BIOMIMETIC PROCESSING OF CERAMICS AND CERAMIC-METAL COMPOSITES

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ABSTRACT

Biomimetic design and processing of laminated B_4C-Al cermets, based on knowledge gained from the microstructure-property characterization of abalone shells, is described. In the nacre section of the shell, the microstructure is highly organized as $CaCO_3$ (aragonite) crystals, with a thickness of 0.25 µm, separated by a layer of organic matter 300-500 Å thick. This organization forms a miniature "brick and mortar" microstructure. The resultant strength and fracture toughness of the nacre, i.e., 180 MPa and 7 MPa-m$^{1/2}$, are many orders of magnitude higher than those of monolithic $CaCO_3$. The processing of laminated B_4C-Al cermets, based on the microstructure of the nacre, was performed by a combination of tape casting of the ceramic and infiltration of the metal. The resultant cermets displayed a 40% increase in both fracture toughness and strength over monolithic B_4C-Al cermets.

INTRODUCTION

The use of composite materials has become popular and frequently necessary to meet the requirements of technology. The employment of composites is well appreciated from the fact that unique arrangements of constituent materials not only satisfy specific requirements but also exhibit properties superior to the sum of each component.

Laminated composites which have planar geometry are one example and can be found both in nature and early civilizations. Examples are seashells, glued woods, and metallic armor. Even though exotic techniques and materials are introduced in the processing of laminated composites for modern applications, the flexibility of offering specific anisotropic properties, such as a specific strength, toughness, and stiffness, makes laminated composites attractive and provides an edge over single-phase materials.

The discovery that modern laminates formed from composites with a nanoscale architecture have enhanced properties has drawn much attention. It has led to the reexamination of the structure-property relationship in composites with different scales of size. Eutectic composites, frequently known as *in situ* composites, exhibit a well-aligned fibrous or platelet-reinforcing phase by directional solidification or by phase transformation, the classical example being the pearlite structure. A wide range of materials belongs to this group such as metal-metal,[1] metal-ceramic,[2] intermetallic-intermetallic,[1] metal-intermetallic,[3] and ceramic-ceramic[4-6] systems. In all cases, the size dependency of properties was observed and is known as the Hall-Petch relationship, $\sigma = \sigma_o + kd^{-1/2}$, for ductile phases and the Orowan relationship, $\sigma_f = YK_{IC}d^{-1/2}$, for brittle phases. Although directional solidification is a thermodynamically-driven process, precise control of the interfacial characteristics and composition of the composites was possible even when the size was reduced to a few microns. Similar microstructures can be obtained at the nanometer range through the use of physical or chemical deposition techniques which are not limited by thermodynamic parameters. The subsequent enhancement of properties results in unique behavior which is not only size dependent[7,8] but also dependent on the nature of the interface,[9,10] a phenomenon known as the supermodulus effect.[11]

A laminated architecture is especially useful in naturally-occurring composites such as seashells where it maximizes strength and toughness, sometimes exceeding the properties of the constituent materials by more than 20 times.[12,13] It should be noted that the biologically-produced laminates are formed *in situ* as are eutectic-like composites and have the same nanometer scale as superlattices. The classical work of Cook and Gordon[14] on the importance of interfacial bond strength in determining toughness can be seen in the enhancement of toughness in laminates as well. Refined models[15,16] are found in brittle matrix composites with all necessary microstructural dependencies. Our interpretation of the enhanced strength of biological laminates requires that a ductile-phase reinforcement be present so that the strength of the composite exceeds that of the strength of the component phases. This behavior has been observed in ceramic-metal composites which have been processed under the presence of strong wetting conditions where a liquid phase has formed between the molten metal and the ceramic phase such as in sintered WC-Co[17-19] and liquid metal-infiltrated B_4C-Al composites.[20-23]

It is therefore apparent that further enhancement of strength and toughness is possible by employing a laminated microstructure with a smaller size scale while keeping the ductile-phase reinforcement, as in B_4C-Al cermets. It will be shown in this study that the properties of laminated B_4C-Al composites indeed exhibit a size dependency in producing desirable enhancements but do so without sacrificing density of the composite. In the following section, therefore, we give a summary of the possible strengthening and toughening mechanisms in the nacre section of the abalone shell and draw certain design guidelines for ductile-brittle laminate materials. This will be followed by a section on the preliminary studies of B_4C-Al laminated structures which already exhibit superior mechanical properties over other existing cermet structures.

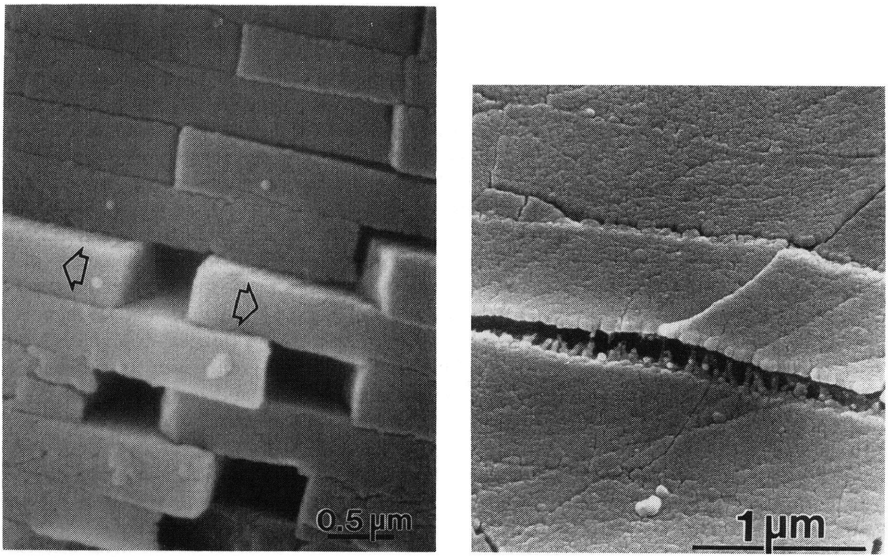

Figure 1. SEM images showing the two possible toughening mechanisms that significantly contribute to the toughening of the nacre section of the abalone shell: (a) sections, (b) ligament formation.

POSSIBLE TOUGHENING MECHANISMS IN LAMINATED MICROSTRUCTURES IN SEASHELL: EXAMPLE, NACRE

Structural components in biological systems such as load-carrying skeletons, grinding components such as teeth, and impact resistant "coats" like seashells, all have highly organized microstructures composed of an organic matrix and an inorganic major phase. In processing these structural components, the organism has full control so that the composite is tailor-made to fulfill certain functions in the body. In all these cases, because of the highly organized microstructures, biological composites have unique properties not yet achieved in synthetic materials. Therefore, it is imperative to examine biological composites to understand the relationship between microstructure and properties. Here we summarize mechanical property-microstructure relations in the nacre of abalone shell, draw some guidelines for laminated materials design, and subsequently apply these to the design and processing of laminated B_4C-Al cermets.

In general, seashells have various microstructures, each designed and processed to have optimum mechanical properties, such as adequate toughness, strength, hardness, or wear-resistance depending on the living environment of the animal. Nacre is a common structure found in many seashells and it primarily provides "toughness" to the shell. In the case of red abalone (*Haliotis refuscens*), the shell in the transverse direction (through thickness) consists of an outer prismatic layer and an inner nacre layer.[12,13] Two forms of $CaCO_3$, calcite and aragonite, constitute the inorganic component of the composite in the prismatic and nacreous layers, respectively.[12] The microstructure and mechanical properties of the nacreous layer are described here only when relevant to the present work.

The nacreous layer is composed of 95% $CaCO_3$ by volume and is organized in a "brick and mortar" configuration with the remaining organic matrix (proteins, macromolecules, and chitin). The $CaCO_3$ layers are individually composed of hexagonal shaped crystallites with a thickness of 0.25 μm. The organic layer between the $CaCO_3$ layers has a total thickness of about 20-50 nm and is composed of several layers of different organic components, the detailed structure of which is still not well understood.[13]

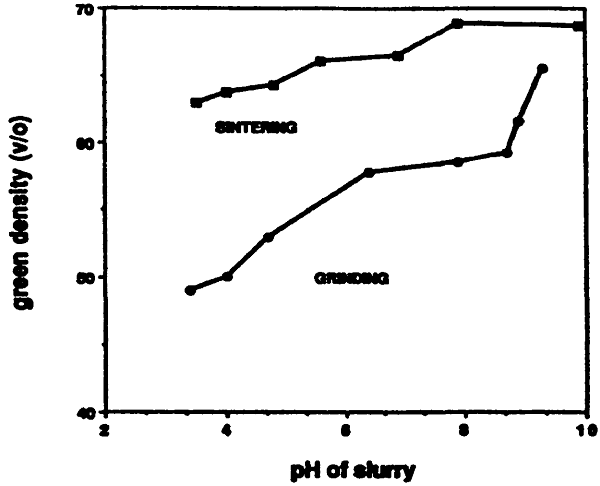

Figure 2. A plot of green-density vs. pH value of the slurry.

The mechanical properties in terms of fracture toughness (a straight notched three-point bend) and fracture strength (four-point bend) have been evaluated in the transverse direction. Typical values of σ_f and K_{IC} are 180 MPa and 7.0 MPa-m$^{1/2}$, respectively. These high values for mechanical properties may be explained based on the behavior of crack propagation during failure. The study of crack propagation features reveals a high degree of tortuosity not seen in monolithic ceramics such as brittle Al_2O_3 or ZrO_2. Certain toughening mechanisms such as microcrack formation, crack branching and blunting, and plate "pull-out" all operate in the nacre. However, the more than 20-fold increase in fracture toughness of the shell, which consists of 95% $CaCO_3$ and 5% organic matrix, compared to monolithic $CaCO_3$, cannot be explained by any of these mechanisms. However, two other mechanisms not usually seen in synthetic composites probably are the causes of the extensive toughness and strength increase. Both sliding of $CaCO_3$ layers on each other and organic "ligament" formation between layers occur when the resolved applied stresses are parallel and perpendicular to the layers, respectively (Figures 1(a) and (b)). The sliding mechanism in the nacre is reminiscent of plastic deformation by the movement of dislocation on slip planes in metals. Therefore, the propagating crack can only advance under constrained crack opening conditions, and only after considerable energy absorption, which results in a toughness increase. Both of these toughening mechanisms require that the organic phase be highly plastic and that the interface between the $CaCO_3$ and the organic phase be "strong."[13] In the above qualitative analysis neither the crystallographic configuration of the individual $CaCO_3$ plates nor the organization of the macromolecules (which are in the liquid crystalline form) is considered.

DESIGN GUIDELINES ON LAMINATED MATERIALS

The unusual combination of mechanical properties in the nacre as compared to synthetic ceramics and composites comes from (i) the intrinsic properties of the component phases (inorganic-brittle and organic-soft), (ii) the unique and highly ordered microstructure, and (iii) the size of the layers. Therefore, a number of design guidelines can be drawn from the study of the seashells. Based on the study of nacre, synthetic composites should possess:

(i) a laminate thickness of the hard-brittle component of less than 1 μm and a soft component of less than 1000 Å;

(ii) a highly plastic soft phase;

(iii) strong interfaces between the soft and the hard phases;

(iv) the ability of the soft phase to bind to the hard phase (strong interfacial bonding) and provide either plasticity to the whole composite (for sliding) or form ligaments to constrain crack opening, depending upon the resolved applied stresses

In practical processing, these guidelines may be difficult to apply. However, they are useful in the sense that they serve as ultimate conditions to be achieved for submicron laminate design. In the present study with B_4C-Al, mimicking lamination even with laminate thicknesses larger than 10 μm resulted in both fracture toughness and fracture strength improvements of more than 40%, as discussed in the next section.

PROCESSING OF LAMINATED B_4C-Al COMPOSITES

Materials

Two types of B_4C powders (supplied by the ESK Company) were used as starting powders. The main difference between the two powders that is of interest for this work was their packing behavior as a function of pH, as shown in Figure 2. ESK 1500 B_4C shows a lower packing green density compared to ESK sintering powder at all pH values.[24] The pH was adjusted with reagent grade HCl or NH_4OH. Rhoplex HA-8, a polyacrylic-based emulsion from Rhom and Haas, was used as a binder. DF-160L foamaster from Henkle was used as a defoamer agent. Finally, aluminum alloy 1100 was used as the source of the metal phase.

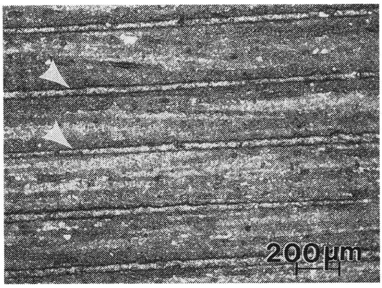

Figure 3. Laminated B_4C-Al composites processed by the first method. Arrows show Al-rich regions.

Fabrication of the Laminated Structure

The laminated composites were formed by three basic methods: (i) Partially sintered B_4C tapes were sandwiched with Al sheets and then heated to induce infiltration. (ii) Green B_4C tapes were stacked, partially sintered, and then metal infiltrated. (iii) Green B_4C tapes of different porosity were laminated (stacked and pressed), partially sintered, and then metal infiltrated.

In the first method, after B_4C tapes were cast, each tape was individually sintered to the desired density between polished graphite discs in order to prevent curling. Sintered tapes were then stacked with Al sheets and the whole stack was then heated to induce infiltration. The resulting structure was a B_4C-Al composite with Al interlayers (Figure 3). In the second method, B_4C tapes were stacked and the entire stack was then sintered. The resulting sintered body was composed of individual tapes of known density which were tightly sintered together but had almost a continuous thin gap between the tapes. The body was then infiltrated with aluminum. The resulting structure was a B_4C-Al composite with a thin (~5 μm) Al interlayer (Figure 4). This method was used when B_4C tapes were thinner than 90 μm. At these thicknesses, tapes could not be sintered by the first method without introducing defects into them. In the third method, tapes of B_4C with different green densities were stacked and laminated under pressure and temperature. The laminated body was then sintered and subsequently infiltrated with Al. The resulting structure is a B_4C-Al composite with graded morphology (Figure 5).

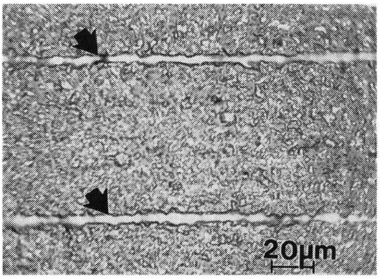

Figure 4. Laminated B_4C-Al composites processed by the second method. Arrows show Al-rich regions.

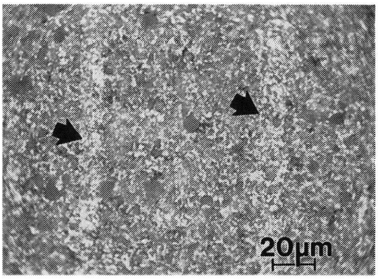

Figure 5. Laminated B_4C-Al composites processed by the third method. Arrows show Al-rich regions.

RESULTS: MICROSTRUCTURES VERSUS MECHANICAL PROPERTIES IN B_4C-Al MICROLAMINATES

The fracture strengths of the B_4C-Al composites were evaluated with four-point bend specimens, having a size of approximately 3 mm × 3 mm × 55 mm with a 1 µm surface finish. The test conditions were as follows: minor span size 12.7 mm, major span size 38.1 mm, and crosshead speed 0.05 mm/min. Fracture toughness was measured using approximately the same size bars with a single straight notch. The notch was cut by a diamond wheel saw with a 250-micrometer width. The tip of the notch was damaged by using 1/4 micrometer diamond paste and a razor blade. The ratio of the notch size to the sample height was 0.33. A three-point bend fixture and a crosshead speed of 0.05 mm/min were used.

Mechanical property testing of laminated B_4C-Al cermets showed an increase in fracture strength and toughness over the same Al-content materials processed with a monolithic morphology. Both the laminated structures with continuous Al layers (methods i and ii) or with graded structures (method iii) showed significant increases in fracture strength over monolithic material (Figure 6). However, the fracture toughness of the structures with continuous Al layers was found to be lower than the monolithic material. Further, as the Al content increased, the value of fracture toughness decreased. This is due to regions in the microstructure where Al is depleted, as shown in the scanning electron microscope (SEM) image (Figure 7). This depleted Al region is partially due to the precipitation of AlB_2 in the Al layers as well as processing defects caused by the infiltration of thin, sintered boron carbide tapes. In a fully dense composite without interfacial reaction products, the Al layers act as effective barrier against crack propagation (Figure 8).

The Al content of laminated samples in Figure 7 was altered by changing the ratio between the Al-rich and B_4C-rich layers in the microstructure. In Figure 9, the fracture strength and fracture toughness values are plotted versus the thickness ratios for laminated samples of Figure 6. It was revealed that a ratio of 6 to 1 of high boron carbide content tape to low boron carbide tape (and hence the Al-rich region in the post infiltration microstructure) with a 33.5 vol. % Al content (Figure 6) results in the highest fracture strength (945 MPa). Samples with a continuous Al layer do not show a maximum in fracture strength and the trend on fracture toughness is the opposite compared to graded samples.

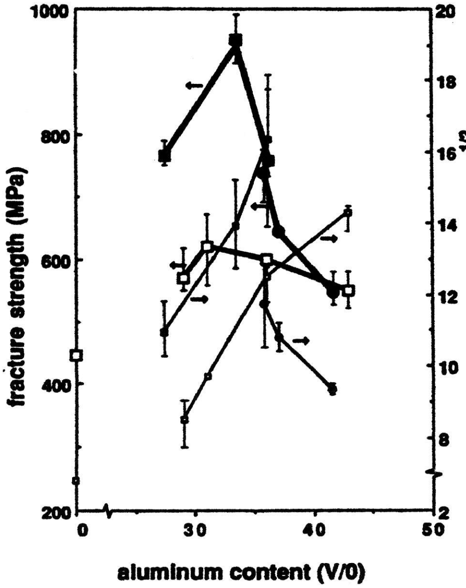

Figure 6. Fracture strength and fracture toughness of B_4C-Al composites. (□) monolith, (●) laminate with continuous Al layers, (■) laminate with graded layers.

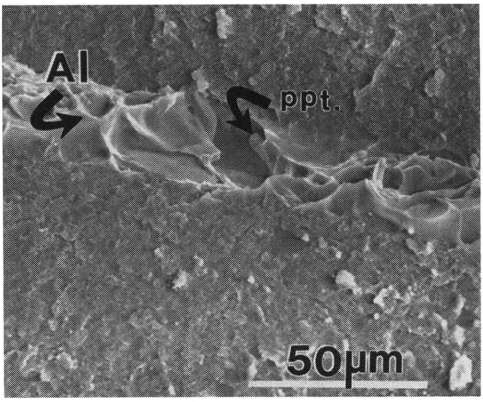

Figure 7. An example of depleted Al region.

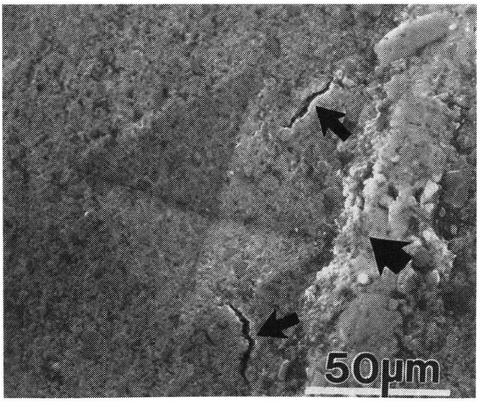

Figure 8. Blunting of a crack at the Al-rich region (SEM image).

After the proper ratio of high B_4C content to low B_4C content (or Al-rich laminae) was determined to be 6 to 1, simultaneous changes in the size of both laminae were made while maintaining the ratio.

The effect of changing the thickness of the laminae on both fracture strength and fracture toughness is shown in Figure 10. As expected from the Hall-Petch relation, the coarsening of the microstructure by increasing the tape thicknesses degraded the mechanical properties, with values approaching those for monolithic samples. Finer 6 to 1 ratio graded laminate structures have not been processed at this time due to the difficulty in casting and handling tapes thinner than 15 μm.

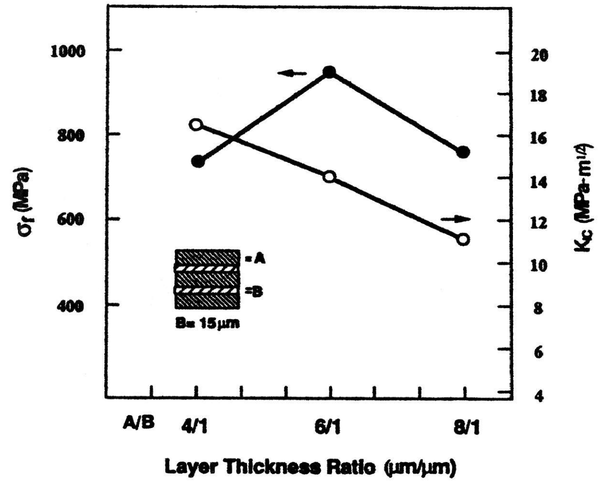

Figure 9. Fracture strength and fracture toughness plotted against B_4C thickness ratios.

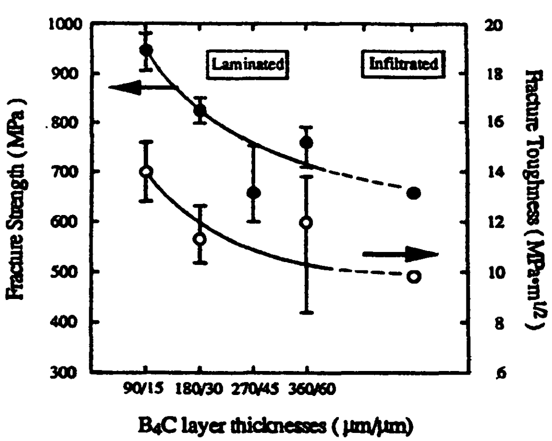

Figure 10. Fracture strength and fracture toughness vs. B_4C thickness plots.

SUMMARY AND CONCLUDING REMARKS

It was illustrated in this work that by processing materials based on the microstructures in biological systems, it is possible to significantly improve their properties. In biological systems, such as in the nacre section of the abalone shell, the microstructure is highly controlled, down to the nanometer scale. In the nacre shell structure, the component phases, $CaCO_3$ (aragonite) and organic matrix (a composite of chitin and macromolecules) form laminates 0.25 μm and 0.05 μm thick, respectively, stacked together to form an overall thickness up to a centimeter. Because of this unique microarchitecture, and also due to the properties of interfaces and the organic layer, unusual toughening and strengthening mechanisms operate, resulting in unexpectedly high mechanical strength and toughness values.

The processed B_4C-Al laminated cermets, based on the design principles outlined in the nacre, also show improvement in mechanical properties, both in fracture toughness and strength. These laminates were processed by tape casting of the B_4C layers which were then infiltrated with molten Al. The resulting microstructure produces layers of B_4C and Al, which are both continuous (unlike in the nacre) and have minimal reaction products at metal-ceramic contacts but still ensures a highly strong interface (like in the nacre).

Neither the fracture toughness nor the fracture strength of the nacre can be predicted based on the known relationships between the fracture toughness and critical flaw size (as in the Griffith relation), nor between the strength and the grain (or laminate) size (as in the Hall-Petch relationship). It should be noted that seashells have many different shapes with different microstructures, but all are based on the same basic components, i.e., $CaCO_3$ and the organic component.[12] Their microstructures have widely varying properties. The organic component can have its own unique "microstructure" in each of these cases. These issues have not been addressed in this paper. Only the gross microstructural features of the nacre have been mimicked in B_4C-Al laminates. In addition, in the case of B_4C-Al cermets, the size of the laminated layer is far from what might be required to achieve the unusual increases in mechanical properties as seen in the nacre. These issues, therefore, call for further detailed studies in the biomimicking area in order to process highly ordered and tailored microstructures to achieve specific, non-isotropic properties in materials.

ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research (AFOSR) and was monitored under Grant Nos. AFOSR-87-0114 and AFOSR-89-0496.

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