

STRUCTURAL CHANGES INDUCED DURING THERMAL SPRAYING OF HYDROXYAPATITE. A COMPARISON OF THREE DIFFERENT SPRAYING METHODS.

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ABSTRACT

HA is commonly applied to orthopaedic implants by thermal spraying. The thermal spraying methods used induce differences, not only in the macroscopic and microscopic properties of the coating, but also at the atomic level, which may compromise the long term stability of the coating. Three different thermal spray methods were investigated to determine the effect each would have on the **final** coating produced at the atomic level. The methods investigated were flame spraying, plasma spraying and high velocity oxy-fuel spraying. All three methods induced a distortion into the hydroxyapatite structure. The high velocity method was expected to produce the highest distortion, but this was not seen due to an annealing effect. Changes were also seen on the chemical level and carbonate found in the precursor powders was removed as determined by both X-ray diffraction (XRD) and Fourier Transform **Infra Red** spectroscopy (**FTIR**). Furthermore, **hydroxyl** groups were removed during spraying, to form oxyapatite.

INTRODUCTION.

Hydroxyapatite (HA) has been established as a material for use in surgery [1,2] and is commonly processed by thermal treatment. However, thermal processing has been shown to induce changes in the structure of HA [3]. Thermal spraying is currently a commonly used method for coating prostheses to produce cementless fixation. The thermal spraying methods **utilise** high temperatures and velocities, to give the desired coating, but these vigorous conditions can induce significant changes in the HA. Microstructural analysis has shown that the thermal processing methods considerably alter the morphology of the powder and XRD also has detected changes in the HA to an amorphous state, to give a **semi-crystalline** coating. However, XRD can detect more subtle changes in the coatings, down to the atomic level, by **Rietveld** analysis. These effects have previously been shown to be significant [3]. The changes detected may be

used, not only to assess the chemical quality of the coating, but also as a means of optimising the coating process.

MATERIALS AND METHODS.

HA was sprayed by three **different** techniques: flame spraying (FS), plasma spraying (APS) and high velocity **oxy** fuel (HVOF) spraying. The powders and variables used are detailed in Table 1.

Table 1. Conditions used for producing coatings.

	FS	APS	HVOF
Gases	Acetylene/ oxygen	Argon/ nitrogen	Propylene/ oxygen
Stand off distance (cm)	10	10	10
Power level (kW)		18	
Torch type	Terodyne	Metco 3MB	Jet Kote II
Powder particle size (μm)	10-40	30-80	10-40
Spraying velocity (ms^{-1})	50-80	150-180	280-320
Spraying temperature ($^{\circ}\text{C}$)	1800	2900	1700

Following coating, the HA was carefully removed from the substrate and analysed by X-ray diffraction (XRD). A data set was **collected** between 5 and $110^{\circ}2\theta$, using a step size of 0.02° and a sample time of 12 seconds. **CuK α** radiation was used. The data set was analysed using General Structure Analysis Software. Samples were also analysed using a Nicolet 800 FTIR spectrometer.

RESULTS

When spraying a powder by thermal methods, there are two main variables in the spraying, namely the temperature and the velocity. The three different methods used in this study were chosen to have markedly different temperatures and velocities, to highlight differences that the techniques may introduce. The first variable examined was the velocity, which was measured indirectly by calculation of any physical distortion in the HA from the distortion of the **PO₄** tetrahedra, as shown in **Figure 1**. The precursor powders show a relatively low distortion index of around 2. Following spraying, irrespective of method, this index increases. Consideration of the source of the distortion leads to the conclusion that velocity is the major influencing factor. However, the HVOF method, while having a **significantly** higher spraying velocity, does not introduce the highest distortion. This result may be **accounted** for by the annealing effect in the HVOF method. The HVOF method has a large heat zone, which extends as far as the substrate. The substrate is heated and thus distortion is annealed out. The APS method however, has a **localised** heat **zone** and no annealing occurs, **giving** the high distortion index.

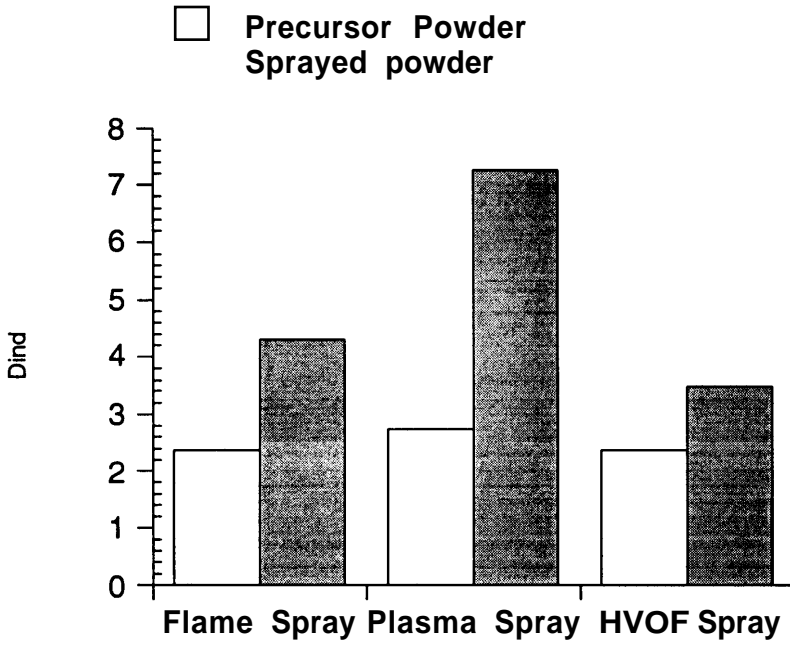


Figure 1. Change in distortion index using different thermal spray methods.

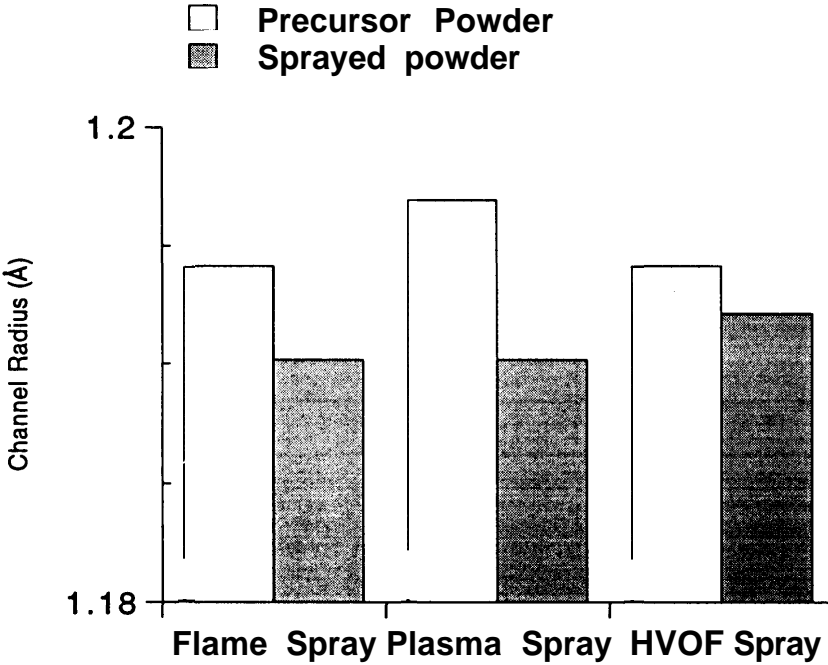


Figure 2. Effect of spraying methods on the hydroxyl channel radius.

Situated within the apatite structure, channels running parallel to the 'c' axis are seen and the radius of these **channels** may be measured, as shown in Figure 2. As expected, a comparison of before and after spraying shows that the channels shrink. In order to determine why the channels are shrinking, further analysis was performed for specific bonds associated with the hydroxyl channels (so designated, because the hydroxyl groups reside within these channels). Measurement of the $\text{Ca}(\text{OH})_2$ bond length reveals significant changes **following** thermal spraying. The precursor powders both show bond lengths of approximately 2.4 \AA . Following spraying, these bond lengths all drop to values of between 2.355 and 2.365 \AA , a **significant** reduction in bond length. Determination of the hydroxyl oxygen occupancy (**not** detailed here) show a reduction in occupancy from above 0.5 to values below 0.5 . A value of 0.5 is expected when hydroxyl groups occupy this site. If carbonate groups are located on this site, the occupancy rises to a value above 0.5 . However, if only oxygen is associated with the site, the occupancy drops to below 0.5 . From the results obtained, it may be inferred that **carbonate** is present in the precursor powder and is lost on thermal spraying. Furthermore, the **high** conditions have also formed oxyapatite. In order to **confirm** this conclusion, **FTIR** analysis was carried out on both the precursor powders and the sprayed surfaces.

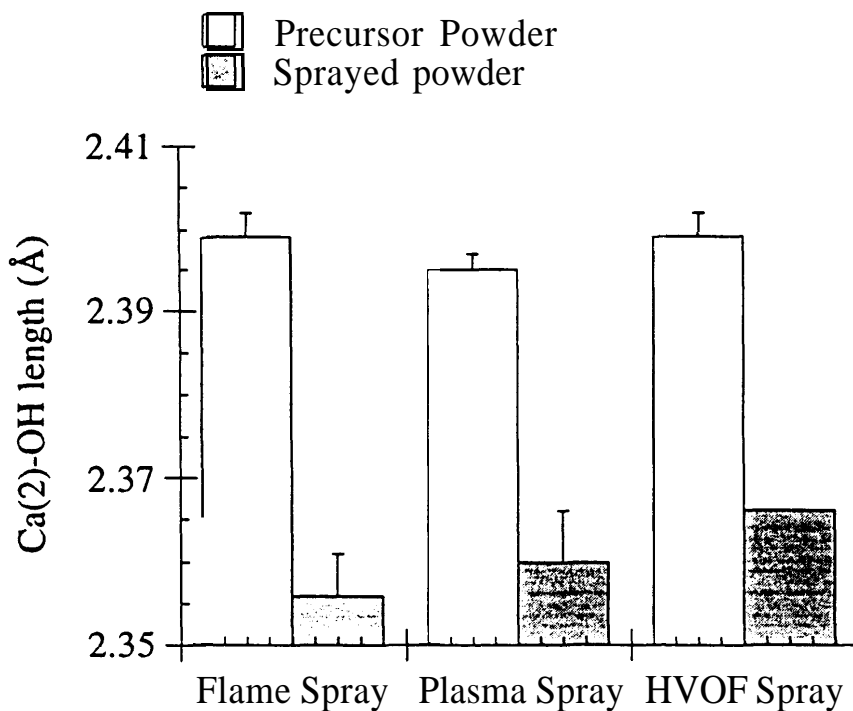


Figure 3. Effect of different thermal spray methods on the $\text{Ca}(\text{OH})_2$ bond length.

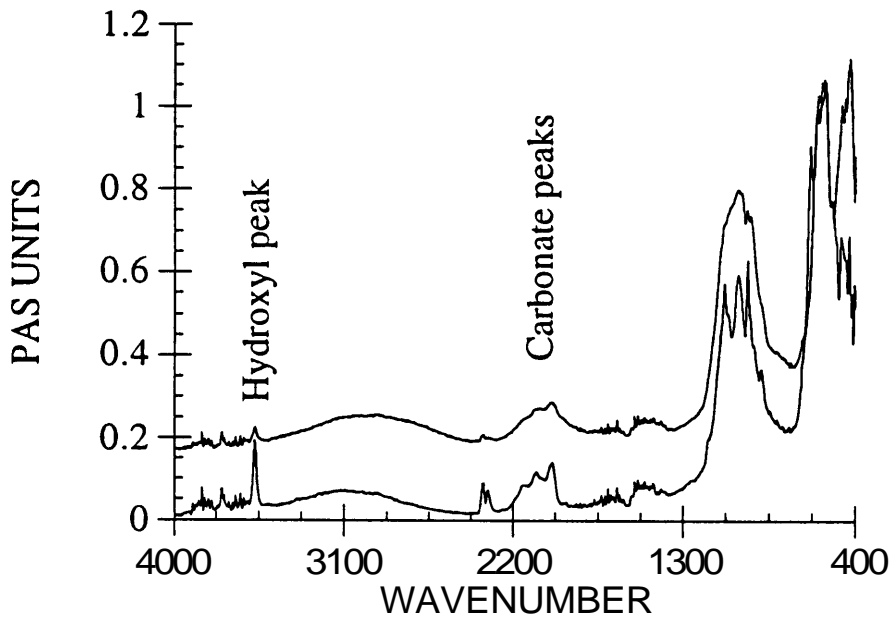


Figure 4. **Infra** red spectra for HA, before (lower) and after (upper) flame spraying.

Labelled in Figure 4 are the peaks of interest, the hydroxyl peaks and the carbonate peaks. It can be seen that the starting powder contains significant amounts of carbonate in the structure. The hydroxyl peaks are also present in the starting powder as expected. Following spraying, the carbonate peaks show a reduction in intensity, indicating loss from the structure and furthermore, the hydroxyl peaks also show a reduction in intensity. Figure 5, shows an FTIR analysis of the precursor powder before and after plasma spraying. This again shows a disappearance of both the hydroxyl peaks and also loss of the **carbonate** groups. Thus the FTIR results confirm the conclusions drawn from the data calculated from Rietveld analysis.

CONCLUSIONS.

The thermal spraying induces considerable changes in the structure of HA, detected by XRD in conjunction with FTIR. XRD analysis is able to detect subtle changes in the structure of the sprayed HA, with distortion induced by the extremely high particle velocities used. Small chemical changes were also detected and **confirmed** by the use of FTIR analysis.

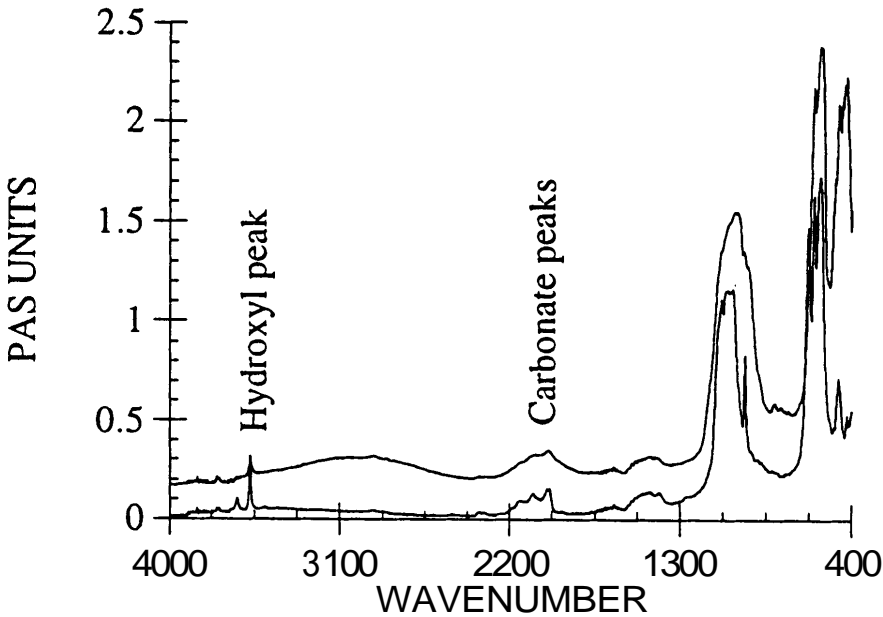


Figure 5. **Infra** red spectra for HA, before (lower) and after (upper) plasma spraying.

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