Nucleation and Growth of Ceramic Films on Metallic Surfaces

Karolyn M. Hansen[§], Andrew S. Mount[*] and Douglas C. Hansen[§]
[§]University of Dayton Research Institute
Dayton, OH 45469 USA
[*]Clemson University
Department of Biological Sciences
Clemson SC 29634 USA

The molluscan shell formation process is a promising model for the development of bio-inspired ceramics for a wide variety of applications in fields as varied as nanotechnology and nanofabrication, nanoelectronics, biomedical engineering, tissue regeneration, adaptive surface coatings, corrosion inhibition, crystal growth and optical gratings, hybrid composite materials and more. A novel mechanism for biomineralization and shell formation in the Eastern oyster (*Crassostrea virginica*) has been elucidated that involves a cellular-mediated process that had previously been unknown[1]. Recent laboratory studies[2] have confirmed that circulating immune blood cells (hemocytes) are directly involved in oyster shell formation, where two mineralized layers of shell (prismatic and foliated) are deposited in conjunction with an organic polymer matrix. The key steps in layered shell formation are: 1) secretion of an organic matrix film for cells to adhere; 2) migration of cells onto this membrane to form a mineralization front; 3) deposition of nanocrystals of intracellular origin by specialized cells; 4) formation of polycrystalline assemblies within cellular agglomerations; 5) epithelial directed growth of polycrystalline assemblies to form a uniform mineralized layer; and 6) subsequent secretion of second organic matrix film onto the mineralized layer. The polymeric organic films may serve an organizing function such as to inform cells where and when to deposit calcite and may serve to delineate crystal structure.

These results challenge the prevailing shell formation paradigm which holds that shell components (calcium carbonate and organic matrix) are secreted in a complex milieu and that assembly into calcium carbonate (aragonite and calcite) shell layers is matrix-mediated. The paradigm shift is this: *initiation and control of molluscan biomineralization is a cellular process*. Using this knowledge, the deposition and growth by cells of these nanoscale composite organic/mineral layers *in situ* on metal alloy substrates and the deposition of nanometer sized ceramic crystals onto metallic surfaces (*ex vivo*) have been achieved.

Figures 1 and 2 demonstrate the cellular deposition of nanocrystals and the growth of polycrystalline assemblies to form a uniform mineralized layer on various metals, respectively. Further success in the formation of a multi-layer, bioceramic coating on an aluminum alloy is presented in Figure 3.

Further elucidation of the cellular processes involved in shell formation will revolutionize the field of ceramics and other nanoscale composite materials research with the ultimate goal being the cell-free nanocrystalline assembly of adaptive bioceramic material systems.

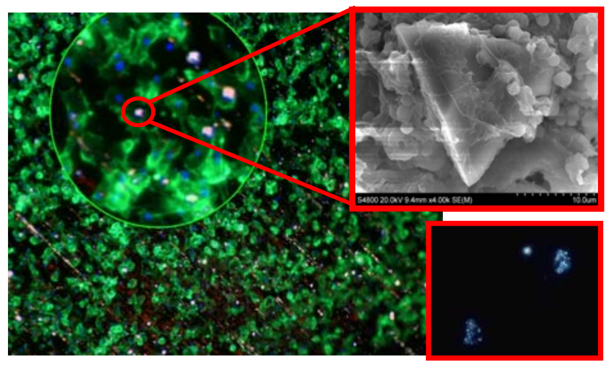

Figure 1. Cellular crystal deposition on Ti6Al4V alloy.

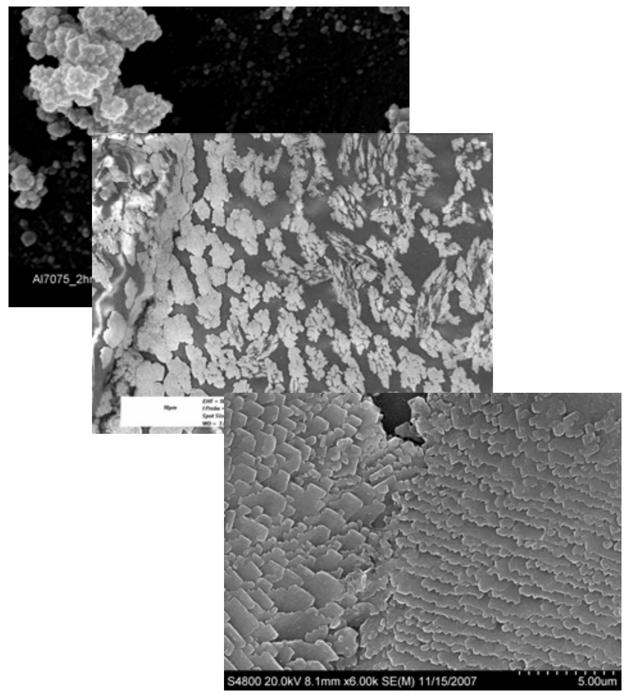

Figure 2. (Top) Nascent crystals on AA7075 alloy
(Middle) Coalescing crystals on AA7075 alloy
(Bottom) Margin of fused crystals on AA7075 alloy

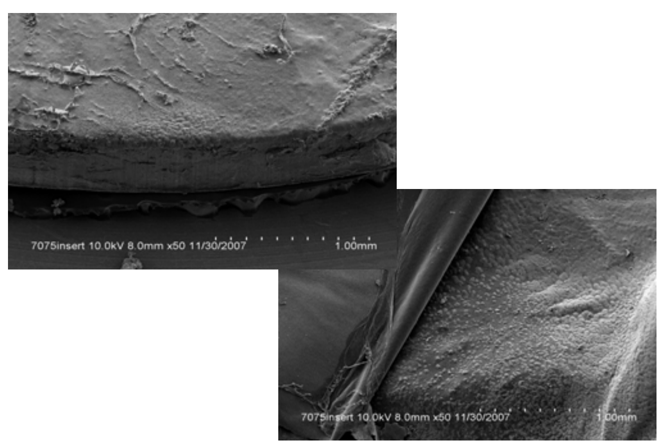

Figure 3. Multi-layer ceramic coating deposited on AA7075 alloy substrate.

REFERENCES

1. Mount, A.S., Wheeler, A.P., Paradkar, R.P. and Snider, D., *Science* **304** (2004) 297.
2. Mount, A.S., K.M. Hansen and D.C. Hansen, *AFOSR Nanotechnology Review* (2008).