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13. ABSTRACT (Maximum 200 words) The grant was initiated on May 1, 1999. In view of the fact that high temperature microindentation testers are no longer in commercial production, we have instead designed, purchased and received an atomic force microscope (AFM) from Digital Instrument. This instrument is configured to perform nanoindentation tests to obtain information on deformation resistance in both elastic and plastic range. The instrument was installed in September 1999 and personnel have been trained to operate the instrument at the same time. We have proceeded with nanomechanical characterization of the bulk silicon nitride and SiAlON's and their interfacial properties. This includes a study of the intergranular glassy phase that is often thought to be a critical factor in determining their mechanical performance.				
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**I. TITLE OF PROJECT**

***A High Temperature Microhardness Tester for Structural Ceramics***

***PROGRESS REPORT***

***September 1, 1999-AUGUST 31, 2000***

***& Final REPORT***

***May 15, 1999-AUGUST 31, 2000***

***U.S. AIR FORCE GRANT NO. F49620-99-1-0269***

**PRINCIPAL INVESTIGATOR**

**I-WEI CHEN**

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## **II. OBJECTIVES**

We will develop nanoindentation and related techniques to investigate the mechanical properties of the new in-situ toughened  $\alpha'$ -SiAlON and other ceramics in the bulk and near the interface. Performance and processing of these materials are often dependent on their intrinsic mechanical properties of the grains and their interfaces. Many of these properties, such as deformation resistance, interfacial friction and debonding strength, fracture toughness and crack deflection can be readily measured using a nanoindentation device.

## **III. STATUS OF EFFORT**

The grant was initiated on May 1, 1999. In view of the fact that high temperature microindentation testers are no longer in commercial production, we have instead designed, purchased and received an atomic force microscope (AFM) from Digital Instrument. This instrument is configured to perform nanoindentation tests to obtain information on deformation resistance in both elastic and plastic range. The instrument was installed in September 1999 and personnel have been trained to operate the instrument at the same time. We have proceeded with nanomechanical characterization of the bulk silicon nitride and SiAlON's and their interfacial properties. This includes a study of the intergranular glassy phase that is often thought to be a critical factor in determining their mechanical performance.

## **IV. ACCOMPLISHMENTS/NEW FINDINGS**

### *Development of Nanoindentation and Imaging techniques using AFM*

We have developed techniques using an atomic force microscope to obtain accurate displacement and nanoindentation measurements. The best displacement resolution obtained is of the order of 1 pm, using techniques involving lock-in amplifiers. This is sufficient for applications that involve piezoelectricity of thin films. For nanoindentation, we have used a diamond tip to map the hardness of silicon nitride across a grain boundary. Much larger depression is seen near the grain boundary, suggesting a softening effect due to the relaxation of mechanical constraints. The measured nanoindentation hardness values are usually higher than the microindentation hardness values, confirming the size effect that is most likely related to nucleation of plasticity. Lastly, the theory of near surface polarization due to a charged, conducting AFM tip has been developed. The nanoindentation technique is also being used to investigate the apparent dependence of microindentation hardness on fracture toughness and microstructure seen in some silicon nitride.

### *Nucleation Control of Microstructure*

The essence of microstructure control that enables the formation of in-situ toughened  $\alpha'$ -SiAlON is to control nucleation of  $\alpha'$  phase so that relatively few nuclei compete for growth. There are three general ways to achieve this goal. First, starting powders can be chosen to be energetically more stable or crystallographically less similar to the product phase. This implies that  $\beta$ -Si<sub>3</sub>N<sub>4</sub> powders are better as the starting powders. The second method is to choose a composition with less stability for the  $\alpha'$  phase. This dictates the choice of larger cations or compositions near the phase boundary. An extension of the second approach is to take advantage the temperature

dependence of the phase stability. This dictates the use of lower temperature for nucleation. We have demonstrated that these three approaches, individually or in combination, with various conceivable variations, can be practiced to render any single phase  $\alpha'$ -SiAlON composition amenable to obtaining a fibrous microstructure.

We have found that for highly stable single phase  $\alpha'$ -SiAlON compositions the above approaches can not be practiced because the driving force is too large and nucleation rate too fast. In such a case, we have introduced seed crystals of single phase  $\alpha'$ -SiAlON composition to predetermine the nucleation statistics. This approach has proved successful. As a result, we are now able to obtain high toughness single phase  $\alpha'$ -SiAlON ceramics of any composition using either  $\alpha$  or  $\beta$ - $\text{Si}_3\text{N}_4$  powders.

A parallel effort has been made to prepare  $\alpha'$ -SiAlON seeds of an appropriate size and shape. It is noted that, to be effective, seeds must have the same composition of the final phase, or have a composition that is thermodynamically more stable. This is a difficult task compared with the other seeding efforts reported in the literature, where the seeding can be provided simply by using compounds of an appropriate phase, e.g.  $\beta$ - $\text{Si}_3\text{N}_4$  or  $\alpha$  SiC. In our case, such compounds invariably dissolve, so the seeds need to have a composition that is stable, i.e., it should be an  $\alpha$ - $\text{Si}_3\text{N}_4$  solid solution itself. This task has been succeeded and a method for obtaining high-yield seed crystals of a variety size, shape and compositions have been developed. The physical chemistry of seed formation and growth has been investigated.

Our research on  $\alpha'$ -SiAlON has also systematically explored the difference between compositions involving (a) rare earth cations of different sizes and (b) alkali earth cations, primarily Ca. The stability of the single phase  $\alpha'$ -SiAlON varies significantly and this has a major impact on the phase nucleation and microstructural development of the ceramics. In addition, the kinetics are influenced by the different liquid viscosity due to the presence of different cations. By controlling these factors separately, it is now possible to obtain the desired microstructure for all the rare-earth cation  $\alpha'$ -SiAlON and for Ca- $\alpha'$ -SiAlON.

#### Mechanical Properties of $\alpha$ -SiAlON

We have investigated the mechanical properties of  $\alpha$ -SiAlON using three methods. Preliminary hardness and toughness data were obtained using the indentation method. Although toughness is usually underestimated by this method, the systematic trend between ceramics of different compositions and different microstructures is usually preserved. A more systematic investigation has been made using R-curve measurements. This was performed in-situ under a microscope in the four-point bending configuration. The R-curves show a very strong correlation with the microstructure and are sensitive to the compositions. The values at small crack extension, approximately 50-100  $\mu\text{m}$ , appear to correspond well to the values of indentation toughness. Very high toughness of 11-12  $\text{MPa m}^{1/2}$  is seen in some microstructures, which compares favorably with the toughness of in-situ toughened  $\beta$ -silicon nitride. Finally, three-point bending has been performed to obtain strength data at room temperature and elevated temperatures, up to 1350  $^\circ\text{C}$ . Strength values

exceeding 1 GPa have been obtained in some ceramics, which can be retained (up to 70%) at high temperatures. Further optimization of the strength-toughness combination seems possible but has not been performed.

#### Thermodynamics of Anisotropic $\text{Si}_3\text{N}_4$ Crystals

The recent observation of Wang, Tien and Chen on  $\beta$ - $\text{Si}_3\text{N}_4$  showed that an elongated rod grown from the liquid can have a concave end. Such morphology implies that material transport must come from the corner, and it in turns implies long range surface diffusion along the side surface. Interface control is obviously an important factor in directing growth anisotropy. We have developed a thermodynamic theory for the chemical potential of surface atoms of an anisotropic crystal, with and without facet, under equilibrium and non-equilibrium conditions. The equilibrium shape has been obtained, and criterion for shape evolution has also been formulated. Using this theory, the evolution of the aspect ratio of grains during phase transformation and Oswald ripening can now be understood. In addition, the case of interface control can also be rigorously treated with respect to the underlying equilibrium conditions to account for different growth scenarios. This theory has been extended to silicon carbide as well. Experimental effort to determine the shape evolution of several anisotropic growth systems is in progress.

#### Microstructure Determination of $\alpha'$ -SiAlON

We have developed a new chemical etching technique that reveals the microstructure clearly under a light microscope. The new technique takes advantage of the bonding difference between nitride and oxide to differentially dissociate the Si-O-Si bond and the Si-N-Si bond. Alternatively, the nitrogen bond can be converted to oxygen bond resulting in a large change in refractive index. This technique makes it feasible to perform quantitative microscopy using image analysis softwares.

A new development in quantifying the microstructure of anisotropic grains has been made. Such microstructure must rely upon information on two-dimensional cross sections. Previous methods measured rectangular shapes on such cross sections; the statistics of such shapes are compared, using reverse transformation, with postulated three-dimensional shape statistics. We have shown that a linear intercept method works equally well for self-similar shapes. The advantage to the linear intercept method is that it is much faster for data collection, and it has much better sampling statistics.

#### **V. PERSONNEL SUPPORTED**

I-Wei Chen (Principal Investigator)  
Joosun Kim (Post-Doc)  
Roman Shuba (PhD student)  
Misha Zenotch (Visiting research student)

## **VI. PUBLICATIONS**

- (a) I-Wei Chen and A. Rosenflanz, "A Tough SiAlON Ceramic Based on alpha  $\text{Si}_3\text{N}_4$  with a Whisker-like Microstructure," *Nature*, 389, 701-04 (1997).
- (b) L-L. Wang, T-Y- Tien, and I-Wei Chen, "Morphology of Silicon Nitride Grown from a Liquid Phase," *J. Amer. Ceram. Soc.* 81 [10] 2677-86 (1998).
- (b) I-Wei Chen, "Modeling Challenges in Ceramic Materials Innovation," *Current Opinion in Solid State & Materials Science*, 3, 538-43 (1998).
- (c) A. Rosenflanz and I-Wei Chen, "Phase Relationships and Stability of  $\alpha'$ -SiAlON," *J. Amer. Ceram. Soc.* 82 [4] 1025-36 (1999).
- (d) I-Wei Chen and M. Engineer, "Model for Fatigue Crack Growth in Grain-Bridging Ceramics," *J. Am. Ceram. Soc.*, 82 [12] 3549-60 (1999).
- (e) A. Rosenflanz and I-Wei Chen, "Kinetics of Phase Transformations in SiAlON Ceramics I. Effects of Cation Size, Composition and Temperature," *J. Europ. Ceram. Soc.*, 19, 2325-35 (1999).
- (f) A. Rosenflanz and I-Wei Chen, "Kinetics of Phase Transformations in SiAlON Ceramics II. Reaction Paths," *J. Europ. Ceram. Soc.*, 19, 2337-48 (1999).
- (g) J-S. Kim and I-Wei Chen, "Microstructure Control of In-Situ Toughened  $\alpha$ -SiAlON Ceramics," *J. Amer. Ceram. Soc.*, 83 [7] 1819-21 (2000).
- (h) L-L. Wang, T-Y. Tien, and I-Wei Chen, "Reply to Comment on "Morphology of Silicon Nitride Grown from a Liquid Phase,"" *J. Amer. Ceram. Soc.*, 83 [3] 677-78 (2000).
- (i) M. Zenotchkine, R. Shuba, J-S. Kim and I-Wei Chen, "R-Curve Behavior of In-situ Toughened  $\alpha$ -SiAlON Ceramics," *J. Am. Ceram. Soc.*, submitted (2000).

## **VII. INVITED TALKS BY PI**

- (a) "Innovations in Processing of Structural Ceramics with High Aspect Ratio Features," International Symposium on Novel Synthesis and Processing of Ceramics, Kurume, Japan, October 1997.
- (b) "Paradigms of Innovations in Materials Research," plenary lecture, Annual Meeting of the Chinese Society for Materials Science, Tainan, Taiwan, November 1997.
- (c) "Phase Relations and Phase Stability in SiAlON Systems," Annual Meeting of the American Ceramic Society, Cincinnati, OH, May 1998.

- (d) "Silicon Nitride at sub 1400°C--Issues and Possible Solutions," Workshop on Ultra High Temperature Ceramics, May 1998, Boulder, CO, May 1998.
- (g) "Silicon Nitride -- A Matter of Kinetics," Conference on New Developments in High Temperature Ceramics, Istanbul, Turkey, August 1998.
- (h) "Silicon Nitride and SiAlON," plenary lecture at the First International Conference on Inorganic Materials, Versailles, France, September 1998.
- (i) "Innovations in Structural Ceramics and Composites," Brown University, Providence, April 1999.
- (j) "Near Surface Ferroelectricity--Theory and AFM Characterization," MRS Fall Meeting, Boston, November 2000.

### ***VIII. TRANSITIONS, PATENTS, AND HONORS***

Samples of in-situ toughened  $\alpha'$ -SiAlON have been provided to a leading US cutting tool manufacturer and a leading German cutting tool manufacturer to evaluate their cutting performance. This evaluation process is on-going as the cutting applications are material specific, depending on the work piece as well as the tool. Thus, composition, microstructure and property optimization is required for each cutting application.

Several patent applications on in-situ toughened  $\alpha'$ -SiAlON have been filed at the US Patent Office. International patents have also been filed. One US patent has been issued. (No. 5,908,798, "In-situ Toughened Alpha Prime Sialon Based Ceramics," I-Wei Chen and Anatoly Rosenflanz.)

Collaborative research with Prof. R. Riedel of Damstadt Technical University of Germany has resulted in the discovery of a new structure of solid solution of Si-Al-O-N. A patent application has been filed with Prof. Chen as a co-inventor.