

# Bio-ceramic Composite Coatings by Cold Spray Technology

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## Abstract

Bioceramics such as hydroxyapatite (HAP) have been conventionally deposited by plasma spray technique. However, due to the inherent high temperature in the plasma, deleterious effects such as evaporation, phase alteration, residual stress, debonding, and gas release etc., commonly occur in these coatings. This paper presents a novel approach to deposit bioceramic coatings at temperatures well below their melting point by cold spray, using composite powders of titanium and HAP. The influence of the process parameters, powder type as well as HAP to titanium ratio has been investigated. It was observed that dense composite coatings, containing up to 30% HAP can be deposited by this technique. Due to widely differing physical characteristics between the powders, as well as the adhesion mechanism, the HAP content in the deposit was a few percent lower than the powder mixture. XRD analysis indicated that the phase composition of the HAP in the deposit was identical to that of the powder. Further, the bond strength of the deposit was comparable/better to that of the plasma sprayed HAP. Coatings deposited using this process hold tremendous potential for improving bone integration of a wide range of dental and orthopedic implants.

## Introduction

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), also known as HAP) has been widely used in dental and orthopedic implants, due to its chemical and crystallographic similarity with bone minerals (Ref 1-3). Lack of cytotoxic effects makes HAP biocompatible with hard tissues, skin and muscle tissues, and thus, it can be bonded to the bone directly. Despite its ideal bioactive properties, poor mechanical strength hinders the use of HAP as a load bearing implant. As a result, the combination of bioactive HAP coating and mechanically strong metals has become a promising approach to fabricate surgical implants for load-bearing applications.

Various techniques, such as dip coating, electrophoretic deposition, hot isostatic pressing, ion-beam sputtering, and plasma spraying have been employed to deposit HAP coatings (Ref 2). Among them, plasma spraying has been most widely investigated. Plasma deposition has some advantages in terms of chemical composition control and process efficiency, however, the long term stability of plasma sprayed HAP is still questionable. Although HAP coating (in appropriate phase) forms a strong bond with the bone, it has been recognized that the mechanical stability of the coating/implant interface is a problem during a surgical operation or after implantation (Ref 2). Additionally, when HAP is plasma sprayed, it may be converted into other calcium phosphate phases such as  $\alpha$ - or  $\beta$ -tricalcium phosphate, tetracalcium phosphate (TTCP) or calcium oxide (CaO) and the crystallinity of HAP may also be lowered due to rapid solidification (Ref 1-3). These alterations in chemistry and crystallinity often deteriorate the novel bioactive properties of HAP as well as its adhesion to the implant. Achieving the appropriate phase and crystallinity in HAP coatings has been an actively pursued research area for years. However, an alternative to plasma spraying that can be employed in industrial scale is yet to evolve.

In this study, we demonstrate a novel approach to fabricate biocompatible composite coatings consisting of HAP and titanium by cold spray technology. Cold spray is a relatively recent spray technology and there are different approaches known by different names such as: "cold gas-dynamic spraying", "kinetic spraying", "high velocity powder deposition", "supersonic powder deposition" etc. Fundamentally, deformable metallic particles (or other feedstock powders) are introduced into a high-velocity, gas dynamic stream (typically formed using a deLaval or similar converging/diverging nozzle, Fig. 1), and directed onto a substrate surface where they impact and form a coating. Cold-spray technologies overcome a number of traditional thermal spray 'shortcomings' such as no melting and solidification process is experienced by the powders. Coatings that have been studied to date show good density and physical

properties for many materials of engineering interest (Cu, Zn, Al, Fe, Ni, Ti and other alloys) (Ref 4-11).

As mentioned above, deformability is a key requirement for cold spray to work on a given powder. Unfortunately, HAP being a ceramic lacks such quality. Ideally, the high impact velocity achievable in modern kinetic spray system can in fact embed ceramic particles onto the surface of a ductile material. However, the coating thickness will be seriously limited. On the other hand, a mixture of ductile metallic and hard ceramic powders can lead to a composite coating. Several studies have demonstrated such composite coatings although the fraction of ceramic particles used in these coatings is still low (Ref 8-10). Further, the hard particles that have been successfully used possess higher modulus compared to that of the ductile component particles in the powder mix. In contrary, HAP, which is similar to bone has lower modulus. To the best of our knowledge, report of successful fabrication of composite coatings consisting of Ti-HAP by cold spray technology is not available in open literature.

In regards to the applicability of composite coating consisting of Ti-HAP for biomedical applications, there is evidence that for bio-integration the surface of the implant need not be completely covered by HAP. In fact, implant surfaces consisting of a fraction of area covered by HAP can effectively integrate to the bone. Composite coatings of Ti and HAP have been sprayed by plasma (Ref 11). In addition to preserving the phase of HAP, cold spray offers an additional advantage due to its operational temperature, that is, an inert environment is not necessary for preventing oxidation of Ti as is the case for plasma spray.

### Experimental

The coatings were sprayed using a CGT KINETIKS 4000 cold spray system. Premixed powders were fed by a high pressure powder feeder into heated N<sub>2</sub> gas stream through a converging-diverging (de Laval) nozzle (Fig. 1). The gas pressure and temperature in the nozzle pre chamber were varied from 25-38 bars and 400-700 °C, respectively. The nozzle was kept normal to the substrates with a standoff distance of 25 mm. Robot traverse speeds, ranging 50-400 m/s were employed to deposit coatings of various thicknesses covering an area of 3"x1.5". Two types of titanium powders used in this study are shown in Fig. 2. The vacuum atomized Cp-Ti (~45µ) was obtained from Crucible Research Pittsburgh, PA. Sponge titanium powder (~45µ) was procured from Titanium Powder Specialists, LLC, Sandy, UT. Commercial high purity HAP powder (CAPTAL 30, Plasma Biotial Limited, UK) was used at 20 and 40 wt% level and mechanically mixed with titanium powders. The powder in the feeder was heated to drive off any moisture prior to deposition.

Coatings were sprayed on grit blasted and acetone cleaned titanium as well as aluminum coupons. Coatings were examined using X-ray diffraction (Rigaku MiniFlex, radiation Cu K<sub>α</sub> = 1.54 Å) and Hitachi SEM. The adhesion strength of coatings was evaluated using a pull-off adhesion bond test fixture shown in Fig. 3. The adhesive used was a heat curable epoxy resin, E900S from Elcometer. Prior to the test the adhesive was cured at a temperature of 120 °C for 1 h. The bond strength of the adhesive was evaluated using an uncoated substrate and was estimated to be > 65 MPa. An average of 3 measurements for each coating is reported. The fraction of HAP in the composite coating was determined using digital image analysis software by PAXit.

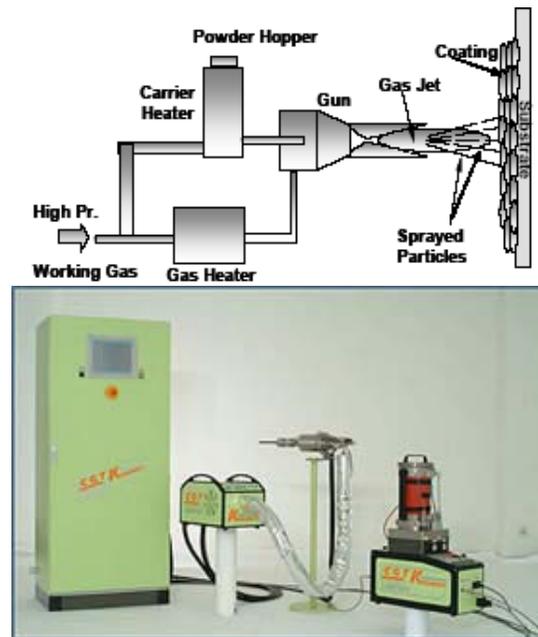


Figure 1: (a) Schematic of cold spray process, and (b) CGT 4000 system used in the present study.

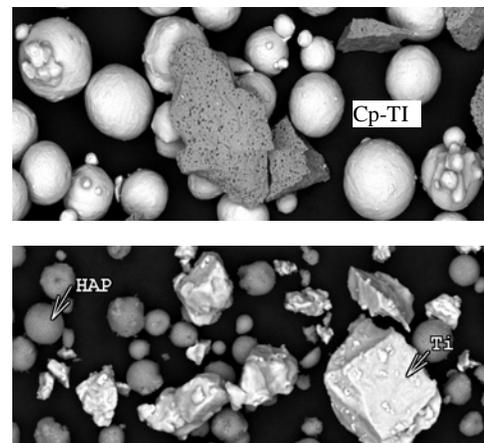


Figure 2: (a) Cp titanium and (b) Sponge titanium with HAP.

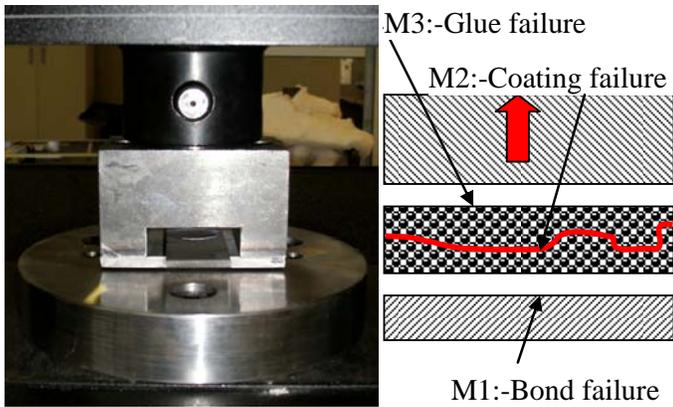


Figure 3: Adhesion strength test fixture.

### Results and Discussion

The deposition characteristics of vacuum atomized Cp-Ti powder is presented in Fig. 4. The coating density increased with increasing gas pressures and decreasing traverse speed, however, as the coating built up, the porosity level slowly increased leading to a gradient coating structure. This behavior has been attributed to the accumulative tamping effect resulting from the successive impacting particles (Ref 6, 18). The thickness of the dense layer increased with increasing pressure and decreasing traverse speed. Increasing the temperature did affect the thickness of the dense layer but the effect was not as significant as the pressure and traverse speed. Coatings with gradient porosity level as shown here are useful for biomedical applications as bone tissues can grow into these open pores creating a mechanical hinge and eliminating the need for cements. However, the cohesive strength of such coatings should be above certain threshold value to act as a mechanical hinge. All the coatings failed in M2 mode (Fig. 3) during adhesion test. As expected, the cohesive strength decreased with the emergence of porosity. The middle coating in Fig. 4, failed at an average value of 15.3 MPa where as the bottom coating averaged to 47.4 MPa. The bottom coating, with its open pore structure is expected to fulfill the requirements of biomedical applications, noting that the currently used plasma sprayed HAP coating adhesion strength averages around ~10-15 MPa. The functionality of this coating can further be enhanced by embedding HAP powder into these pores that would promote bone in growth. However, when Cp-Ti and HAP powder mixture was sprayed together, it was very difficult to build up the coating within the pressure and temperature bounds investigated here (~38 bar and 700 °C). Fig. 5 shows the X-ray map of the coating cross section. Only a contiguous thin layer (~10 $\mu$ ) of coating consisting of Ti (yellow) and HAP was possible. It appears that the difficulty in spraying spherical Cp-Ti get augmented in the presence of HAP powder. This issue needs further examination and will be addressed later. However, the thin layer observed here may be sufficient to promote bone in-growth if sprayed on the top of a coating shown in the bottom of Fig. 4.

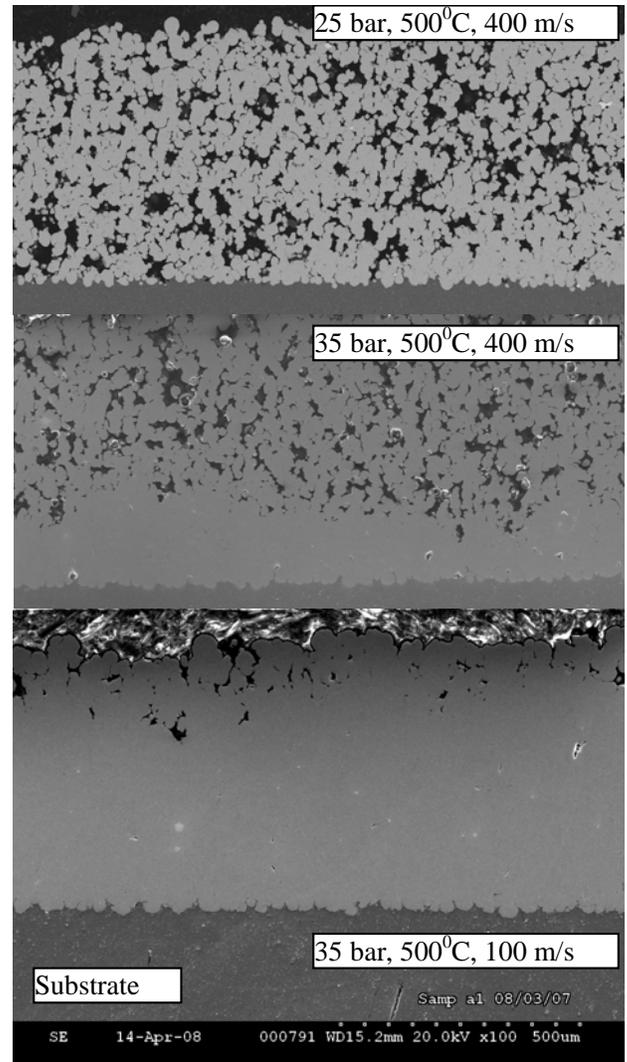


Figure 4: Cross section view of Cp-Ti sprayed at different conditions.

Contrary to the behavior of Cp-Ti powders, the sponge titanium sprayed very well as demonstrated in Fig. 6. Dense coatings were achieved with equivalent process parameters that led to porous coatings in the case of Cp-Ti. In a significant number of adhesion tests, failure occurred within the resin, indicating that the bond strength was higher than the epoxy strength. Many studies (Ref 18, 19, 20) investigated spraying of angular and sponge Ti powder with nitrogen gas and have invariably observed porous coatings. Further, these studies also reported that Ti particles didn't deform significantly during the deposition process and the occurrence of porosity was linked to this observed lack of compaction. Only, when helium gas was used, dense coatings were possible. In our experiments, a significant level of plastic deformation was observed as shown in the bottom of Fig. 6. It is to be noted that the pressure levels were higher in our experiments compared to the earlier studies mentioned above.

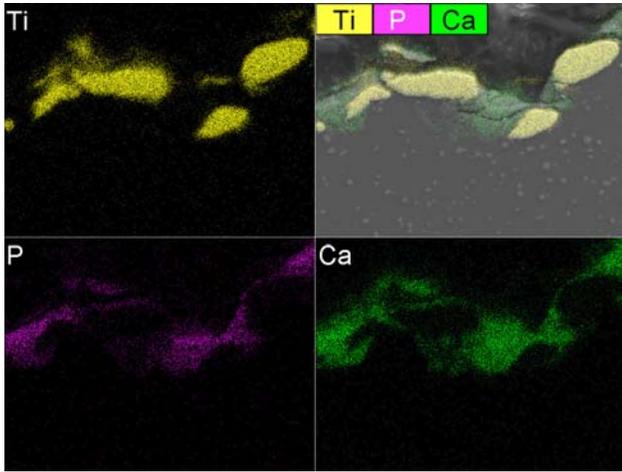


Figure 5: Cross section view of Cp-Ti + 20 % HAP at 38 Bar & 700 °C.

HAP particles were successfully deposited. The encapsulation of HAP particles within the Ti matrix is shown in Fig. 8. The corresponding XRD (Fig. 9) of the coating as well as the precursor powders show that the phases of both the powders were unaltered in the coating, which bears tremendous potential especially for HAP. Image analysis indicated that these coatings encapsulated nearly 16 % HAP and 4% of HAP powder from the powder mixture were lost during the deposition process. The adhesion strength of these coatings averaged to 24.45 MPa. However, most of the failure occurred in the coating. Increasing the deposition temperature helped the deposition density reaching a maximum at 600°C. Further increase in pressure and temperature didn't improve the process any further. Very little porosity was observed in these coatings. The deposition efficiency was almost halved by the addition HAP powder to the sponge powder.

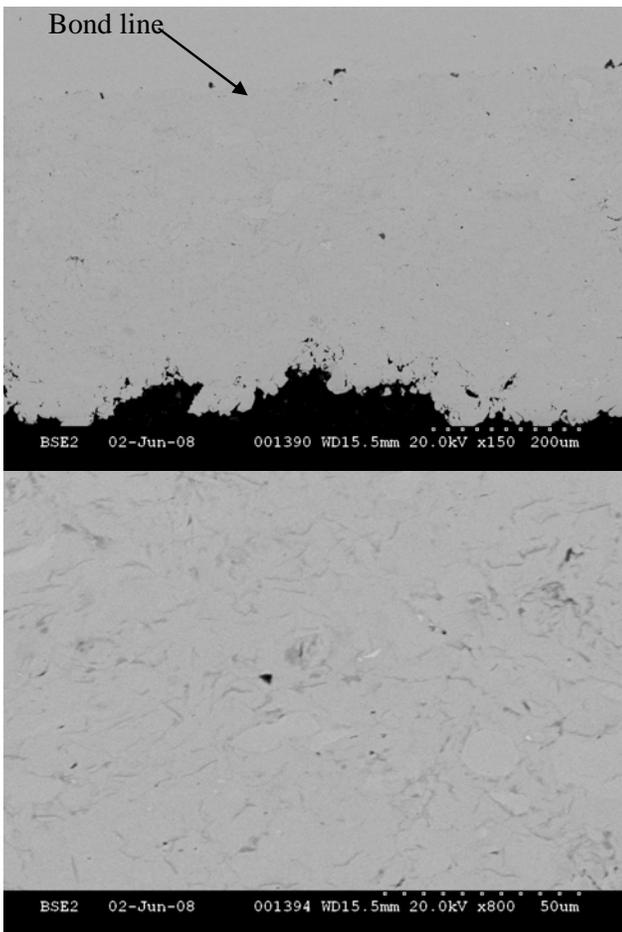


Figure 6: Cross section view of Sponge-Ti at 35 Bar & 500 °C.

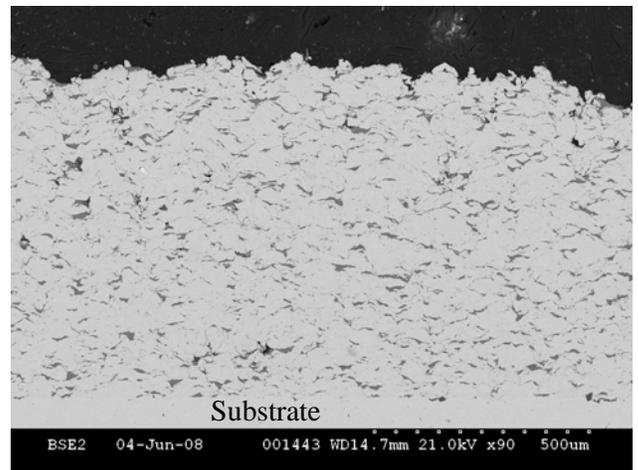


Figure 7: Cross section view of Sponge-Ti +20% HAP at 35 Bar & 600 °C.

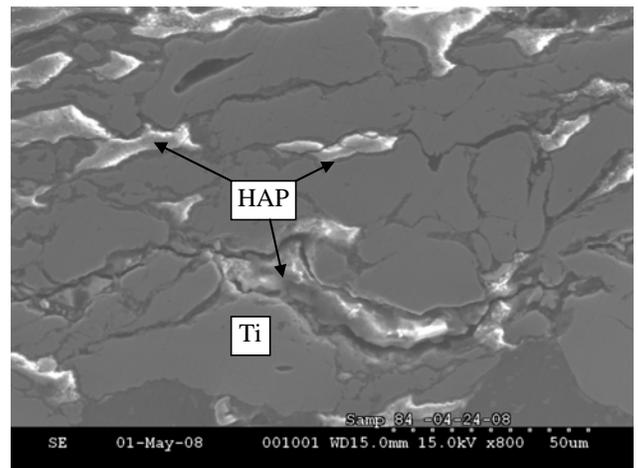


Figure 8: High magnification view of Sponge-Ti + 20% HAP coating in Fig. 7 (etched to reveal the boundary).

The microstructure of sponge Ti and HAP coating is shown in Fig. 7. As seen here a very dense coating with well distributed

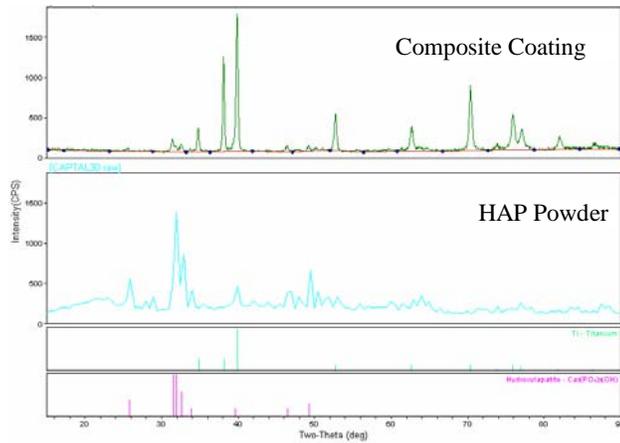


Figure 9: XRD of Sponge-Ti + 20% HAP composite coating made at 35 Bar & 600 °C.

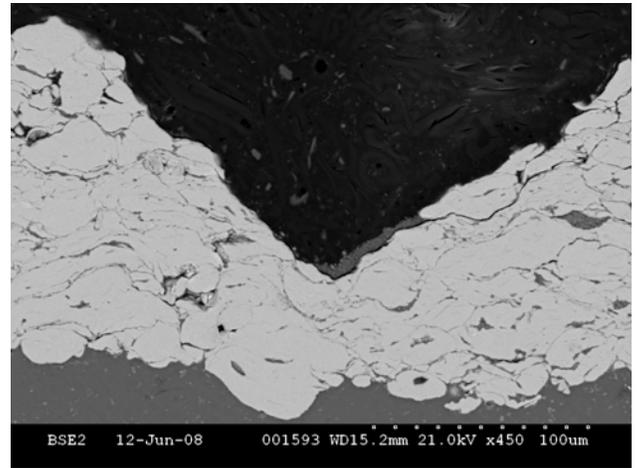


Figure 12: Valley formation due to the presence of broken HAP particles.

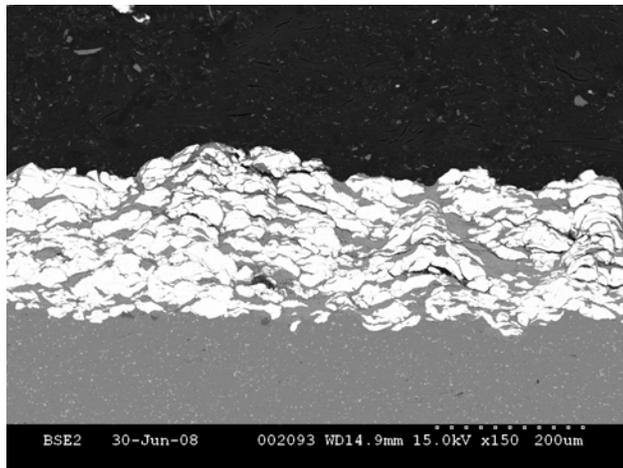


Figure 10: Cross section view of Sponge-Ti + 50% HAP composite coating made at 30 Bar & 700 °C.

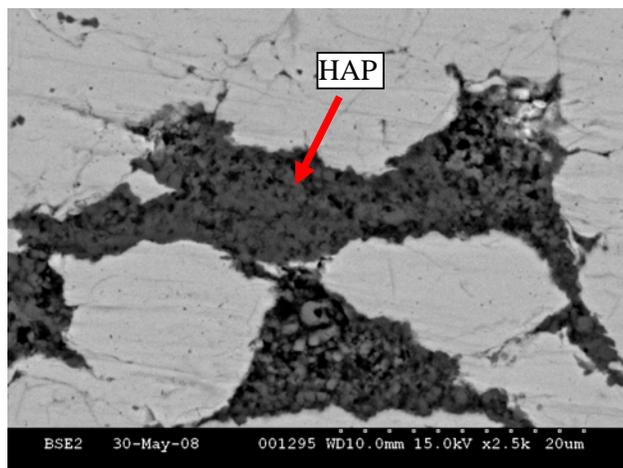


Figure 11: Breaking of HAP particles at 38 bars.

The microstructure of a coating with 50% HAP powder is shown in Fig. 10. Although a significant level of HAP powder was encapsulated in the coating, voids were observed in these coatings. Detailed examination revealed that these voids were filled with broken HAP particles as shown in Fig. 11. Some HAP powders get crushed into fragments due to high impact. It was observed that decreasing the pressure to 30 bar and increasing the temperature to 700°C favored the deposition. Further, the loss of HAP powder in the coating increased to 15%. Often broken HAP particles inhibited further deposition leading to valley formation in the coatings as shown in Fig. 12. Thus, thicknesses more than 8 milli-inches could not be achieved. In adhesion tests, the failure always occurred in the coating and the strength values averaged to 18.2 MPa. Note that this value is comparable to that of plasma sprayed Ti-HAP composites (Ref 11).

It was observed that some HAP particles were nicely compacted whereas some were loosely stuck in between the titanium particles. It is understood that successful bonding of an impacting particle requires localized deformation and adiabatic shear instabilities, which occur at sufficiently high impact velocities, the so called critical velocity (Ref 12). This critical velocity is believed to be a function of material properties and our system is not expected to attain such critical velocity required for ceramic materials. The formation of dense coatings as observed here requires an understanding of how two different types of particles with different size distributions, morphologies, densities, and mechanical properties compact together.

It has been (Ref 13) observed that inclusion of a ceramic component in the powder mixture causes a continuous activation of the surface which actually aids the metal deposition process. In fact, some low pressure systems depend on the use of such hard ceramic particles to successfully deposit coatings. The overall deposition efficiency reaches an

optimum value and then declines when the ceramic fraction in the powder mix increases significantly. The existence of such an erosive regime i.e., erosion of the coating material by hard particles competing with the process of coating build-up does not seem to be plausible here. Because the HAP particles are inherently fragile and crush easily on the impact compared to other ceramic particles such as alumina. The mechanics of composite formation, especially how crushable particles become trapped in the coating and how cold spray and particle parameters affect this process need further attention.

### Conclusions

We demonstrated that HAP powders can be cold sprayed simultaneously with titanium to form thick biocompatible composite coatings, without compromising the phase constituents of HAP. Further we demonstrated that very dense coatings of pure Ti and Ti-HAP composite can be achieved using sponge powder and nitrogen process gas. The adhesion strength of the composite coatings compared or exceeded the reported values of comparable plasma sprayed coatings. These results are encouraging from the point of process economics as well as potential applications of these novel coatings.

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