

TECHNOLOGY ADVANCES

Bioactive Glass Coating for Titanium Bone Implants Strengthens Their Adhesion

Scientists in the Materials Sciences Division (MSD) at Lawrence Berkeley National Laboratory (LBNL) have developed a bioactive glass coating for titanium bone implants that avoids large thermal stresses while strengthening glass/metal adhesion. The composition of their glass system is related to that of Bioglass[®], developed by Larry L. Hench of Imperial College of Science, Technology, and Medicine. Within Hench's SiO₂-CaO-Na₂O-P₂O₅ system, these scientists substitute MgO and K₂O for CaO and Na₂O. These additions alter the thermal expansion and softening points such that enameling can be carried out below the transformation of Ti in the alloy Ti-6Al-4V (955–1010°C), without generating large thermal stresses. Generally, to encourage bonding, titanium bone implants are coated with a bioactive material that promotes the formation and adhesion of hydroxyapatite (HA), the inorganic component of natural bone. However, because of the difference in the thermal expansion coefficients of the ceramic and metal, large thermal stresses are generated during processing that lead to cracks at the interface and compromise adhesion. Furthermore, chemical reactions between the ceramic and metal can weaken the interface, reducing the strength of the coated system. Controlling the interfacial reaction between the glass and the alloy is critical. Furthermore, the researchers have developed an enameling technique for coating titanium-based alloys.

This new family of bioactive silicate glasses alters the thermal expansion and softening points of the glasses, avoiding the generation of large thermal stresses and restricting the processing to temperatures below the α - β transformation of Ti (882°C). The silica content of the LBNL glasses is between 46 and 69 mol% and the coefficients of thermal expansion (CTEs) between 8.8 and 15.1 $\times 10^{-6}$ °C⁻¹. This range includes the CTEs of the Co-Cr-Mo alloys (e.g., Vitallium) frequently used for implants (12–13 $\times 10^{-6}$ °C⁻¹) and Ti or Ti-6Al-4V (~9–10 $\times 10^{-6}$ °C⁻¹). Preliminary *in vivo* testing was performed using bulk pieces of porous glass, demonstrating that when the silica content is below 57 wt%, bone grows inside the pores and at the same time the glass is replaced by mature osseous tissue.

The scientists fabricated coatings on Ti-Ti-6Al-4V and Co-Cr-Mo alloys following a conventional enameling procedure in which they painted glass powders on the metal surface and subsequently annealed

the samples in air or nitrogen. The annealing temperatures and times were between 800°C and 900°C and between 30 s and 2000 s. The final thickness of the coatings ranged between 30 and 150 μ m.

For Ti alloys the main reaction forms titanium silicide (Ti₅Si₃). The interfaces with optimum adhesion have a nanostructured interfacial silicide layer ~100–150 nm thick. In indentations performed on polished cross sections of these coatings, cracks did not propagate along the glass/metal interface, but rather tended to be driven into the glass coating, which is a qualitative indication of relatively strong glass/metal adhesion. During initial *in vitro* tests of bioactivity, the coatings developed a layer of HA on their outer surface on exposure to simulated body fluid.

In general, fabrication of coatings for implants involves a compromise between adhesion, mechanical stability, and bioactivity. However, glasses with thermal expansions close to those for Ti alloys have a high silica content, which reduces their bioactivity. The range of glass compositions that satisfy the requirements of bioactivity and low thermal stresses is extremely narrow. Therefore, the LBNL group is developing coatings of functionally graded glass and glass/HA to reduce thermal stress and improve adherence and long-term stability while maintaining a highly bioactive surface. The resorbability rates and bioactivity of graded composites can be adjusted by changing their composition, thereby allowing custom designing of implants for specific applications. By controlling the gradient in the glass composition along the coating, the researchers expect that good adhesion to the metal will be combined with rapid biofixation and long-term stability.

In recent tests, the LBNL scientists fabricated graded coatings by sequentially depositing layers of glass or glass/HA mixtures and subsequently firing in air or

N₂ under conditions that provide better adhesion for the glass in contact with the alloy (Figure 1). To coat Ti alloys, they used glasses with a high silica content for the layer in contact with the metal because the glasses' thermal expansion is closer to,

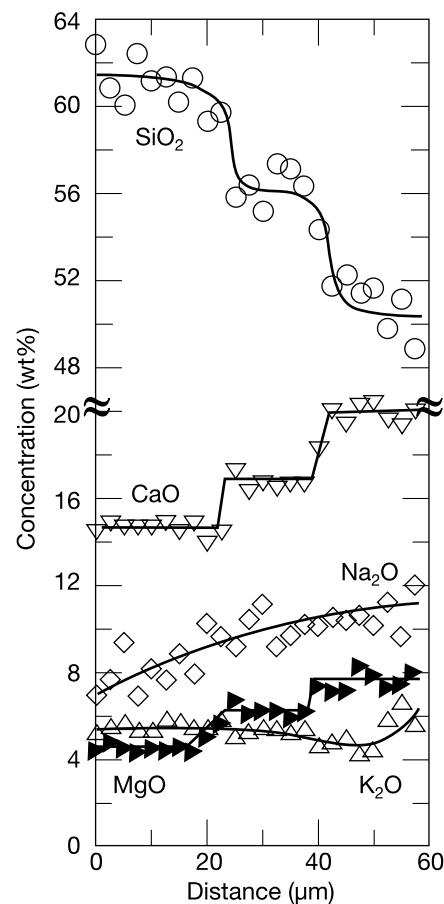
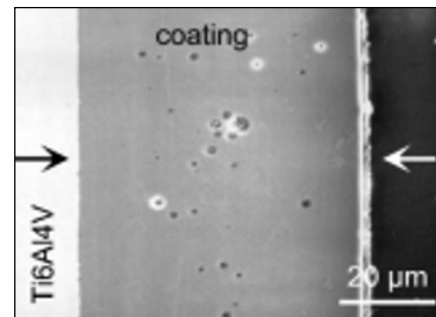


Figure 1. Elemental analysis, by energy-dispersive spectroscopy (EDS), along the cross section of a multilayer glass coating shows a stepwise distribution of the glass components that corresponds to the composition of the deposited glass layers. The smoother profile of Na₂O is due to its faster diffusion in silicate glasses, which allows for some interdiffusion between layers even for the shorter firing times.

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and in some cases lower than, that for the alloy—high silica glasses are more resistant to corrosion in body fluid and can effectively protect the alloy, increasing the long-term stability of the coating. The edge stresses were reduced by using graded coatings thereby allowing the use in the coating surface of more bioactive compositions that otherwise would crack when applied directly to the metal. In addition, the researchers designed gradients in which the residual stress distribution of the coating changes from a surface under tension to a compressive stress at the glass-to-metal contact. Recent theoretical and experimental studies have shown that such stress distributions are effective in arresting crack growth.

Graded coatings have been fabricated at LBNL with a corrosion-resistant glass protecting the metal, and surface silica content—as low as 53 wt%. Also, layers containing as much as 50 wt% synthetic HA were fabricated using this approach, with no appreciable degradation of the inorganic component. All the coatings formed apatite on their surfaces when tested *in vitro*. No appreciable corrosion was observed in the high-silica layers in contact with the metal. Work is ongoing to characterize the behavior of the glass in cell cultures, and, in cooperation with researchers and orthopedic surgeons at the University of California at San Francisco, systematic *in vivo* studies are planned for the more promising coating compositions on Ti-6Al-4V and Co-Cr implants.

Titanium and cobalt-chromium alloys continue to be widely used for orthopedic implants because of their desirable mechanical properties. Due to failure, though, most hip implants typically must be replaced within 15 years, and nearly 20% of hip replacement surgeries are for replacing the original, failed implant.

Acknowledgment

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Opportunities

The LBNL developers suggest that this bioactive glass could also be used by itself in implants where mechanical strength is not essential—such as in middle ear devices—and particles could be used where soft tissue augmentation is needed or in bone restoration in periodontal treatment. A patent application has been filed. The developers welcome inquiries about joint research and development projects. Licensing is also possible.

Source: For R&D projects, contact Dr. Antoni P. Tomsia, Principal Investigator, MS 62-203,

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Textured Silicon Nitride Retains High Flexural Strength and High Toughness

Because of its relatively good mechanical properties at elevated temperatures, silicon nitride (Si_3N_4) has been commercialized for applications such as automotive engine components and cutting tools. Nevertheless, its wide adoption as an engineering material has been limited due to brittleness leading to low reliability. In conventional silicon nitride, high strength and high toughness appear to be incompatible. Researchers at Japan's National Industrial Research Institute of Nagoya (NIRIN) have developed a processing strategy for controlling the size and orientation of large columnar grains in self-reinforced silicon nitride. The size of large columnar grains in sintered silicon nitride could be controlled by seeding of $\beta\text{-Si}_3\text{N}_4$ single crystal particles (see Figure 1c). In addition, textured silicon nitride with unidirectional alignment of large columnar grains—namely, control of grain orientation—could be achieved by the combination of seeding and tape-casting process (see Figure 1d). The textured silicon nitride exhibits high

strength, high fracture toughness, and high Weibull modulus for strength.

Silicon nitride has two crystalline phases: a low-temperature phase, $\alpha\text{-Si}_3\text{N}_4$, and a high-temperature phase, $\beta\text{-Si}_3\text{N}_4$. Silicon nitride powder consists mainly of the α -phase. During sintering (typically 1600–1700°C in nitrogen at atmospheric pressure), $\alpha\text{-Si}_3\text{N}_4$ particles dissolve in a liquid phase and precipitate as small, uniform needlelike grains of $\beta\text{-Si}_3\text{N}_4$ (Figure 1a), indicating the preferential growth in the crystallographic [001] direction of the β -phase. This material has a high bending strength of about 1 GPa, reflecting the fine, uniform microstructure; but it has a fracture toughness as low as 5 $\text{MPa m}^{1/2}$ (Figure 2a).

However, when sintered at higher temperatures under high nitrogen pressure (gas pressure sintering) to suppress decomposition, a unique microstructure is developed in which large columnar grains are dispersed in a fine-grained matrix (Figure 1b). The high fracture toughness (above 10 $\text{MPa m}^{1/2}$) of silicon nitride with this type of bimodal microstructure is attributed to the large columnar grains acting as reinforcements similar to whiskers in composite materials. But the flexural strength of these *in situ* composites or self-reinforced materials is low (~600 MPa) compared with the material with uniform microstructure, because the large grains act as flaws.

The development of a bimodal microstructure is closely related to two phenomena during sintering: α -to- β phase trans-

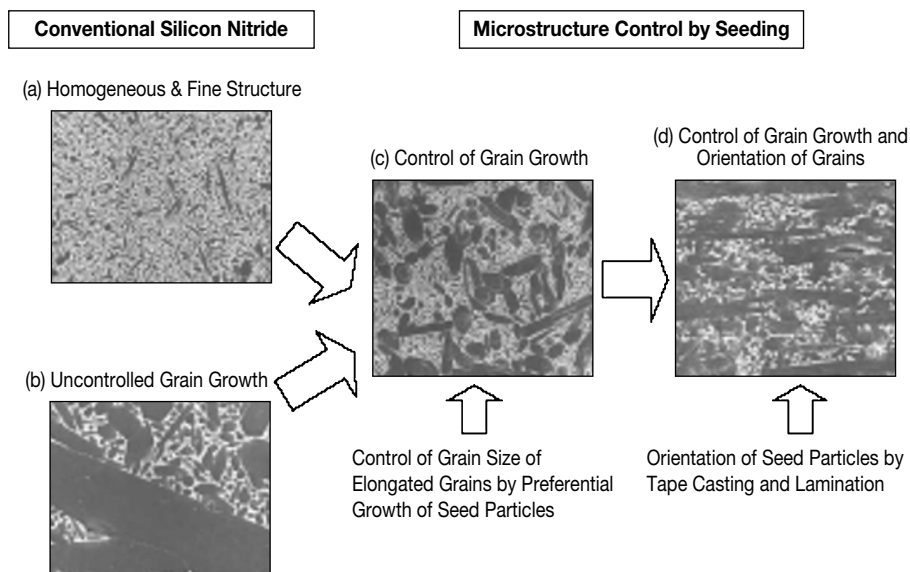


Figure 1. Microstructures of (a) conventional silicon nitride, (b) conventional toughened silicon nitride, (c) seeded silicon nitride, and (d) seeded and tape cast silicon nitride.

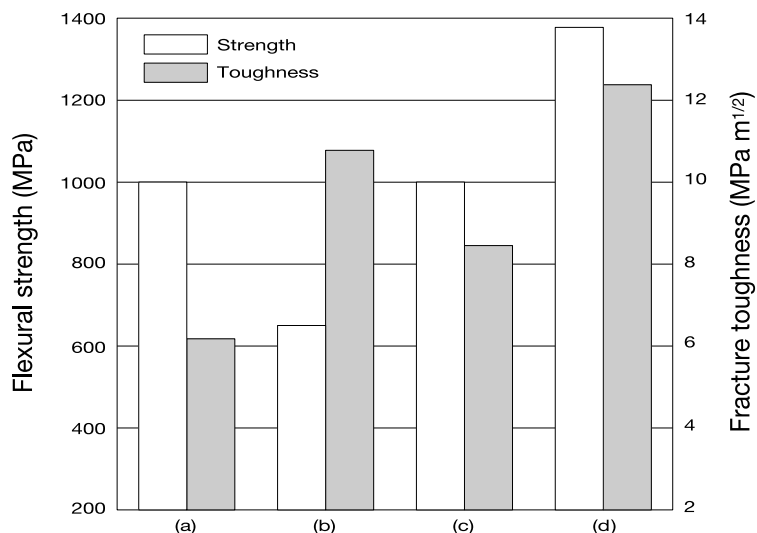


Figure 2. Comparison of the mechanical properties of (a) conventional silicon nitride, (b) conventional toughened silicon nitride, (c) seeded silicon nitride, and (d) seeded and tape cast silicon nitride.

formation and the solution reprecipitation of β -grains. The former occurs primarily at the early stage of sintering and the latter at the final stage. Commercial α - Si_3N_4 powder includes a few percent of β - Si_3N_4 particles. It has been shown that preexisting β -particles are the preferential nucleation sites for the newly formed β - Si_3N_4 phase during α -to- β transformation. In the final stage of sintering, the small β -grains dissolve in the liquid phase and reprecipitate on the larger β -grains owing to the difference in the solubility of the grains; the smaller grains are more soluble than the larger ones. Consequently, the number and size of β - Si_3N_4 particles present in the starting powder play important roles in determining the final microstructure. This is why the microstructural control of self-reinforced silicon nitride is difficult to achieve by conventional sintering technology.

Based on this grain-growth behavior analysis, the NIRIN researchers developed their method involving seeding with a small quantity of β - Si_3N_4 single crystal particles. For grain growth, the seed particles should be larger than the silicon nitride powder. In addition, their size distribution should be uniform in order to avoid growing undesirable excessively large grains.

The researchers synthesized seed particles satisfying these requirements by calcining a mixture of silicon nitride, yttrium oxide (Y_2O_3), and silica (SiO_2) powders, followed by an acidic rinse. The addition of these seed particles to Si_3N_4 powder produces a bimodal microstructure in

which large columnar grains with a uniform size distribution are dispersed in a fine-grained matrix (Figure 1c). As a result of this microstructural control, the fracture toughness was improved ($\approx 8 \text{ MPa m}^{1/2}$) without a reduction in flexural strength ($\approx 1 \text{ GPa}$) (Figure 2c).

The combination of seeding with particles that have an anisotropic shape (e.g., platelike or columnar) with a forming process that generates shear stress (e.g., tape-casting, extrusion) was found to have the further advantage of enabling the development of a textured microstructure. For example, highly anisotropic silicon nitride in which large columnar grains are almost unidirectionally oriented can be obtained by combining seeding with tape casting (Figure 1d). This material is fabricated from 200- μm thick green sheets prepared by casting a slurry containing an organic binder, raw Si_3N_4 powder, and 5 vol.% of columnar-shaped seed particles, then punching each sheet into a rectangular shape, and laminating together about 50 sheets aligned in the casting direction. The oriented columnar grains in the sintered material (Figure 1d) were grown from seed particles aligned parallel to the casting direction during forming.

The resulting textured silicon nitride has both high flexural strength (over 1.4 GPa) and high fracture toughness (over $12 \text{ MPa m}^{1/2}$) in the direction parallel to the grain alignment. The developers said that these values have not been obtained together previously in an engineering ceramic (Figure 2d). They suggest that the oriented columnar grains seen in

Figure 1d effectively serve as barriers to inhibit crack propagation, thereby contributing to the high fracture toughness, and the combination of the high toughness and the precise control of grain size results in the high strength.

Opportunities

Two U.S. Patents for this process (5,674,793 and 5,705,449) have been awarded to the Agency of Industrial Science and Technology (AIST), Ministry of International Trade & Industry (MITI), Japan.

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Control of Temperature Gradient at Interface during Joining Expands Potential for High-Performance Materials

The development and exploitation of various high-performance materials, such as high-strength aluminum and titanium-based alloys, nickel-based superalloys and metal matrix composites, exhibit potential applications, particularly in transport industries. However, the lack of a reliable and economical joining method for some of these materials has drastically limited their use. To answer this need, a bonding method has been developed in the Department of Materials Science and Metallurgy at the University of Cambridge, which results in joints with strengths and reliabilities as high as those of the parent materials (e.g., similar and dissimilar combination of aluminum-based alloys and composites). The key feature of this method is to impose a temperature gradient and control the temperature profile across the liquid phase in order to produce bond lines with nonplanar morphologies.

In this method, an interlayer of a suitable composition is inserted between the pieces to be joined, and one of the pieces is heated to the bonding temperature while the other piece is kept slightly colder by using an appropriate heat sink. The bonding temperature is always lower than the melting point of the base materials, and the formation of the liquid phase at the bond line is normally due to solid-state interdiffusion between the interlayer and the base material since this results in the formation of a low-melting-point eutectic phase (e.g., using a copper interlayer when bonding aluminum alloys). Alternatively, an interlayer initially of eutectic composition can be used, and this melts at the bonding temperature which is chosen to be just above the eutectic's melting point. For example, a Ni-P interlayer can be used when bonding nickel alloys. A wide range

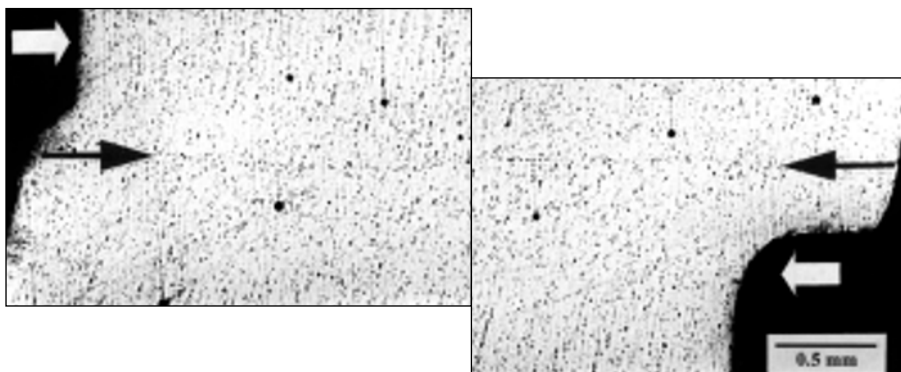


Figure 1. Cross section of an Al-6082 bond with sinusoidal interface (shown by black arrows) using the temperature gradient bonding method and which subsequently withstood 251 MPa in a shear test. White arrows show the direction of the applied shear force and the extent of lateral plastic deformation.

of bond-line morphologies, from fairly flat to wavy and even fully dendritic, have been produced when joining aluminum alloys using copper interlayers.

Results of mechanical tests have shown that nonplanar interfaces (i.e., wavy or sinusoidal) result in extremely reliable bonds with shear strengths comparable to those of the parent materials. Figure 1 shows results for the aluminum alloy 6082 in the fully aged condition. The topography of fracture surfaces shows that the apparent fracture area increases due to the development of a sinusoidal interface, and this is the cause of the higher bond strengths compared with bonds with planar interfaces produced using conventional diffusion bonding processes. Apparently bond strength is improved due to the increased surface area of the interface.



Figure 2: Cross section of a dissimilar joint of Al-6082 alloy and an Al/SiC particulate composite made using the temperature gradient bonding method.

Furthermore, the bonding conditions should be precisely optimized to achieve a nonplanar interface while avoiding formation of any dendritic structure.

In this method, unlike conventional

transient liquid phase (TLP) diffusion bonding, bond formation through solidification does not require diffusion of solute in the solid phase. Instead the bonding time depends on the diffusivity of the solute in the liquid phase and also on the magnitude of the imposed temperature gradient. Consequently, bonding times are considerably shorter than those required in conventional TLP diffusion bonding process.

In addition to bonding aluminum alloys to themselves, they can also be joined to aluminum metal matrix composites. Bonds with shear strengths as high as that of the parent aluminum alloy have been produced. Figure 2 shows the bond line of a joint where the silicon carbide particles in the composite have penetrated into the aluminum alloy. This result confirms the potential of the method for the joining of dissimilar materials. Preliminary experiments on bonding nickel alloys with a nickel/phosphorous interlayer have also been very promising. Hence, the method is potentially applicable to a wide range of alloys and composites.

Opportunities

The approach described has been patented, and research is continuing to extend the method to other advanced materials. The researchers are interested in hearing from those interested in developing and/or licensing this method for commercial applications.

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