



## QUANTITATIVE PHASE ANALYSIS OF CERAMIC COATINGS

### INTRODUCTION

Medical and dental implants employing hydroxylapatite (HA) plasma-sprayed coatings on a structural substrate are widely used in orthopedic and dental applications. Both the crystallinity of the coating and the presence of contaminant phases are believed to affect the biological response to the ceramic coating. The potential for variation in the plasma-spraying process has led to the need to accurately characterize the crystallographic properties of the coatings after deposition (ASTM F1185-88).

During the plasma-spray process, powdered HA is deposited on a substrate at elevated temperatures in a controlled atmosphere. Variation in either the plasma-spray conditions or in the composition of the starting HA powder can affect the crystallinity of the coating and result in the occurrence of one or more contaminant phases:  $\alpha$  or  $\beta$  forms of tricalcium phosphate (TCP),  $\text{Ca}_3(\text{PO}_4)_2$  calcium oxide, CaO; or  $\beta$ -calcium pyrophosphate,  $\text{Ca}_2\text{P}_2\text{O}_7$ .

Lambda Research has developed a rigorous quantitative phase analysis method capable of quantifying any or all of the contaminate phases and determining the percent crystallinity from the total fraction of crystalline phases present in the sample. The method has been described in detail at the ASTM Symposium on Characterization of Performance of Calcium Phosphate Coatings for Implants and will be published in the proceedings of the meeting. [1] Copies of the paper are available.

The software eliminates the inherent subjectivity of manual methods and allows quantification by any method with introduction of the "packing" factor to provide for less than theoretical density in the samples investigated.

There are three primary methods [2, 3] of x-ray diffraction quantitative analysis: 1) direct comparison, 2) internal standard, and 3) external standard. The first method requires advance knowledge of the sample crystallinity, which may not be known for plasma-sprayed coatings. The internal standard method can be applied to partially amorphous samples, but is only applicable to powdered samples to which a measured amount of a standard can be added.

The external standard method was selected because it is applicable to partially amorphous multiphase solid samples. The diffraction pattern is obtained non-destructively from the coating surface and compared to an external standard. The percent crystallinity of the multiphase coatings is taken to be the sum of all crystalline fractions present. The balance is the remaining amorphous fraction.

### THEORETICAL DEVELOPMENT FOR THE EXTERNAL STANDARD METHOD

The packing factor is defined for a mixture as the ratio of the mechanical density of the mixture,  $\rho_m$ , to the weighted average x-ray (theoretical maximum) density,  $\rho_{xm}$ .

$$P = \frac{\rho_m}{\rho_{xm}}$$

For a powder samples placed in an unpolarized x-ray beam, the integrated intensity of the (hkl) peak of the  $i^{\text{th}}$  phase is proportional to the power per unit length of the diffraction circle at a distance R from the sample, [4].

$$I_i^{hkl} \propto \left[ \frac{I_o}{16\pi R} \left( \frac{e^4}{m_e^2 c^4} \right) \frac{\lambda^3 M_{hkl} F_T^2}{V_a^2} (LP) \right] V_i \quad (1)$$

where:

- $I_o$  = intensity of the incident x-ray beam
- R = radius of the goniometer
- e = electron charge
- $m_e$  = mass of electron
- $\lambda$  = wavelength of radiation used
- $M_{hkl}$  = multiplicity factor
- $F_T$  = structure factor
- $V_a$  = unit cell volume
- LP = Lorentz Polarization Factor
- $V_i$  = effective diffracting volume

For a given reflection from a given phase I, the expression for the integrated diffraction intensity reduces to:

$$I_i^{hkl} = K_i^{hkl} V_i \quad (2)$$

where  $K_i^{hkl}$  is a constant for a given phase I and (hkl) reflection and is proportional to the quantity in square brackets in (1), and  $V_i$  is the effective volume of phase I in the mixture.



The effective volume can be expressed in terms of the volume fraction of the  $i^{\text{th}}$  component for an infinitely thick sample as:

$$V_i = \frac{A_o P C_i}{2\mu_m} \quad (3)$$

assuming that the sample is homogeneous so that the packing factor, P, and the volume fraction,  $C_i$ , are constant with depth.

Substituting (3) into (2) and including all constants in  $K_i^{hkl}$ , the diffracted intensity of a reflection (hkl) due to a phase i of volume fraction  $C_i$  in a mixture is given by:

$$I_i^{hkl} = \frac{K_i^{hkl} A_o P C_i}{\mu_m} \quad (4)$$

or, dropping the hkl superscript, the intensity in terms of the weight fraction  $W_i$  is

$$I_i = \frac{K_i A_o P}{X_m \rho_i} \cdot W_i \quad (5)$$

where  $X_m$  and  $\rho_i$  are the mass absorption coefficient of the mixture and density of the  $i^{\text{th}}$  phase.

If diffraction data are collected for the mixture and the pure phase under identical conditions, then the ratio of the intensity measured for the unknown and the pure samples will be:

$$\frac{I_i}{I_i^p} = W_i \frac{X_i P}{X_m P^p} \quad (6)$$

where  $I_i^p$  and  $P^p$  are the diffracted intensity and packing factor of the pure phase.

Solving for the weight fraction,  $W_i$ ,

$$W_i = \frac{I_i}{I_i^p} \cdot \frac{X_m}{X_i} \cdot \frac{P^p}{P} \quad (7)$$

Equation (7) is the working equation for the external standard method. Measurements are made of the integrated intensities of the same diffraction peaks from phase i in the mixture and for a pure sample to obtain the integrated intensities,  $I_i$  and  $I_i^p$ . The weight fraction,  $W_i$ , is calculated from the ratio for intensities.

The complexity of the analysis of multiple phases in a mixture can be greatly reduced if all of the pure phase peak intensities are referenced to a single standard. The reference intensity ratio (RIR) for a phase i has been defined as:

$$RIR_i = \frac{I_i}{I_s} \quad (8)$$

where  $I_i$  is the intensity of the 100% peak of phase i, and  $I_s$  is the intensity of the 100% peak of reference phase s, taken by convention to be corundum in a 50:50 mixture by weight.

The integrated intensity of any diffraction peak from a phase with arbitrary Miller indices (hkl) can be expressed as a fraction of the intensity of the strongest diffraction peak,  $I_i^p$ , of that phase by the relative intensity. Then,

$$W_i = \left[ \frac{I_i^{hkl}}{I_i^{REL}} \right] \cdot \left[ \frac{X_m}{X_s} \right] \cdot \left[ \frac{P_s^p}{P} \right] \cdot \left[ \frac{1}{I_s^p \cdot RIR_i} \right] \quad (9)$$

where  $I_i^{hkl}$  is the integrated intensity of (hkl) reflection for phase i, and  $I_i^{REL}$  is the relative intensity of (hkl) reflection phase i.

If the RIR values for all components in a mixture are known relative to the reference phase, s, a single determination of  $I_s^p$  in conjunction with the measurement of  $I_i^{hkl}$ , under identical experimental conditions, allows solution of the entire system of weight fractions,  $W_i$ . The use of RIR values is much faster and less prone to error than the determination of all weight fractions from equation (7), which would require reference to the integrated intensities of the 100% peak of each phase in its pure form. The only disadvantage to the method is that the packing factor of the standard and the sample must either be equal or known.

## EXPERIMENTAL METHOD

### RIR Values

The RIR values were determined for each crystalline phase which may occur in the ceramic coatings using commercially available pure samples of HA,  $\beta$ -TCP and CaO. The RIR value for  $\alpha$ -TCP was obtained from a mixture of  $\alpha$ - and  $\beta$ -TCP after quantification for the amount of  $\beta$ -TCP in the mixture. Alpha-quartz was selected as a suitable internal standard for the determination of the RIR values because peak interference was minimal and a fully dense sample of fine grained

quartz (novaculite) was available as a stable external standard. Several repeat diffraction patterns were obtained from which the integrated intensities of the strongest peak of each phase could be measured. Between each run, the mixture was remixed and packed to reduce any error due to inhomogeneity during a single run.

**Data Reduction Strategy**

Known mixtures of HA,  $\alpha$ -TCP,  $\beta$ -TCP, and CaO were prepared for the purpose of developing a data collection and reduction strategy and for eventually testing the validity of the RIR values and relative intensities necessary for the calculation. A diffraction pattern for known mixtures containing nominally 70% HA is shown in Figure 1.

Actual plasma -sprayed coupons have varying degrees of a glassy amorphous phase characterized by the broad amorphous "hump" near 29 deg. as seen in Figure 2. The amorphous background was approximated locally by fitting Pearson VII function profiles to the background and the neighboring peaks to deconvolute the overlapping peaks as shown. Regions of true background were selected for any combination of crystalline and amorphous phases. After careful study of the complex diffraction patterns of the known mixtures and actual coating samples, a data reduction strategy was developed for acquiring the integrated intensities necessary to quantify mixtures of  $\alpha$ -TCP,  $\beta$ -TCP, CaO, and HA. Provision is made for interference effects from  $\beta$ -Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, although this phase is not quantified because RIR values have yet to be determined.

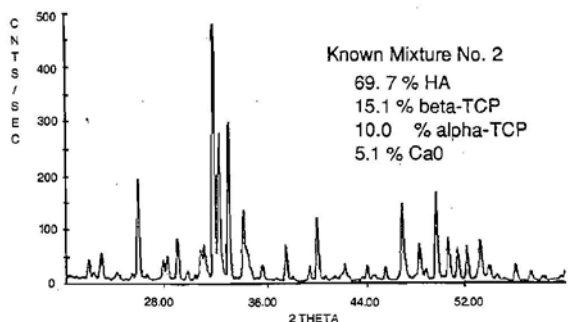


FIG. 1 – Diffraction pattern, known mixture No. 2, nominally 70% HA

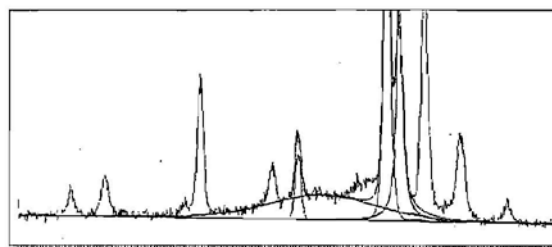


FIG. 2 – Pearson VII function deconvolution of amorphous hump and diffraction peaks in a plasma-sprayed coating

**Known Mixture Tests**

The method and the experimentally determined constant were tested by reducing the external standard method to a direct comparison method by assuming 100% crystallinity, and performing quantitative analysis of the fully crystalline known mixtures prepared by weight from the pure powders. One mixture containing nominally 85% HA, 10%  $\beta$ -TCP, 3%  $\alpha$ -TCP, and 2% CaO was prepared to closely simulate the composition of actual plasma-sprayed coatings containing small amounts of contaminants in a relatively pure HA matrix. Repeat measurements were made, rehomogenizing the sample between each measurement. The results, presented in Table 1, demonstrate both the accuracy and the repeatability of the method using the data reduction strategy on well-crystallized samples. Repeatability within one weight percent was observed for the major HA phase, and within three weight percent for the minor  $\alpha$ -TCP and  $\beta$ -TCP phases. The average weight fraction obtained for each phase was within three weight percent of the actual measured values for each phase.

The high relative error in determination of the individual  $\alpha$ -TCP and  $\beta$ -TCP fractions is due to compounding of error in separation of the contributions of each phase to the 30.5 to 31.6 deg. integration range when only small quantities of the phase are present. The combine diffractions of  $\alpha$ -TCP and  $\beta$ -TCP phases are 13.0±0.6 weight percent. The actual combined fraction is 13.1 percent.

	% HA	% $\beta$ -TCP	% $\alpha$ -TCP	%( $\alpha$ + $\beta$ )TCP	% CaO
1	87.1	8.5	4.2	12.7	0.2
2	86.2	10.5	3.1	13.6	0.2
3	86.6	13.0	0.4	13.4	0.05
4	87.8	12.0	0.2	12.2	0.08
5	87.1	6.4	6.1	12.5	0.3
6	86.1	12.6	1.3	13.9	0.08
Avg	86.8±0.6	10.5±2.6	2.5±2.3	13.0±0.6	0.2±0.1
Actual	84.9	10.1	3.0	13.1	2.0

TABLE 1 – Repeatability test on a known mixture.



	% HA	% β-TCP	% α-TCP	% (α+β)TCP	% CaO
1	87.1	8.5	4.2	12.7	0.2
2	86.2	10.5	3.1	13.6	0.2
3	86.6	13.0	0.4	13.4	0.05
4	87.8	12.0	0.2	12.2	0.08
5	87.1	6.4	6.1	12.5	0.3
6	86.1	12.6	1.3	13.9	0.08
Avg	86.8±0.6	10.5±2.6	2.5±2.3	13.0±0.6	0.2±0.1
Actual	84.9	10.1	3.0	13.1	2.0

TABLE 1 – Repeatability test on a known mixture.

The method was applied to a study of nine HA plasma-sprayed coating samples from a variety of sources chosen to represent a wide range of crystallinity. The results were presented in Table 2. The crystallinity of the samples varied from 37% to 84%. The samples were found to contain from 1.6 to 58% β-TCP, from 0.0 to 1.9% α-TCP and a maximum of 0.4% CaO.

The method has been shown to provide both reproducibility and accuracy on the order of ± 2% for the HA and CaP phases and for the combined alpha and beta TCP on well-crystallized known mixtures. Accuracy on the order of ± 3 to 5% is typical for plasma-sprayed coating containing up to 50% amorphous material.

Quantitative analysis techniques have been developed at lambda Research for a variety of ceramic and metallic systems, using both internal and external standard techniques and direct comparison methods, depending on the nature of the specimen and phases to be analyzed. The automation and freedom from the subjectivity of annual peak and background fitting allow relatively inexpensive and accurate phase analysis of complex systems with one or two day delivers, once the technique has been established.

If you have interest in quantitative analysis, please contact our laboratory to discuss your application.

## REFERENCES:

- [1] Prevey, P.S. and Rothwell, R.J., "X-ray Diffraction Characterization of Percent Crystallinity and Contaminants in Plasma-Sprayed Hydroxylapatite Coatings," *Characterization and Performance of Calcium Phosphate Coatings for Implants*, ASTM Syp 1196, Emanuel Horowitz, and Jack E. Parr, Eds., American Society for Testing and Materials, Philadelphia, 1993.
- [2] Klug, H.P. and Alexander, L.E., *X-ray Diffraction Procedures*, 2nd ed., John Wiley & sons, New York, 1974, pp 541-554.
- [3] Cullity, B.D., *Elements of X-ray Diffraction*, 2nd ed., Addison-Wesley, Reading, Mass, 1978, pp 409-417.
- [4] Warren, B.E., *X-ray Diffraction*, Addison-Wesley, Reading, Mass., 1968, p 49.
- [5] Bish, D.L. and Post, J.E., "Modern Powder Diffraction", Review in Mineralogy Vol. 20, 1989, pp 106, 109, The Mineralogical Society of America.

## NEW X-RAY FLUORESCENCE TECHNIQUE

An x-ray fluorescence technique has been developed for the determination of the Ca/P molar ratio in hydroxylapatite powders on coatings. The method is accurate to ± 1% and is calibrated with gravimetric standards.

## NEW LABS FULLY ACCREDITED

Moving into our expanded facilities has necessitated a complete review of our A2LA accreditation status and GE 8-400. We are proud to report that our new laboratories meet or exceed all standards for A2LA accreditation and on-site audits, and our 8-400 certification has been expanded to cover retained austenite, % volume, Laue single crystal orientation, qualitative and quantitative phase analysis. Copies of our updated certification status are available on request.

