Visualizations of Molecular Dynamics Simulations of High-Performance Polycrystalline Structural Ceramics

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Abstract

Initiated by the Department of Defense (DOD) High Performance Computing Modernization Program (HPCMP), the Data Analysis and Assessment Center (DAAC), serves the needs of DOD HPCMP scientists by facilitating the analysis of an ever-increasing volume and complexity of data [1]. A research scientist and HPCMP user ran nanoscale molecular dynamics simulations using Large-scale Atomic/Molecular Massively Parallel Simulator code (LAMMPS) from Sandia National Labs. The largest simulation contained over 70 million atoms (Fig. 7). Data sets this large are required to study crack propagation and failure mechanisms that span multiple length scales with atomic resolution. The DAAC developed new methods to visualize the time evolution of data sets this large. The size and complexity of the molecular dynamics simulations and the analytics required the use of DOD HPCMP High Performance Computing (HPC) resources.

Research Scope and Objectives

Synthetic ceramics are generally strong but brittle and flaw-intolerant materials, rendering them unsuitable for most structural applications, while biomaterials composed primarily of brittle ceramics are able to achieve exceptional combinations of stiffness, strength and toughness. Nature combines materials into complex hierarchical structures to achieve exceptional mechanical properties. The increased demand for stronger and lighter materials is driving researchers to explore new methodologies to increase the toughness and overcome the brittleness of synthetic ceramic materials. In this paper we use a structural mechanics approach to analyze the

properties of different nacre-like material designs for a material composed of silicon and carbon. Molecular dynamics (MD) is used to study the design parameters required to reproduce the mechanistic behavior observed in nacre and identify the parameters necessary to prevent unstable crack propagation in a synthetic silicon carbide (SiC) ceramic. We also investigate the relationship of the tensile strength of the grains and shear strength of the matrix on grain pullout and the strain hardening mechanism produced by the grain shape.

Natural processes for fabricating biological materials take place in aqueous solutions at room temperature using resources available in the environment. These processing requirements result in a large number of biological materials comprised from a comparatively limited range of elements. Nevertheless, many biomaterials exhibit remarkable mechanical properties despite the structural weaknesses of their individual components. Advances in micro- and nano-scale in situ experiments and computational techniques are shedding light on the delicate structure-property relationships required to reproduce the mechanistic behavior found in biomaterials [2,3,4,5,6,7,8,9]. Some underlying strategies are beginning to emerge that reflect general design concepts for achieving optimal performance from materials assembled from components with disparate and seemingly incompatible properties.

Researchers are attempting to engineer synthetic materials using design principles found in nature. Recent manufacturing techniques designed to produce synthetic nacre-like structures such as those designed through ice templating [10,7], thin film deposition [11,12,13], layer-by-layer deposition, and

additive processing [14,15,16,17] techniques show the performance and behavior of nacre can be reproduced using a wide range of material combinations with varying degrees of success [18,14].

The design strategies for nano- micro-engineered synthetic materials are not constrained by the processing requirements of natural materials. Thus, synthetic material designs are free to explore a wide range of structure and material combinations that are not accessible to natural materials. A detailed understanding of the general design concepts and the structure-property-relationships responsible for the mechanistic behavior and mechanical properties observed in nature may result in new composite designs using synthetic materials. In some cases, it may be desirable to replace the constituent materials found in nature with synthetic engineered materials that are amenable to advanced manufacturing techniques. However, the choice of synthetic materials is much more extensive compared to natural materials. In many cases, it may not be possible or desirable to replicate the complex hierarchical structure of biomaterials. The goal is to determine structural arrangements and material combinations that can be achieved using advanced manufacturing techniques to produce structural composites with mechanical properties that exceed both natural and state-of-the-art synthetic materials [19].

The biological “brick- and-mortar” hybrid design is characterized by a layered structure consisting of strong inorganic platelets embedded in a soft, organic matrix. The properties of these materials can be tuned by manipulating the individual components to achieve performance and functionality that are inaccessible to monolithic materials. It is widely recognized that tablet sliding is a key mechanism in the toughness of nacre [20,21,22,23] and that the aspect ratio is used to strike a balance between the widely different strengths of the soft matrix and brittle mineral [24]. It has also been proposed that a strain hardening mechanism on the local scale is required to promote tablet sliding on a large scale. Strain hardening at the local scale is generated by the waviness of the tablet surfaces in natural materials [20]. Studies suggest that the “brick-and-mortar” structure allows large sliding deformation of tablets and suppresses the strain localization and crack

propagation in the brittle inorganic platelets.

In this paper, we conducted a sensitivity analysis to gain insight into the causal relationships between crystalline structure, crystal size, grain boundary properties and the mechanical properties of the ceramic. A parametric study was performed using a two-dimensional representative volume element (RVE) consisting of a 2×2 arrangement of grains to analyze the parameters required to increase fracture toughness and strain hardening at the component level. The results were then tested on a larger system to determine the material response on a larger scale.

The simulations identify the design parameters and failure mechanisms necessary to reproduce the mechanistic behavior responsible for fracture toughness of a “brick-and-mortar” material composed of silicon and carbon. This research was able to identify the parameters that promote flaw tolerance and suppress crack propagation. The research also evaluated the parameters required to promote grain sliding and “dovetail-type” grain locking mechanisms necessary to suppress strain localization and spread crack formation over large volumes. The results indicate that there a number of designs that can produce strain hardening in the material and suggest additional designs that can be used depending on the level of control that can be obtained over the manufacturing process.

HPC simulations coupled with physics-based material models are having a significant impact on the design and performance of micro- and nano-engineered materials. Historically material development has been almost exclusively empirically based, with materials going through cycles of build/test, rebuild/retest to understand material behavior or to achieve performance goals. The tests are usually performed at the macroscale, whereas material response begins at the nano- to micro-scale. High-fidelity physics-based calculations coupled with HPC allow constitutive properties of materials to be determined based on the atomic and molecular structure of the material.

The atomic stress is calculated based on the virial theorem [25] and the equation for the i, j components (where i and $j = x, y$) of the symmetric stress tensor is given by:

$$\sigma_{ij} = \frac{\sum_k^N m_k v_{ki} v_{kj}}{V} + \frac{\sum_k^N r_{ki} f_{kj}}{V}$$

The time average of the atomic stress tensor summed over all the atoms in the system provides a bridge that links results of molecular dynamics simulations with structural mechanics. The maximum and minimum principal stress components are given by:

$$\sigma_p = \frac{(\sigma_{xx} + \sigma_{yy})}{2} \pm \sqrt{\frac{(\sigma_{xx} - \sigma_{yy})^2}{4} + \tau_{xy}^2}$$

and the maximum shear stress is given by:

$$\tau_{\max} = \sqrt{\frac{(\sigma_{xx} - \sigma_{yy})^2}{4} + \tau_{xy}^2}$$

The principal stress is used to evaluate the material performance as a result of variations in design parameters. Simulations of the RVE's were used to analyze the parameters required to increase fracture toughness and strain hardening at the component level. Strain was applied by increasing the length of the RVE's in steps. This was accomplished by scaling the positions of the atoms by an amount that varied along the longitudinal axis of the system depending on the x-coordinate of the atoms. The maximum principal stress was then allowed to approach equilibrium after each strain increment. The equilibration process gave the material time to respond to the increase in strain and to any structural changes that take place during failure processes before increasing the strain. The strain was not allowed to increase until the material had time to respond to bond breaking, defect formation and migration, sliding between grains (intergranular failure) and grain fracture (transgranular failure), and the resulting structural changes that take place during these processes.

While the principal stress provides a quantitative measure of material performance (Fig. 1), visualizing the time evolution of atomic stress provides qualitative information that allows the failure mechanisms to be observed with atomic resolution. This information provides valuable insight into the evolution of stress and the subsequent failure mechanisms resulting from the applied strain. Visualizing the time evolution of atomic stress provides information on the design parameters that suppress and arrest crack growths as well as the impact the parameters have the load transfer between grains and defect migration (Fig. 3). It also provides

valuable information on the effect the design parameters have on producing stress concentrations that can lead to crack initiation and propagation (Fig. 4). The results of the of the RVE simulations were evaluated to narrow the scope of the parameters to the design parameters that promote grain sliding, suppress strain localization and spread crack formation over large volumes before attempting to run larger simulations (Fig. 5-7).

Visualization Process

The simulation results were used to produce still images and animations of the position of the atoms over time. Visualizing the simulation data from LAMMPS required the development of a custom program to extract the 3D position and the energy value of each atom. To represent each atom on a rendered image, a sphere was generated in VTK using the 3D position as the center point of the sphere. In addition, aesthetics determined the radius of the spheres.

To create the appearance of a mesh, VTK primitive tubes, which represented the bonds between the atoms, were used to connect them. Atoms within 2.8 angstroms of each other were connected using a version of the k-nearest neighbor algorithm. This algorithm first sorted the atoms into buckets, based solely on their Cartesian position, which prevented the exponential increase in runtime complexity. Next, the straight-line distance between each atom in the bucket was calculated. The atoms located within the desired range were connected with a tube using VTK.

Colors were applied to the spheres and tubes based on the energy and stress values. The tubes were a special case because the ends of the tubes were colored the same as the atoms they were connecting, which, in some cases, required two differently colored atoms. VTK automatically colored the rest of the tube by smoothly blending from one end to another. After the color was applied, the geometry was appended into a PLY file (Stanford ASCII Polygon Format).

Using this process to prep the data for visualization worked well until the atoms numbered over 15 million, at which point the run-time of the analytics increased beyond an acceptable measure. A modification was needed; therefore, a new step was added that placed each atom into one of 100 possible lists. Each list contained atoms from inside a

boundary that represented $\sim 1/10$ of the x and y domain ranges. Atoms along the boundaries were also included in adjacent lists to ensure the program created tubes between all qualifying atoms. Then, HPCMP systems processed each list according to the previously described custom program. The advantage of using HPC systems is that it allowed the program to run parallel on multiple cores and make full use of the large amount of RAM available. Likewise, using HPC systems reduced runtime to a few hours instead of a few days.

Visualization Results and Impact

Figure 2 shows the final result for a relatively small data set containing 143,536 atoms. In this simulation, the material was subjected to an external force that continued until the structure failed. The spheres and tubes were colored by the stress applied in the horizontal direction.

Figure 3 represents a change in the processing steps. The simulation contained over 256,080 atoms, which required the use of cubes instead of spheres to reduce the polygon count. The number of polygons in each tube was also reduced.

Figures 2 and 3 were created by importing the PLY files into Autodesk's 3D Studio Max (3DS Max). Once the geometry was imported, a light was added to the scene, and an image was rendered and saved.

These images allowed the researcher to see the results of the simulations in a much higher quality than ever before. This is significant because high resolution images allow the entire result of the simulation to be seen at once, instead of smaller images where tiny details may go unnoticed. In addition, a movie was made from each set of results, which allowed the simulations to be viewed in high definition.

Visualizing the large simulation that contained 15,102,976 atoms presented a unique opportunity to render the final time step in ultra high definition. The goal was to view the image on a 4K monitor to allow the observer to see the results in as much detail as possible. Representing 15,102,976 atoms and their connecting tubes required over 350 million polygons. Normally, this is considered overkill because there are not 350 million pixels on the screen. In this case, high-resolution graphics are required to capture

failure mechanisms that operate across multiple length scales covering three orders of magnitude. Material failure is initiated with bond breaking at the atomic level (10^{-10} M). Interactions between the structural elements are designed to produce toughening mechanisms that operate at the nanoscale (10^{-9} M). The evolution of these cracks produces fracture patterns at the microscale (10^{-6} M). The high-resolution graphics capture the synergy between these mechanisms across multiple length scales, and provide a better understanding of the failure mechanism and design requirements for advanced materials. Figure 5 shows the result. The red and green boxes identify two areas of interest discovered while viewing the image on a 4K monitor. The researcher verbalized how these details would have been otherwise overlooked at normal rendering resolutions.

The total number of atoms in Dr. Cornwell's simulations have continued to increase. The process described above works well for less than 20 million atoms. The new simulations contain more than 70 million atoms. A new method was developed to visualize the results.

The DAAC supports a visualization program named VisIt [1]. This program can visualize data that resides on the HPC systems in a client-server mode. The DAAC developed a VTK script to translate the LAMMPS output into VTK files. Each atom is represented by a VTKPoint object. The atoms are colored by stress, which is appended to each point as a scalar value. The VTK files are then opened up in VisIt. Figures 4, 6, and 7 illustrate the results. VisIt accomplishes the monumental feat of drawing more than 70 million atoms (Fig. 7) at once by representing each atom with a "sphere imposter," which is a 2D representation of a 3D sphere.

Why HPC Matters

Usually, material development has been exclusively build/test, then rebuild/retest to understand the behavior of the material and to achieve performance goals. Such physical experimentation is relatively slow and costly. For Dr. Cornwell, access to HPC systems allows the simulations to be performed at the nano-to-micro scale, where material response begins.

The HPC resources and high-resolution graphics improve the quality of research by extending the size and complexity of problems that can be solved with the aid of modeling and simulation.

HPC systems, also aid visualization efforts, that allow large data sets, which contain millions of points and polygons, to be processed and rendered quicker than ever before. The DAAC continues to improve on techniques and adopt new strategies that take advantage of the opportunities that HPC offers.

Conclusion

An integrated computational experiment approach to materials science has the potential to accelerate materials development, improve design optimization, and unify design and manufacturing. The traditional approach to materials development cannot keep pace with the demand for advanced materials. This is driving the search for a new solution to materials development. Biomaterials are constructed from a relatively small set on elements using a wide range of hierarchical structures. The structure-property relationships of these materials are designed for a specific set of loading conditions. Developing nano- micro-engineered materials will require a detailed understanding of the delicate structure-property relationships required to reproduce the mechanistic behavior and the mechanical properties of materials found in nature. It will also require the manufacturing technology necessary to rapidly and systematically produce these structures.

High-fidelity physics-based simulations coupled with HPC allow constitutive properties of materials to be determined based on the atomic and molecular structure of the material. High-resolution graphics allow the time evolution of the failure mechanisms to be observed with atomic resolution. This provides valuable information on structure-property relationships required to develop the general design concepts in terms of the relative properties of the constituent materials. A detailed understanding of the structure-property relationship in terms of the relative properties of the materials would provide the necessary data descriptors for data driven discovery. Data driven discovery has the potential to further accelerate the discovery of advanced materials.

Atomistic simulations complement experimental efforts to develop advanced materials and guide the

design optimization of materials. The results of this project demonstrate the potential benefit of an integrated computational experiment approach to materials development. Access to HPC resources coupled with physics-based material models and high-resolution graphics extends the size and complexity of problems that can be solved with the aid of modeling and simulation.

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References

- [1] DAAC. Welcome to DAAC (Data Analysis and Assessment Center). [Online]. <http://daac.hpc.mil/>
- [2] Espinosa, Horacio D.; Juster, Allison L.; Latourte, Felix J.; Loh, Owen Y.; Gregoire, David; Zavattieri, Pablo D., "Tablet-level origin of toughening in abalone shells and translation to synthetic composite materials," *Nature Communications*, vol. 2, no. 173, p. 1, Feb 2011.
- [3] D. Grégoire, O. Loh, A. Juster, and H.D. Espinosa, "In-situ AFM Experiments with Discontinuous DIC Applied to Damage Identification in Biomaterials," *Experimental Mechanics*, vol. 51, no. 4, pp. 591-607, 2011.
- [4] Zaiwang Huang and Xiaodong Li, "Origin of flaw-tolerance in nacre," *SCIENTIFIC REPORTS*, vol. 3, no. 1693, 2013.
- [5] Denvi Lau, Oral Büyükoztürk, and Markus J. Buehler, "Characterization of the intrinsic strength between epoxy and silica using a multiscale approach," *Journal of Materials Research*, vol. 27, no. 14, pp. 1787-1796, 2012.
- [6] Horacio D. Espinosa, Jee E. Rim, Francois Barthelat, and Markus J. Buehler, "Merger of structure and material in nacre and bone –

- Perspectives on de novo biomimetic materials," *Progress in Materials Science*, vol. 54, no. 8, pp. 1059-1100, 2009.
- [7] S. Deville, J. Adrien, E. Maire, M. Scheel, and M. Di Michiel, "Time-lapse, three-dimensional in situ imaging of ice crystal growth in a colloidal silica suspension," *Acta Materialia*, vol. 61, no. 6, p. 2077, 2013.
 - [8] Maximilien E. Launey, Markus J. Buehler, and Robert O. Ritchie, "On the Mechanistic Origins of Toughness in Bone," *Annual Review of Materials Research*, vol. 40, p. 25, 2010.
 - [9] Maximilien E. Launey and Robert O. Ritchie, "On the Fracture Toughness of Advanced Materials," *Advanced Materials*, vol. 21, pp. 2103–2110, 2009.
 - [10] Sylvain Deville, "Freeze-Casting of Porous Biomaterials: Structure, Properties and Opportunities," *materials*, vol. 3, pp. 1913-1927, 2010, Review - freeze-casting.
 - [11] Kotov Nicholas A., Magonov Sergei, Ozturk Birol Tang Zhiyong, "xx".
 - [12] Paul Podsiadlo et al., "Ultrastrong and Stiff Layered Polymer Nanocomposites," *SCIENCE*, vol. 318, pp. 80-83, 2007.
 - [13] Lorenz J. Bonderer, André R. Studart, and Ludwig J. Gauckler, "Bioinspired Design and Assembly of Platelet Reinforced Polymer Films," *Science*, vol. 319, pp. 1069-1073, 2008.
 - [14] I Corni et al., "A review of experimental techniques to produce a nacre-like structure," *Bioinspiration & Biomimetics*, vol. 7, 2012, TOPICAL REVIEW.
 - [15] Nahum Travitzky et al., "Additive Manufacturing of Ceramic-Based Materials," *Advanced Engineering Materials*, pp. 1-26, 2012.
 - [16] Jianfeng Wang, Qunfeng Cheng, and Zhiyong Tang, "Layered nanocomposites inspired by the structure and mechanical properties of nacre," *Chem. Soc. Rev*, vol. 41, pp. 1111–1129, 2012.
 - [17] Alberto Ortona, Claudio D'Angelo, Sandro Gianella, and Daniele Gaia, "Cellular ceramics produced by rapid prototyping and replication," *Materials Letters*, vol. 80, pp. 95–98, 2012, hybrid methodology that can realize cellular ceramic structures of any shape by combining 3D printing of polymer inks with replication.
 - [18] Jee E. Rim, Pablo Zavattieri, Allison Juster, and Horacio D. Espinosa, "Dimensional analysis and parametric studies for designing artificial nacre," *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 4, no. 2, pp. 190-211, February 2011, combination of simulations and experiments.
 - [19] Hongqing Wang, Yong Chen, and David W. Rosen, "A Hybrid Geometric Modeling Method for Large Scale Conformal Cellular Structures," in *ASME 2005 International Design Engineering Technical Conferences and Computers and Information in Engineering Conference*, vol. 3, 2005, scale up: hybrid geometric modeling method to create CAD models of large-scale conformal cellular structures.
 - [20] Tang H. , Zavattieri P.D. , Li C.-M. , Espinosa H.D. Barthelat F., "On the mechanics of mother-of-pearl: A key feature in the material hierarchical structure," *Journal of the Mechanics and Physics of Solids*, vol. 55, pp. 306-337, 2007.
 - [21] Vincent J. F. V., Turner R. M. Jackson A. P., "Comparison Of Nacre With Other Ceramic Composites," *Journal Of Materials Science*, vol. 25, pp. 3173-3178, 1990.
 - [22] Chang-an Wang, Yong Huang, Qingfeng Zan, Hai Guo, and Shengyou Cai, "Biomimetic structure design — a possible approach to change the brittleness of ceramics in nature," *Materials Science and Engineering C*, vol. 11, pp. 9-12, 2000, two kinds of ceramic composites: Si₃N₄/rBN composite imitating bamboos, laminated Si₃N₄/rBN composite imitating nacre in structure.
 - [23] S.P. Kotha, S. Kotha, and N. Guzelsu, "A shear-lag model to account for interaction effects between inclusions in composites reinforced with rectangular platelets," *Composites Science and Technology*, vol. 60, no. 11, pp. 2147–2158, 2000.
 - [24] Huajian Gao, "Application of fracture mechanics concepts to hierarchical biomechanics of bone and bone-like materials," *International Journal of Fracture*, vol. 138, pp. 101–137, 2006, Fracture mechanics concepts are applied to gain some understanding of the hierarchical nanocomposite structures of hard biological tissues such as bone, tooth and shells.
 - [25] A. P. Thompson, S. J. Plimpton, and W. Mattson, "General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions," *J Chem Phys*, vol. 131, p. 154107, 2009.

Figure 1 The principal stress provides an average measure of material performance for the entire system. The first drop in stress is due to the failure in tension of the amorphous SiC grain boundary at the ends of the grain. This is followed by strain hardening due to the increase stress gradient along the grain boundary at the top and bottom of the grain. The second decrease in stress is due to failure of the grain boundary in shear at the top and bottom of the grains. The subsequent increase in stress is due to the compressive forces produced as the two dovetails attempt to slide past one another during grain sliding. The material fails once the grain breaks or the grains completely pull apart.

Figure 2: Structural Failure of Dovetail Geometry. The visualization shows the grain boundary fail in tension followed by failure of the grain in tension. This occurs when the angle of the dovetail or shear strength of the grain boundaries are too high to allow the grains to slide. (Dimensions: 50.8 nm x 19.3 nm x 1.5 nm)

Figure 3: Structural Failure of Modified Dovetail Geometry Pattern. The visualization shows shear failure of the dovetail section of the grain, load transfer across the grain boundary, and the migration of defects in the crystal structure of the grain. (Dimensions: 50.8 nm x 34.5 nm x 1.5 nm)

Figure 4: Close view in VisIt illustrating failure by sheering. The grain shears along a crystal plane. The two halves of the grain shift relative to each other and form a notch at the bottom center of the grain. This notch acts as the initiation point for a crack that forms later in the simulation.

Figure 5: 16x HD Rendering of large-scale simulation revealing previously unobserved behavior. Distortions at the local level causes failure of the grain boundaries, between the top and bottom of the grains, in tension rather than shear as shown in the insets. (Dimensions: 406.4 nm x 254.4 nm x 1.5 nm)

Relative Stress

Figure 6: Simulation results for a system containing 16X32 arrangement of grains that were $250\text{\AA}$ long with an aspect ratio of 8 and a dovetail angle of 32 degrees. The dovetail structure allows large sliding deformation of grains, produces strain hardening, and suppresses the strain localization.

Relative Stress

Figure 7: The simulation of a 6X18 array of grains that were $1500\text{\AA}$ long and $250\text{\AA}$ wide. The entire system contained 73654704 atoms. The shallow dovetail angle of 6 degrees allowed for a much more gradual compression of the grains during grain sliding. As with the other larger simulations, the design produced large sliding deformation of grains, strain hardening, and suppresses the strain localization. (Dimensions: $0.9120\mu \times 0.5537\mu \times 1.5\text{ nm}$)