

NANO-MECHANICAL PROPERTIES OF HYDROXYAPATITE COATINGS WITH A FOCUS ON THE SINGLE SOLIDIFIED DROPLET

K.A. Gross and S. Saber-Samandari

¹ *Department of Mechanical and Manufacturing Engineering, University of Melbourne, VIC 3010, Australia*

*email: kgross@unimelb.edu.au

ABSTRACT

Hydroxyapatite (HAp) is a common implant material choice for orthopaedic implants and is mostly used as a coating to improve the biocompatibility of implants and stimulate tissue growth. This is a desirable material for implants, but the thermal instability requires strict control of the processing conditions to produce a crystalline coating. A coating with well molten particles has been produced from flattened solidified droplets. This development has allowed further investigation of the coating surface with nanoindentation, profilometry and electron microscopy. Instrumented indentation testing, also known as depth-sensing indentation or nanoindentation, was used to gather information on the hardness and elastic modulus. It was found that the surface topography can lead to elevated values of the hardness and elastic modulus. The micromechanical properties will be higher when conducted on a sloped surface. It is recommended that any micromechanical data from a thermally sprayed coating be accompanied with topographic map of the flattened solidified droplet.

KEYWORDS: hydroxyapatite, thermal spraying, solidified flattened droplet, nanoindentation, hardness, elastic modulus.

INTRODUCTION

Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is widely accepted a biocompatible material, which resembles the mineral component of bone and teeth [1, 2]. A combination of amorphous and crystalline phases results from the spraying process leading to variable solubility, dictated by the amount of the amorphous phase. While some manufacturers prefer a more crystalline coating, others prefer a faster dissolving coating. The advantage lies in the supply of calcium and phosphate ions that stimulate bone tissue growth towards the surface. A balance must be reached between the solubility and time that the coating is required on the implant surface.

The use of a coating on a metallic implant overcomes the brittleness, poor impact resistance and low tensile strength [3]. The ideal scenario is established whereby metal ion release is reduced by the coating and a bioactive surface is presented to the body [1, 4, 5]. This is an old strategy, but one that still plays an important role for permanent implants such as hip prostheses.

Thermal processing of hydroxyapatite is challenging. The complexity of plasma processing requires a high degree of skill to ensure that the desired product is deposited. Every particle travels through the heat source and is subjected to a unique processing environment dictated by the thermo-kinetic history of the particle. Several approaches are being used to provide a reproducible environment. Axial powder delivery versus transverse delivery provides injection directly into the heat source. A narrow particle size distribution provides each particle with a comparable heat history. Air plasma spraying causes turbulence that introduces cold pockets into the spray stream. Turbulence can be reduced by plasma spraying in a vacuum or with a flame.

Historically, a solidified deposited droplet would contain an amorphous phase in addition to hydroxyapatite, when air plasma sprayed. The control of particle melting leads the way to a predictable solidified droplet microstructures. Analysis of the solidified droplet requires an array of new microcharacterization and microtesting techniques. Electron microscopy has long been a useful technique to visually identify the appearance of the deposit. Micro-Raman now provides the ability to assess the

chemical bonding within each flattened droplet. Micro-X-ray diffraction, available at synchrotron light sources, provides an analysis of the crystal structure. Nanoindentation is a new capability for assessing mechanical properties at the 1-10 micron level. These tools can provide a unique insight into the quality of each deposited droplet.

The processing conditions will be optimized to completely melt the particles and create well-flattened solidified droplets, suitable for micromechanical testing. Instrumented indentation testing, also known as depth-sensing indentation or nanoindentation, is ideally suited for measuring hardness and elastic modulus of thin films/coatings [6, 7]. Other investigators have assessed the mechanical properties of the hydroxyapatite coating using nanoindentation [8-11] but, there are no reports on single splats. This study will investigate the mechanical properties of HAp coatings with a focus on the single splat.

METHODS

Coating Production

Spray dried hydroxyapatite supplied by CAM Implants was dry sieved to produce a powder size of 60-80 microns. This powder was flame sprayed with a Metco 6P II gun at a spray distance of 12.5 cm after preheating the grit blasted rectangular (2 cm x 2 cm) titanium substrate. A slow traverse speed was selected to decrease the cooling rate of the solidifying droplet and aid the crystallization of the droplet during solidification. The resulting microstructure of the solidified droplet was an $\langle 001 \rangle$ oriented crystal structure as confirmed by X-ray diffraction (not shown here). The coating conditions were not optimized to decrease the crack size, but to ensure a crystalline coating.

Coating Characterization

Coatings were sputter coated with gold and then examined with a XL30 Philips scanning electron microscope (SEM) at an accelerating voltage of 20 keV to confirm a well spread solidified droplet. Micro-Raman was used to ascertain the bonding within the solidified droplet.

Mapping the Topography

The undulations of the solidified droplet are difficult to ascertain with a scanning electron microscopy and so the nanoindenter was used to determine the topography of the individual solidified droplet. The nanoindenter was rastered across the surface using a

load of 0.05 mN where each traverse was separated by 0.5 micron. This resolution was selected to determine the topography of a slice of the solidified droplet and not to seek further information about the indentation location.

Nanoindentation

A series of indentations, exactly 90 indentations, were made on top of a single droplet in the matrix of 10 x 9 to cover the most portion of the droplet. Indentations were separated by a distance of 8 microns. In this study, hardness and elastic modulus were determined using the method of Oliver and Pharr [7]. The indentations were conducted using the load control mode, i.e. a loading process was applied to a maximum of 30 mN and then reversed for a pre-set peak load. The initial load was preset to 0.01 mN and a loading/unloading rate was 2 mN/S. A dwell time, the peak load-holding period, was set to 5 seconds and a holding time of 30s at 90% of the unload was selected for thermal drift correction.

RESULTS AND DISCUSSION

Solidified Droplet Topography

The outside of the particle was well molten as shown by the smooth appearance of the solidified droplet, Fig. 1. The droplet shape indicates that the droplet spread without forming any stringers and satellite droplets. This confirms that spreading occurred above the critical temperature under which splashing occurs.

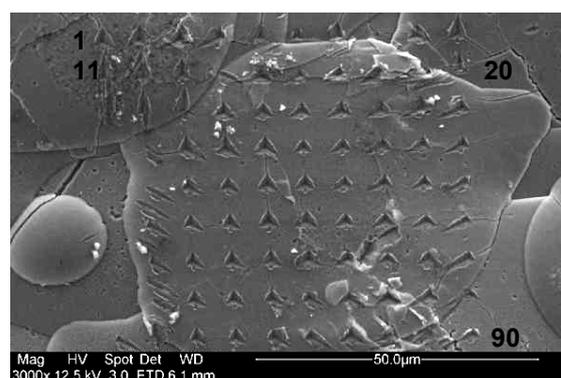


Fig. 1: An indented flattened solidified droplet with reference to specific indentations.

The variation in the height across the droplet is difficult to ascertain from the SEM micrograph, and so a topographic image provided a closer insight. Figure 2 shows that the traverse over the 60 micron flattened droplet led to a 4 micron vertical displacement from the side of the droplet to the

centre. The centre area is only about 40 micron wide where the vertical displacement varies by less than 0.5 micron. It is difficult to determine whether this vertical displacement is associated with the waviness of the underlying coating, or whether this droplet has not completely flattened. The assessment of the droplet flattening would be more easily ascertained by depositing the droplet onto a polished flat surface.

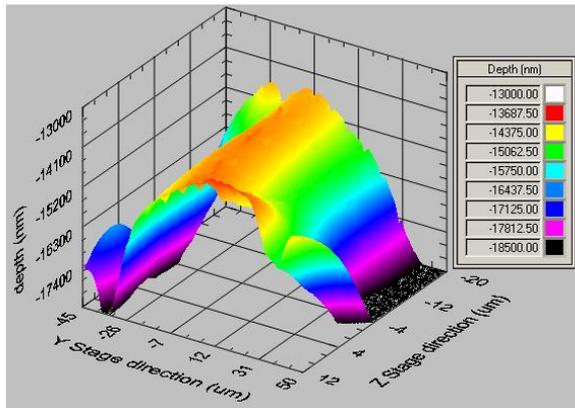


Fig. 2: Topographic slice of the flattened droplet.

Mechanical Properties of a Flattened Droplet

Values of hardness and elastic modulus were obtained from the grid of indentations. The separate indentations were labelled with a number, for ease of reference to the flattened solidified droplet, Fig. 1. It can be seen that the elastic modulus has a base value of about 100 GPa, a value representative of hydroxyapatite, Fig. 3. The elastic modulus appears to peak periodically. This is attributed to the indentations on the sloped component of the solidified droplet resulting in smaller indentations.

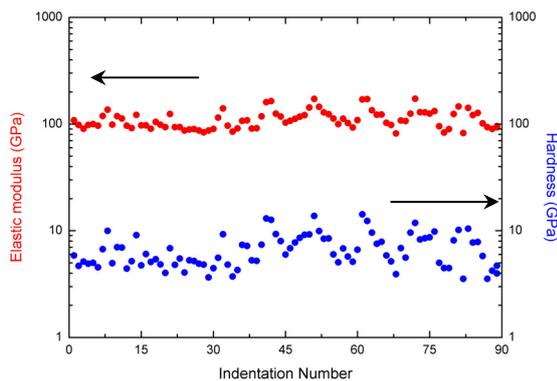


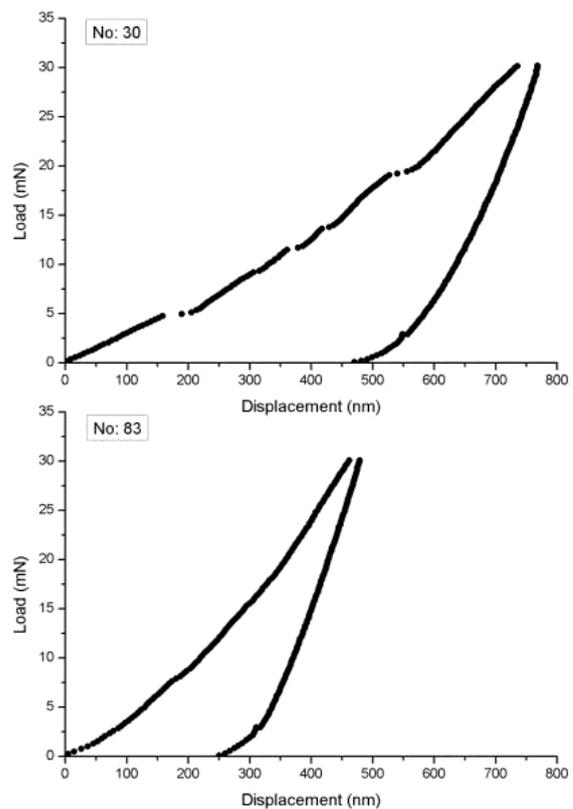
Fig. 3: Hardness and elastic modulus from indentations on the solidified flattened droplet.

Hardness follows the same pattern as observed for the elastic modulus. The hardness of the hydroxyapatite coating is about 7 GPa, Fig. 3, in agreement with hardness measured from a polished sintered apatite.

The higher hardness values are attributed to indentations on the inclined surface.

The variation in the hardness of the single flattened solidified droplet is attributed to the microstructure. For example, an indentation produced close to an existing crack results in a hardness of 4.4 GPa. This may be due to the ease of material movement close to a crack or from a tensile residual stress. The origin of the lower hardness value would require a more detailed examination using other techniques. Closer examination of the loading curve for indentation number 30 shows a sudden displacement, Fig. 4a. This behaviour suggests the growth of microcracks during loading.

Where an indentation is made on a sloped section, the smaller indentation area results in a higher hardness. The value reported for indentation number 83 is 12.6 GPa, Fig. 4b. The higher value occurs from the larger surface slope, compared to an indentation on a flat surface, indentation number 57, Fig. 4c.



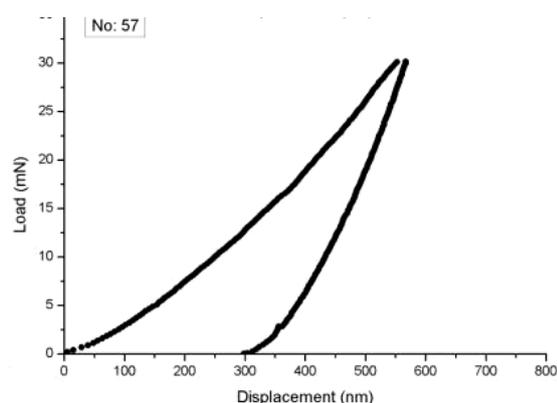


Fig. 4: Loading-unloading curves for an indentation (a) adjacent to a crack (indentation # 30), (b) on a sloped section (indentation # 83) and (c) on the top flat surface (indentation # 57).

Hardness is a more sensitive tool for the examination of micromechanical properties. A variation can arise from a different crystal structure (or chemical phase), grain size, crystal orientation or residual stress. The contribution of these individual factors cannot be determined from this study and more detailed information is required from other micro-characterization and testing techniques.

These results suggest that it is imperative to obtain a flat surface perpendicular to the axis of the nanoindenter to obtain a representative value of hardness. The formation of well flattened solidified droplet in a hydroxyapatite has enabled the measurement of micromechanical properties from the surface of a coating. Any report on the micromechanical properties of a surface should be accompanied with topographic information of the material surface. Such flat surfaces will be achievable with control of the droplet temperature and velocity before impact and the solidifying conditions at the substrate.

Conclusions

A grid of indentations over a flattened solidified droplet has shown that the angle of the surface must be well controlled to avoid a higher elastic modulus and hardness. A report on micromechanical properties of thermally sprayed particles must be accompanied with a topography map.

References

1. K. de Groot et al., "Plasma sprayed coatings of hydroxylapatite", *J. Biomed. Mater. Res.*, vol [21], 12, (1987) 1375-1381.
2. L.L. Hench, "Bioceramics: From concept to clinic", *J. Amer. Cer. Soc.*, Vol [74], (1991), 1487-1510.
3. M. Jarcho, "Calcium phosphate ceramics as hard tissue prosthetics". *Clin. Orthop.*, Vol [157], (1981) 259-279.
4. C.C. Berndt et al. "Thermal spraying for bioceramic applications", *Materials Forum*, Vol [14], (1990), 161-173.
5. Y.C. Tsui, C. Doyle, and T.W. Clyne, "Plasma sprayed hydroxyapatite coatings on titanium substrates Part I: Mechanical properties and residual stress levels", *Biomaterials*, Vol [19], 22, (1998), 2015-29.
6. M.F. Doerner, M.F., D.S. Gardner, and W.D. Nix, "Plastic properties of thin films on substrates as measured by submicron indentation hardness and substrate curvature techniques", *Materials Research*, Vol [1], (1986), 845-852.
7. W.C. Oliver and G.M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments", *Materials Research*, Vol [7], (1992), 1564-1583.
8. R.R. Kumar and M. Wang, "Modulus and hardness evaluations of sintered bioceramic powders and functionally graded bioactive composites by nano-indentation technique", *Materials Science & Engineering A*, Vol [A338], (2002), 230-236.
9. H. Pelletier, et al., "Mechanical properties of pulsed laser-deposited hydroxyapatite thin film implanted at high energy with N and Ar ions", *Nuclear Instruments and Methods in Physics Research B*, Vol [216], (2004), 269-274.
10. V. Nelea, et al., "High-energy ion beam implantation of hydroxyapatite thin films grown on TiN and ZrO₂ inter-layers by pulsed laser deposition", *Thin Solid Films*, Vol [453], (2004), 208-214.
11. P.S. Uskokovic, et al., "Micromechanical properties of a hydroxyapatite/poly-l-lactide biocomposites using nanoindentation and modulus mapping", *European Ceramic Society*, (2006), **In Press, Corrected Proof**.
12. C.M. Lepienski, et al., "Factors limiting the measurement of residual stresses in thin films by nanoindentation", *Thin Solid Films*, Vol [447-448], (2004), 251-257.
13. R. Saha, and W.D. Nix, "Effects of the substrate on the determination of thin film mechanical properties by nanoindentation", *Acta Materialia*, Vol [50], 1, (2002), 23-38.