The Mechanical Behavior of Surface-Modified Ceramics

Grant No. DE-FG02-86ER45252
FINAL REPORT FOR PERIOD
June 1, 1990 - May 31, 1994

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1. Project Title: The Mechanical Behavior of Surface-Modified Ceramics

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4. Project Overview

A. Project Objectives:

To understand crack nucleation, formation and growth on the surfaces of brittle materials that are being acted on by macroscopic residual stresses and relate this behavior to the failure criterion and strength distribution parameters.

B. Relationship to DOE Mission:

Ceramic materials are playing an increasingly important role in the development of new energy systems and technologies, e.g., solid state electrolytes in energy storage applications, high temperature engine components, nuclear waste disposal, high temperature superconductors, thermal barrier coatings, etc. Within these applications, the mechanical behavior of these materials is often a critical factor in their successful use. In particular, ceramic materials are often subjected to macroscopic residual stresses and indeed, if these stresses are compressive, are used to strengthen the materials. Prior to the current work, it was realized that fracture under the action of these residual stresses was not understood in a fundamental way. In the current project, there is a strong emphasis on understanding how the residual stresses influence strength variability and damage tolerance of brittle materials. This approach also allows the development of guidelines such that new materials could be designed to satisfy specific requirements, especially in the areas of improved material reproducibility and enhanced structural reliability.

C. Relationship to Other DOE Projects:

Within the Materials Science Programs funded by the Office of Basic Energy Sciences, there are several projects that are considering various aspects of the mechanical behavior and reliability of ceramic materials. For example, there are projects at the following institutions;

- University of Illinois on high temperature mechanical behavior (Socie, Stubbins),
- LBL on fatigue (Ritchie),
- ORNL on toughening mechanisms (Becher et al.),
- Carnegie Mellon on ceramic-matrix composites (Steif),
- Michigan State University on breakdown in random media (Duxbury)
- University of Michigan on design of oxide ceramics (Chen)
- North Carolina on crack growth resistance in ceramics (Scattergood)
- Rockwell International Science Center on fatigue in ceramics (Cox et al.)
- University of Utah on zirconia composites (Shetty)

Clearly the work in the current project is also of importance to DOE programs, in which the use of ceramics is being contemplated. Examples can be found in various sectors of the overall DOE research program, e.g., conservation (batteries, engine components, fuel cells), renewable energy resources (energy storage), fossil energy (MHD), transportation, engines, etc.

D. Project History

1) DOE Funding

Direct Research Funding: \$409,071

Overhead: \$122,562

Total Funding: \$531,633

2) Current Contract DE-FG02-86ER45252

Performance Period June 1, 1986 - May 31, 1994

5. Scientific and Technical Content

A. Major Activities

The work in the project has been focussed on the following areas

- 1) Indentation fracture behavior of ion-exchanged glasses,
- 2) Strength variability of residually-stressed brittle materials,
- 3) Fracture behavior of SiC-coated graphite,
- 4) Sub-critical crack growth in stress-free and ion-exchanged glasses.

B. Scientific Issues

The mechanical behavior of ceramics can be strongly influenced by the presence of macroscopic residual stresses and yet there has been few attempts to understand the effect of these stresses on crack nucleation, formation and propagation. It is of particular importance to be able to incorporate the effect of these stresses into existing fracture mechanics theory, as this is the key framework for being able to predict the reliability of brittle materials. The lifetime of brittle materials is often controlled by their resistance to sub-critical crack growth and again, the role of residual stresses in influencing this type of crack growth is poorly understood.

In the design of structures involving ceramics, there has been substantial concern about the wide variability in the strength of these materials and initial work in this project showed that residual stresses could increase this variability. It was clearly important to define the material parameters that needed to be controlled, so that residual stresses could be introduced in an optimum way. Clearly, it would be of particular interest to determine whether the residual stress profiles could be designed in such a way as to decrease strength variability.

Ceramic coatings and films are often used to improve the resistance to various degradation processes, e.g., thermal barrier coatings, corrosion-resistant coatings, scratch-resistant coatings, etc. These coatings are often in a state of residual stress and it is critical to understand the material parameters that control the fracture behavior of these materials. In particular, it would be particularly useful to identify situations in

which cracks could be arrested so that the damage tolerance of these coatings could be improved.

C. Experimental and Theoretical Approach

1) Indentation fracture behavior of ion-exchanged glasses

The approach was to use indentation cracks to study the behavior of cracks on residually-stressed surfaces. The idea was to establish the basic mechanics so that the effect of the residual stresses could be incorporated into the existing indentation fracture mechanics theory. There was also a strong emphasis on direct observation of the crack formation and propagation process, measuring the changes in crack size and shape during loading. The loading was to be accomplished using a custom-designed, fully-instrumented device that could be mounted on an optical microscope.

2) Strength variability of residually-stressed brittle materials

It was recognized early in the project that macroscopic residual stresses often act to increase strength variability and yet there were no theories available to allow this effect to be incorporated into the structural and material design methodology. Thus, the overall fracture process on residually-stressed surfaces was also to be evaluated theoretically to determine the role of the residual stresses on strength, especially in terms of its effect on strength variability. It was expected that this approach would also allow residual stresses to be introduced in an optimum way into ceramic components and that the subsequent fracture behavior could be predicted.

3) Fracture behavior of a SiC-coated graphite

It was known that ceramic coatings and films are often in a state of macroscopic residual stress after their fabrication. The aim of this work was to use a commercial material and determine the best approach for characterizing and understanding its mechanical behavior, especially in terms of the processing conditions used to deposit the coating. It also became clear in this work that the coated material was a simple type of layered structure and as such, could be used to understand damage tolerance in a brittle laminated structure.

4) Sub-critical crack growth in stress-free and ion-exchanged glasses.

A similar scientific approach to that described in 1) was used for observation of sub-critical crack growth and the way it is influenced by residual surface stress. This work combined data from dynamic fatigue experiments on the stress-free and residually-stressed glasses with direct observation of the crack growth. As indentation

cracks were to be used for these observations, it is necessary to show that the data obtained from indentation crack growth is consistent with previous studies and the dynamic fatigue measurements made in the current study. Thus, the primary aim was to determine the crack velocity-stress intensity factor behavior using indentation cracks for the base glasses (prior to ion exchange). In the next phase of the work, the aim was to introduce indentation cracks into the ion-exchanged glasses and study the crack growth behavior as a function of the exchange conditions.

D. Importance of Problem

It will allow the reliability of ceramics containing residually-stressed layers to be incorporated in design methodology and this will enable the success of a wide variety of energy technologies that depend on the current or future use of ceramic materials.

6. Project Output (1990-94)

A. Major Accomplishments

1) Indentation fracture behavior of ion-exchanged glasses

In considering cracks on residually-stressed surfaces, there are two important limiting conditions; 1) cracks under the action of uniform residual surface stress and 2) cracks subjected to a thin layer of residual stress. In studying the literature, it was concluded that the former situation was well understood both experimentally and theoretically but this was not the case for the latter. Thus, the initial emphasis of this section of the project was to consider indentation cracking on surfaces that possessed a thin layer of surface compression (Ref.1). It was found that existing theory was unable to predict the lengths of radial indentation cracks on such surfaces and that crack shape was probably being influenced by the surface stresses. It was also shown that the strength of such indented materials was not being influenced by the surface stress unless the surface was ion-exchanged after indentation. Finally, it was also found to be more difficult to form indentation cracks on residually-compressed than stress-free surfaces. In order to gain further insight into the indentation crack process, it was decided that direct observation of the indentation crack formation and growth processes was needed.

Direct observation of the indentation process (Ref. 2, 13) uncovered some previously unreported phenomena, e.g., the observation of cone cracking under sharp indenters on glasses considered to be "normal" (alumino-silicate) and the complete absence of median cracking on ion-exchanged soda-lime silica glass. The overall effect of the residual compressive stress was to alter the flaw morphology formed

during the indentation process, from median to radial, i.e. restricting the indentation flaw depth. The formation of lateral cracks was retarded by the residual surface compression. Experiments on tempered glasses have yielded identical results, i.e., a complete suppression of median cracking and a preference for the radial crack morphology. This is an important result indicating for materials with residual surface compression, the damage due to contact events not only initiates at higher loads but will be more surface localized. In view of the altered indentation crack morphology, previous analyses which assumed that the flaw shape was semi-circular must be modified. The growth of indentation cracks on ion-exchanged glass surfaces was also studied and it was found to occur primarily at the segment of the crack front furthest away from the surface. Within the above work, a simple experimental technique for measuring surface stress was analyzed theoretically and evaluated (Ref. 3, 13)

2) Strength variability of residually-stressed brittle materials

It was shown early in this project that macroscopic surface residual stresses can have a pronounced effect on strength variability and if a material follows a Weibull distribution in the stress-free state, the surface stress can lead to non-linearities in this distribution that must be understood in the design process. In order to understand this variability in more detail, materials with flaws which experience various stabilizing and destabilizing fields during their extension to failure were examined theoretically (Ref. 8, 13). General forms for the crack size distribution were assumed and fundamental statistical descriptions, i.e., mean and standard deviation, were used to characterize the strength and variability. The results of the analysis were insensitive to the crack size distribution assumed and indicated in the cases studied that the variability did not necessarily depend on the critical microstructural parameters in the same fashion. This indicates optimum microstructures and stress profiles must exist in which increases in strength can be balanced against increases in strength variability. Directions for altering the microstructure of materials in order to obtain this balance were discussed.

Stabilization of the fracture process and resistance to strength degradation have been observed for materials with increasing fracture resistance curves. In our studies, the possibility of using **residual compressive stresses to induce crack stabilization** was examined theoretically and validated (Ref. 5-7, 13). The approach outlined in these papers represents a new way to improve the strength of materials using surface compression and in a way in which the material shows increased strength, flaw tolerance and substantial reductions in strength variability. It was therefore concluded that residual stress profiles, if properly designed, can be used to

improve mechanical reliability in ways which are usually associated with microstructural toughening mechanisms.

3) Fracture behavior of a SiC-coated graphite

The primary areas of interest in the mechanical characterization of this simple layered structure were the measurement of the Young's modulus of the coating, the coating residual stress and the overall fracture behavior (Ref. 4, 9-12). The major source of experimental error in the modulus measurement was due to coating thickness variability. The residual strains in the coatings were measured through the use of the strain gage/polishing technique. The results showed the stresses were compressive and were higher than those expected from the thermal expansion mismatch.

The fracture behavior of the β -SiC coated graphite was examined in 4 point flexure. When the coating thickness exceeded a "critical thickness" of $\sim 50 \mu\text{m}$, catastrophic failure of the sample was observed. However, when the coating thickness was less than $\sim 50 \mu\text{m}$, crack arrest and multiple cracking was observed in the coating under tension, despite the fact that graphite has a lower fracture toughness than SiC. The ability to arrest cracks in this fashion in a brittle material would be a very useful attribute in structural applications and indicates that layered structures may be very attractive candidates for improved structural materials. In order to understand the conditions for the arrest of the initial crack, the process was modelled using fracture mechanics (Ref. 11, 12). The results of this analysis are important for the fracture behavior of brittle laminates of all types, indicating that crack stability and arrest can be designed into these brittle composite materials in a variety of ways.

4) Sub-critical crack growth in ion-exchanged glasses.

Dynamic fatigue tests have been performed on the two baseline glasses (soda lime silica and aluminosilicate) with and without ion exchange and the data is in general agreement with the literature. This data was obtained for both indented and non-indented glasses. In addition to the dynamic fatigue data, in-situ observations of the sub-critical crack growth process were made on the two glasses. It is felt the in-situ observations are a key aspect of this project and have lead to a much better understanding of the sub-critical crack growth process. The data for the in-situ observations was obtained using indentation cracks on ion exchanged surfaces and was compared with those obtained on stress-free surfaces. The loading apparatus also allowed measurement of the stress intensity factor (K) and the crack velocity (v). Indeed this procedure for the two glasses gave K - v data, which is in good agreement with the literature (Ref. 14, 16). In order to overcome the complications of the localized indentation residual stresses, cracks were

grown subcritically to sizes $> 200 \mu\text{m}$ before measurements were performed. In this work, it was first necessary to define the changes in crack shape that occur during the subcritical growth process. This was accomplished by unloading specimens at various points during the crack growth and this imprinted crack front traces on the fracture surface.

The changes in crack shape that occur during subcritical crack growth had not been analyzed previously and thus, theoretical simulations were performed to understand this effect (Ref. 15, 16). The crack shape after indentation was found to change rapidly into a shape that was dependent primarily on the applied stress distribution. For example, there is a continuing change in crack shape with crack extension for an applied bending stress. The crack shape was also found to depend on the subcritical crack growth parameters for the particular glass/environment system. The changes in crack shape were also shown to be important in lifetime predictions.

The experiments on the ion-exchanged glasses has demonstrated a further change in crack shape occurs in the presence of surface compression (Ref. 16). For these cases, the cracks can no longer be considered semi-elliptical but rather they have a shape somewhere between a semi-ellipse and a complete ellipse, i.e, the major axis of the ellipse has moved away from the surface. Moreover, it is found the subcritical growth was occurring only below the exchanged layer. The complex crack shape does not allow easy quantification of the subcritical growth as the stress intensity factors associated with cracks of such shapes are not known. It was, however, possible to measure the changes in crack shape as a function of the ion exchange conditions.

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13. R. Tandon, "Influence of Residual Stress-Induced R-Curves on the Fracture Behavior of Brittle Materials", Ph.D. Thesis, The Pennsylvania State University, 1992.
14. P. Dwivedi and D. J. Green, Determination of Subcritical Crack Growth Parameters by In-situ Observation of Indentation Cracks, submitted to J. Am. Ceram. Soc. May 1994.
15. P. Dwivedi and D. J. Green, Indentation Crack-Shape Evolution during Subcritical Crack Growth, submitted to J. Am. Ceram. Soc. July 1994.
16. P. Dwivedi, Crack-Shape Evolution during Subcritical Growth of Cracks in Glass, Ph.D. Thesis, The Pennsylvania State University, 1994.
17. P. Dwivedi and D. J. Green, Indentation Crack-Shape Evolution during Subcritical Crack Growth in Ion-Exchanged Glasses, in preparation.

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