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Crystallinity of Hydroxyapatite Coatings for Implant Application

Materials Science & Technology

C. R. Bradbury
Empa Feuerwerkerstrasse 39, 3602 Thun

K. Maniura, S. Lischer, A. Grubelnik, & Q. Ren
Empa, Lerchenfeldstrasse 5, 9014, St. Gallen

P. Gruner
Medicoat AG, Gewerbe Nord, 5506, Mägenwil

A. Roques
Finsbury Orthopedics, Randalls Road, KT22 7BA, Surry

Introduction

A common feature of implants is to modify the surface to promote osseointegration. This has significant benefits for the patient with faster recovery times.

One of the best surface modification used today is the application of Hydroxyapatite (HA) onto the surfaces that require osseointegration. The HA ceramic coating adheres strongly to the metal implant surface and has a chemical composition similar to that of bone. This HA coating of calcium and phosphate helps to promote fast bone growth and forms a secure bond to the implant.

To assure the compositional purity and adhesion of the HA coating, Vacuum Plasma Spraying (VPS) is a commonly used method to apply such coatings. This method uses a high energy plasma to partially melt the HA particles and propel them at high velocity at the implant surface to form a continuous HA ceramic film on the surface.

Design of Experiment

Design of Experiment (DoE) is a statistical approach to setting up and analyse experiments. It has the advantage of reducing the number of required experiments to achieve the same statistically valid result. The crystallinity of the HA coatings was investigated using a 3^2 full factorial design with a centre point. All experimental data were analyzed using a statistical package called 'Design Expert'. The factors varied were;

1) Stand off distance (200mm, 350mm)
2) Plasma Energy (21.5 kW, 29.6 kW)
3) Chamber Vacuum (350 mbar, 150 mbar)

The experimental design allows to determine the particular factors which have the highest bearing on the crystallinity. The experimental design space is graphically represented in Figure 1.

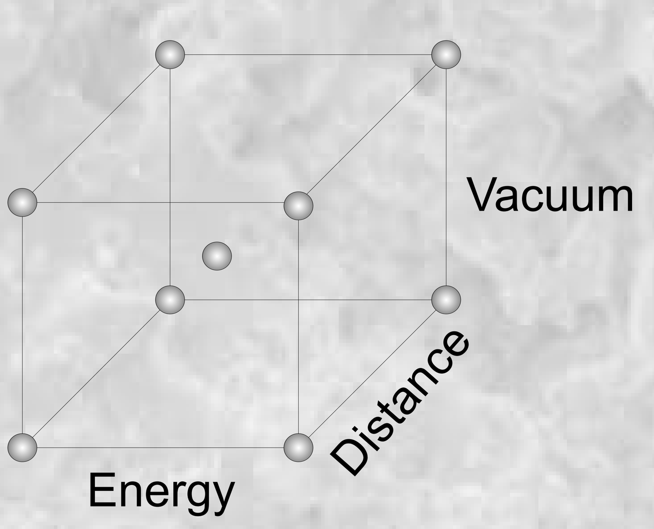

Figure 1 : A graphical representation of the experimental space as defined by Design of Experiment.

X ray Diffraction

The X-ray Diffraction (XRD) is a useful and versatile tool to assess the spraying of HA coatings. XRD allows the crystallinity to be measured by the reduction in intensity of the diffraction peaks and also the quantity of impurities to be quantified. The crystallinity was measured on the, as sprayed, coatings and for the impure phases, HA coating were heated to 1000°C for 3 hours to remove the amorphous phase. The Rietveld refinement was used to fit the diffraction pattern and determine the quantity of the foreign phases in the HA coatings.

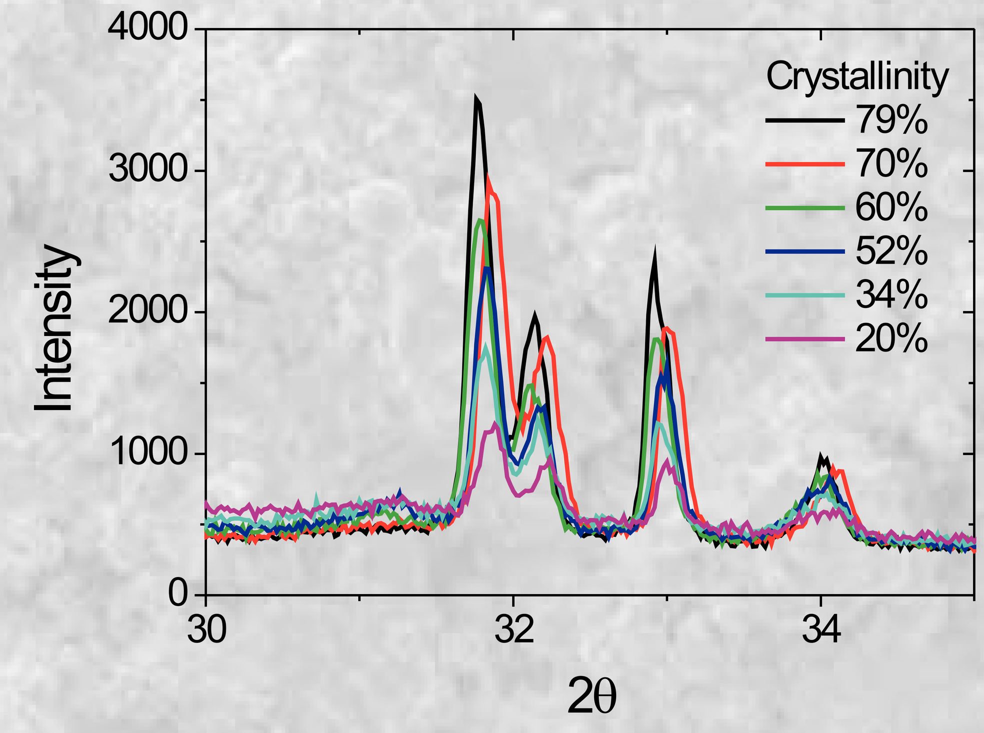

Figure 2 : XRD patterns of the HA coatings with different crystallinity. The lower crystallinity results in a decrease in the intensity of the diffraction peaks.

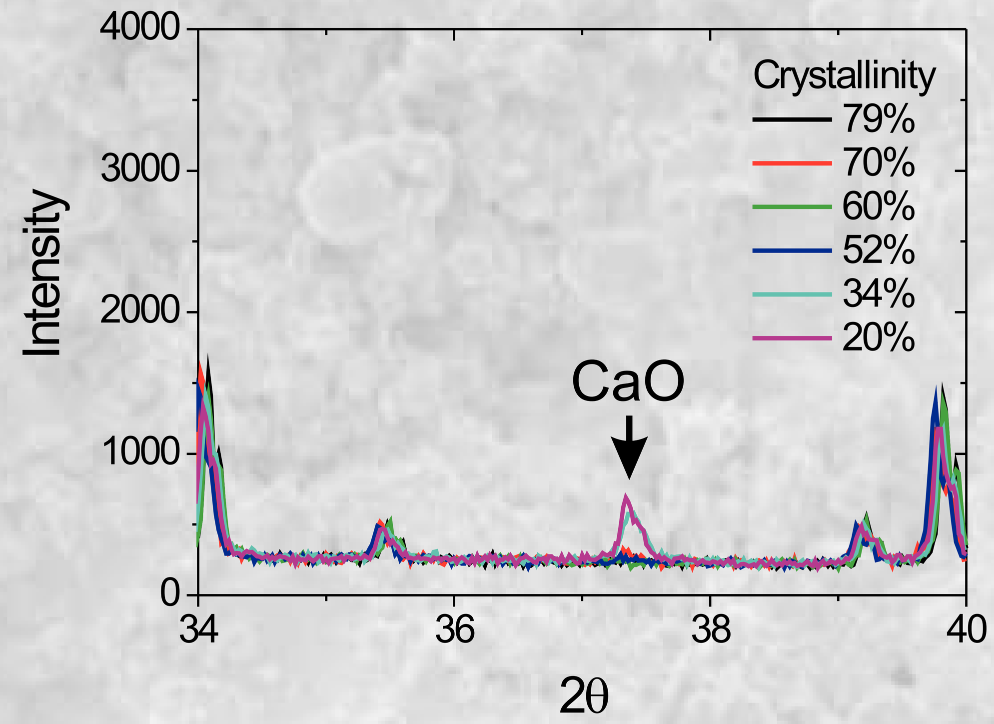

Figure 3 : XRD patterns of the HA coatings with different crystallinity. The CaO impurity has been highlighted to illustrate the impurity at low crystallinity.

Dissolution Experiments

The dissolution of HA coatings has important implications for the application of implants. The dissolution of the HA coating relates to impurities such as tricalcium phosphate and calcium oxide. Also the amount of the amorphous phase HA has a significant contribution to the dissolution of the HA coating. The dissolution of HA coatings with three different crystallinity was measured with a calcium selective electrode - ASTM F1926-03. Figure 4 shows the amount of calcium that has dissolved from the HA coating over time. The rate of dissolution for the HA coating followed the crystallinity, where the lowest crystallinity showed the highest rate of dissolution, while the highest crystallinity was the slowest. The amount of the calcium liberated after 21 days becomes relatively constant at 0.5 $mg.cm^{-2}$. Also the crystallinity of all samples measured after dissolution converge to the same crystallinity.

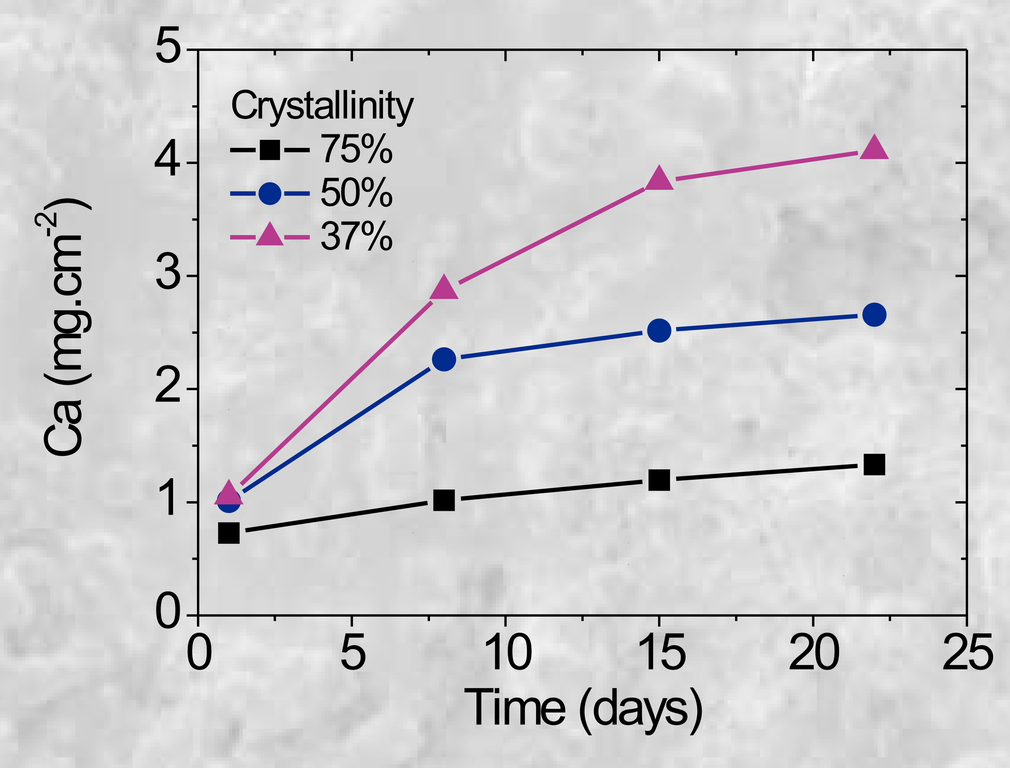

Figure 4 : Dissolution of the HA coatings over time. The dissolution was measured with a calcium selective electrode according to ASTM F1926-03.

Mechanical Properties

The surface roughness was measured by optical profiler for the HA coatings of different crystallinity (Figure 5). This Average Surface Roughness (R_{SA}) decreased when the crystallinity decreased below 60%. The DoE analysis determined the major factor controlling the surface roughness was the vacuum in the VPS chamber

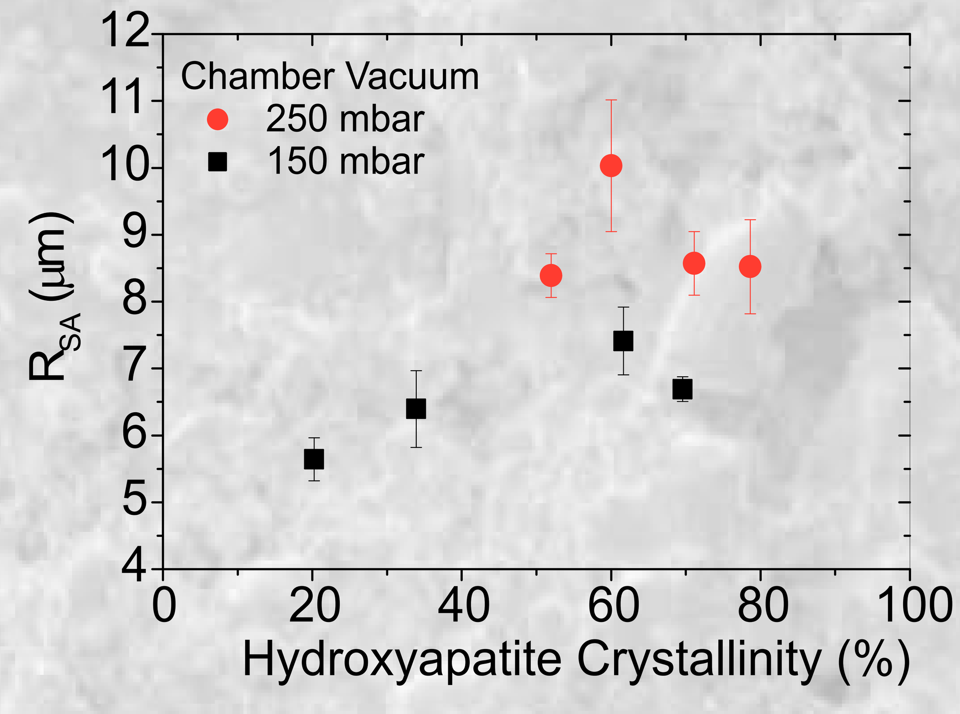

Figure 5 : The Average Surface Roughness (R_{SA}) measured by an optical profiler versus crystallinity at two chamber pressures.

The HA coatings were subjected to shear tests based on DIN EN15340. This involves measuring the force required to remove the HA coating 125µm from the surface (Figure 6). The shear force increases with the crystallinity and the DoE analysis determined the controlling factor was the energy of the plasma used during spraying. This effect would also correlate with the porosity of the coatings. The increased shear force correlates to an improved adhesion of the coating to the surface. The 20% crystalline sample was brittle and resulted in a large variation in shear strength. HA coatings below 20% crystallinity would have potential failure problems if used for implants.

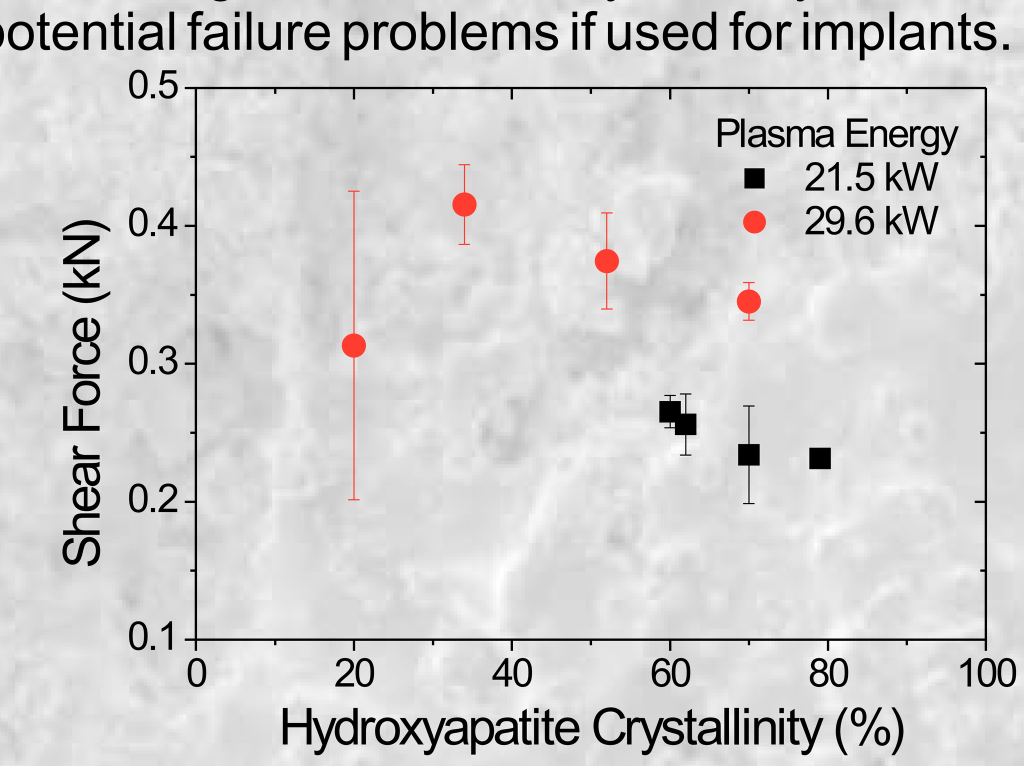

Figure 6 : The shear forces required to remove 125µm of the HA coating versus crystallinity.

Conclusions

The application of the DoE with a 3^2 full factorial design allows the crystallinity of the HA coatings to be controlled. The HA coatings crystallinity and impurities were measured by XRD. The dissolution of the HA coating was faster with lower crystallinity. Also after dissolution the amorphous phase was removed resulting in an increase in crystallinity. The mechanical properties showed a decrease in R_{SA} and increase in shear strength with decreasing crystallinity.

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