



SURFACE ENGINEERING

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Factors Affecting HA Coating Integrity

The most common coatings for orthopedic implants are sintered porous coatings (spherical beads, irregular particles, wire mesh, etc.), plasma sprayed titanium coatings, and hydroxylapatite (HA) coatings. The HA coating process is by far the most complex, requiring a high level of expertise and process control to provide a safe coating. HA coatings are particularly demanding in that the chemical, mechanical and morphological characteristics must be very carefully monitored.

Chemical Properties

The coating process begins with a highly crystalline pure HA powder. ASTM and FDA requirements state that the powder must be at least 95% HA, and conform to strict trace elemental requirements. The plasma spray process degrades both the crystallinity and HA content. HA goes through a phase transformation to tricalcium phosphate and other calcium phosphates due to the high temperatures required in the process. The greater the extent of degradation, the more resorbable the coating becomes.

The FDA requires that the coating shall not be below 62% crystallinity. There are specific variables that can contribute to a loss of crystallinity and HA content including; dwell time, distance, powder density, powder size, powder morphology, gun configuration, humidity, gas purity, gas type, etc. Controlling these variables, while spraying implants with irregular geometries and varying levels of heat dissipation, is critical to yield a successful coating. Distance is a particularly important variable, resulting in a reduction in crystallinity and HA content the further you spray from the part. Implants having complex geometries therefore present a challenge, necessitating the use of robotics to maintain an optimal distance. Other factors such as oxidation of the implant and masking materials may make it difficult to spray implants at the optimal distance.

Mechanical Properties – Coating

Mechanical property considerations are no less important than the chemical properties. In fact, coating failure may be a result of synergetic effects resulting in partial dissolution of the coating, leading to a compromise in mechanical

properties. In addition to the aforementioned variables, degree of melting, surface preparation and substrate material composition all play a strong role in coating adhesion. Grit blasting is essential to achieve a bond between the coating and substrate. Factors such as media type, blast pressure, blast distance, blast duration and the resulting morphology of the surface must be carefully controlled. The most critical factor, however, is how the HA cools upon impact and after being in contact with the implant. The use of a pre-heat cycle might benefit coating adhesion, by allowing the coating to “splat” more efficiently into the roughened surface. However, the rate of cooling of a pre-heated part, verses that of a room temperature part, may have a strong effect on the resulting chemical properties. The cooling rate is obviously also affected by the mass of the part.

Mechanical Properties – Substrate

The HA coating process may affect the underlying substrate in one of two ways; the roughening of the substrate and the thermal effects due to the coating. Titanium and its alloys are known as *notch sensitive* materials. The roughness created by the grit blasting process must be controlled to minimize a potential compromise in fatigue properties. However, this roughness must contain enough surface area for coating adhesion. The end result is that the blast process alone may cause as much as a 15% reduction in endurance limit. Since porous coatings must be roughened for HA adhesion, great care must be taken not to compromise bead to bead attachment.

The thermal effects of the coating process may be potentially more significant than the grit blast process. Titanium and its alloys react with embrittling elements in air (i.e.; C, N₂, H₂, and O₂) as low as 600°F. A significant loss in fatigue strength may be observed if the implants become exposed to a high enough temperature. This necessitates the use of robotics to control exposure through control of traverse rate and part assimilation, as well as the possible need for auxiliary cooling. Thermal affects are a prime concern when dealing with high surface area substrates and thin sections. Porous coatings may lose their strength in necked areas due

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to embrittlement. Devices such as dental implants, with typical wall thicknesses under a millimeter, might also lose fatigue strength if heated for too long at high temperature.

Morphological Properties

Morphological characteristics of the coating must be taken into account, along with the chemical and mechanical characteristics. The most influential variables controlling coating morphology are powder size and distribution, powder density, and degree of melting. If one uses a powder with a wide distribution of particle sizes, in order to achieve a well melted coating, the finer particles will degrade in the process of melting the larger particles. This will result in a degradation of chemical properties. Another approach would be to more closely tailor the process to melting the finer particles, creating a 'bricks and mortar' type coating. This is equally dangerous as the unmelted form of the powder may have inferior mechanical properties (especially if one starts with a relatively porous particle.)

Even with optimal particle size and distribution, the degree of melting must be carefully controlled. There is a fine line between undermelting a coating and overmelting it. Due to chemical considerations, one may seek to reduce phase transformations and a loss in crystallinity by undermelting the coating. Typically this does not result in an improvement in chemical properties, but does lead to porosity. Porosity has the obvious effect of decreasing mechanical properties and abrasion resistance. It also allows for the less obvious synergistic effects of increased coating dissolution (due to increased surface area and possible 'through thickness' accessibility of body fluids) and a resulting rapid loss of mechanical integrity. Overmelting of a coating is equally as dangerous as undermelting. Some degree of cracking of an HA coating can be expected due to differences in the coefficient of thermal expansion between the coating and substrate. What is critical is to confine the cracking to a shallow depth on the surface. Overmelting a coating may lead to 'through thickness' cracking and possible delamination (separation of the coating from the substrate.) Again, this level of cracking may lead to increased susceptibility of the coating to dissolution and possible loss of adhesion.

Clinical Implications

It is clear that many variables affect the integrity of an HA coating. The most critical issue is controlling these variables on a day to day basis, under 'real world' conditions. The plasma spray process is highly susceptible to a loss of process control. For example, an anticipated degree of gun wear will be inevitable due to the high temperatures used. Gun wear obviously changes the morphology of surfaces (i.e. the anode and cathode) changing the resulting electrical profile of the flame. Typically, what is observed is an increase in voltage, at a given amperage, resulting in a different melting profile of the coating. Another problem with gun wear is that it will deposit a copper alloy (anode) and a tungsten alloy (cathode) within, and on top of the coating. Quality control becomes critical to ensure that these materials are minimized.

Gun wear is just one of many equipment characteristics that could unknowingly change the coating, and in inexperienced hands go

unnoticed until it fails in the patient. The consequences of losing coating integrity are well documented for hip prostheses. Early coating failures lead to results such as osteolysis and third body wear to the articulating surfaces. Most HA coatings are not highly resorbable, which has led to evidence of failed coatings showing up in the lymph nodes. While the quality of most U.S. produced coatings are now acceptable, this was not always the case. The advent of an FDA guidance document in the early 1990's, as well as ASTM standards, have raised the general quality of domestic coatings. However, the inconsistency of regulations and patient follow-up in Europe has resulted, in some cases, in lower quality, cost-driven coatings that are still being produced to this day.

Summary

In summary, HA coatings are very difficult to develop and control. Numerous variables must be controlled in a 'real world' environment, where the slightest loss of control could lead to disastrous results. It is no wonder that there are only three companies in the U.S. that HA coat for themselves, and only three or four that serve the remainder of the industry. Bio-Coat is proud to have achieved the position of being the largest HA coater in the world since the mid-1990's. Process control and materials expertise have led to no known published case where a Bio-Coat implant has failed due to the coating over our 12 year span in business.

Editor: Frederick (Rick) S. Georgette is President of Bio-Coat, Inc., Southfield Michigan. Rick has been an active member in the Society for Biomaterials and ASTM for the past 22 years. At ASTM, Rick has chaired several task forces, primarily those dealing with metallic and ceramic coatings. He has received several awards at ASTM, including twice receiving the prestigious Leroy Wyman award.

Rick has authored and co-authored several papers and patents in the porous coating, ceramic coating and metallurgical areas. Rick worked for both Richards Medical Company (now Smith and Nephew Orthopaedics) as well as Intermedics Orthopedics (now Centerpulse Orthopedics) before founding Bio-Coat in 1990. Part of a three-company group, Bio-Coat, Bio-Vac and Bio-Vac Spain provide porous coatings, HA coatings, and plasma sprayed titanium coatings for the orthopedic and dental fields.

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