown in Fig. 3. The residual stress through the coating thickness of sample APS2 is

TABLE I Details of sample preparation

Spraying parameters	Nomenclature	Coating thickness (μm)	Deposition rate (μm/cycle)
APS. Ar/N standard	APS1	96 ± 15	48 ± 7
APS. Ar/N overheated	APS2	212 ± 20	106 ± 10
APS. Ar/N underheated	APS3	112 ± 12	56 ± 6
APS. Ar/He standard	APS4	109 ± 11	13.6 ± 3
APS. Ar/He overheated	APS5	126 ± 12	31 ± 3
APS. Ar/He underheated	APS6	156 ± 11	13 ± 1
CDS. Standard	CDS1	148 ± 8	24.6 ± 1.3
CDS. Overheated	CDS2	167 ± 13	28 ± 2

shown in Fig. 4 and the residual stress measurements of the heat-treated samples APS1 and APS5 can be seen in Figs 5 and 6, respectively.

4. Discussion

The range of spraying parameters used result in different cooling rates and coating characteristics. This is reflected in the range of residual stresses which are shown in Fig. 1 for all the APS coatings. The percentage crystallinity obtained from the XRD patterns for the APS coatings can be related to the deposition rate/pass as shown in Fig. 2, this also indicates different cooling rates for each coating.

The overheated coating, CDS2, has a significantly higher residual stress and thickness relative to the standard CDS1, which can be seen in Fig. 3. The CDS process, which is a low-temperature and high-velocity technique, should be beneficial when spraying hydroxyapatite as phase changes, primarily to tricalcium phosphate, at high temperature will be minimized. The process relies on the higher velocity of the gas stream to accelerate the particles to a speed high enough to cause deformation of particles on impact with the substrate and thereby enhance adherence. The overheated coating, CDS2, would cause a steeper temperature gradient and hence a higher residual stress. The apparent residual stress is smaller in the CDS than that for the APS coatings, which would make the CDS coating less prone to spalling.

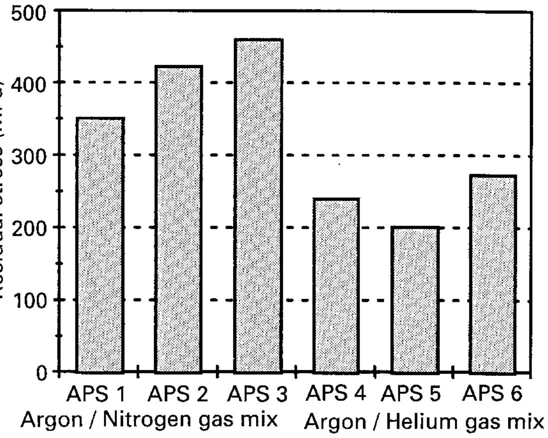

Figure 1 Residual stress in air plasma sprayed coatings.

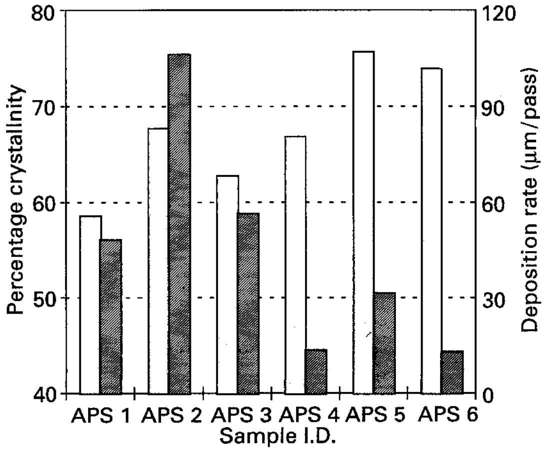

Figure 2 Relationship between percentage crystallinity (■) and deposition rate/pass (▨) for air plasma sprayed coatings.

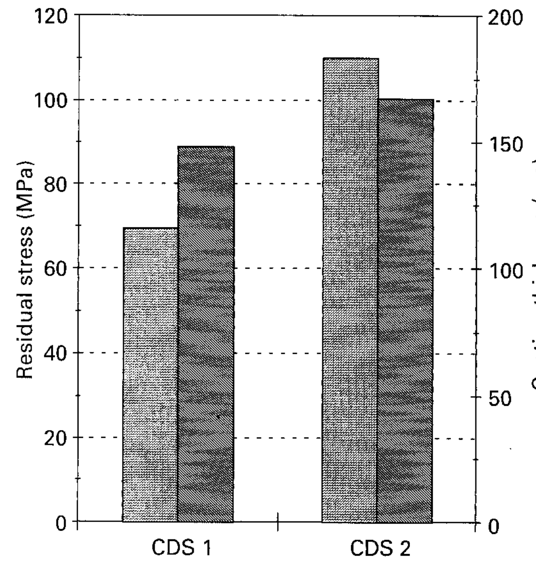

Figure 3 Relationship between residual stress (▨) and coating thickness (▧) for high-velocity oxy fuel sprayed (CDS) coatings.

As the thickness of the APS coating was reduced by progressively removing the surface the residual stress decreased, as shown in Fig. 4. This is not unexpected since the residual stress in the coating builds up with the increasing number of layers deposited by the spraying process.

Residual stress measurements on both standard and overheated air plasma sprayed coatings showed a similar reduction after heat treatment in the range 600 to 900 °C (Figs 5 and 6). These reductions in residual stress are due to a combination of stress relieving of the substrate and crystallization of amorphous hydroxyapatite in the coating. Above 900 °C phase changes in the plasma sprayed hydroxyapatite coating

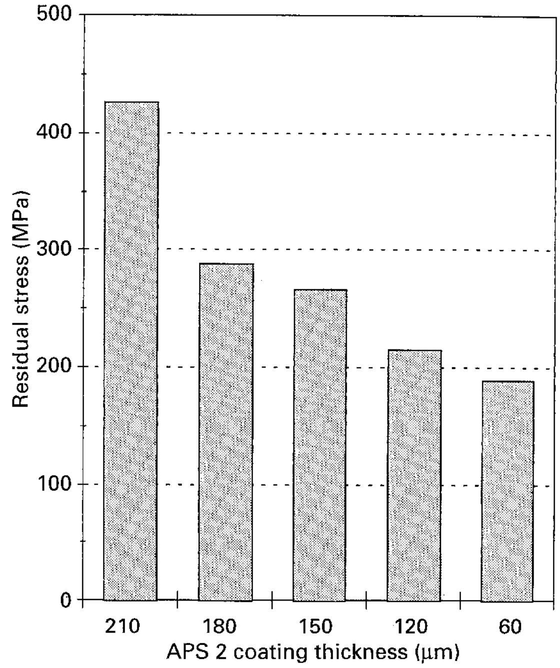

Figure 4 Residual stress through the thickness of air plasma sprayed coating, APS2.

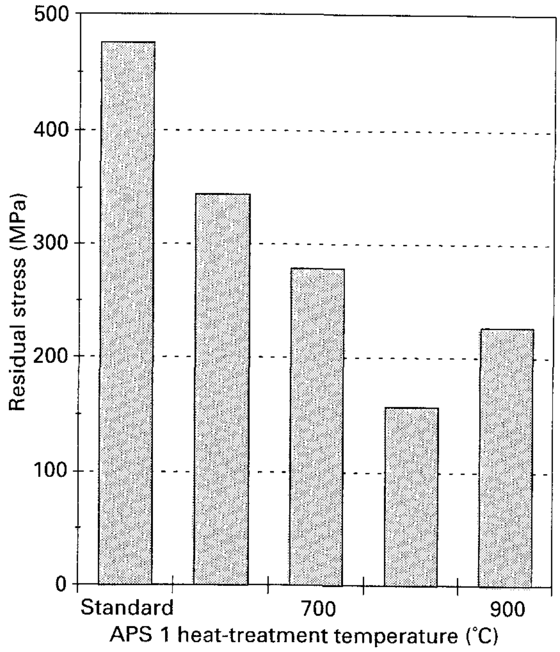

Figure 5 Effect of temperature on residual stress for air plasma sprayed coating, APS1.

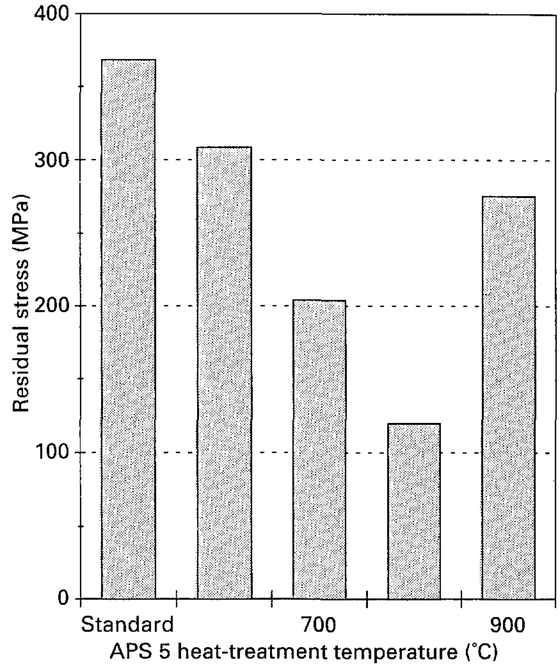

Figure 6 Effect of temperature on residual stress for air plasma sprayed coating, APS5.

can occur, this is indicated by a peak shift resulting in an increase in residual stress.

The XRD technique has proved to be a successful method for measuring residual stresses in hydroxyapatite coating on a titanium-alloy substrate. It has been shown that such stresses are sensitive to spraying parameters and that the newer high-velocity oxy fuel spraying process results in lower residual stress than the conventional air plasma spraying process. Heat treatment of the coating has been shown to significantly reduce the residual stress in the coating.

Acknowledgements

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