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Development of X-Ray Methods for Analyzing Rough-Wear Surfaces on Ceramics

P. J. Blau

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DEVELOPMENT OF X-RAY METHODS FOR ANALYZING ROUGH-WEAR SURFACES ON CERAMICS

TECHNICAL SUMMARY OF COMPLETED ORNL SUBCONTRACT 19B07733B

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DEVELOPMENT OF X-RAY METHODS FOR ANALYZING ROUGH-WEAR SURFACES ON CERAMICS

P. J. Blau

ABSTRACT

This report summarizes research performed by Virginia Polytechnic Institute and State University under subcontract to Oak Ridge National Laboratory. The work, funded by the Energy Conversion and Utilization Technologies Program of the U.S. Department of Energy, began January 1, 1983, and ended September 30, 1987. The research has resulted in the successful completion of Bing Hwang's Ph.D. degree in Materials Engineering Science from Virginia Polytechnic Institute and State University. The reference to Dr. Hwang's thesis is *Near Surface Wear Structure of Ceramic Components*, Virginia Polytechnic Institute and State University, Blacksburg, Va., May 1987.

The purpose of the research was to develop novel X-ray diffraction and fluorescence methods for probing the near-surface (<1 μm deep) zone of worn ceramics. An important aspect of the work in regard to fundamental tribology research was to overcome the difficulties associated with X-ray analysis of rough surfaces. Fully and partially stabilized zirconia (PSZ) were selected as the materials to be examined by the X-ray techniques being developed. The specific characteristics of the worn ceramic surface of most interest were phase content, particle size, and near-surface strains.

This summary outlines the major findings of this work. Details of the mathematical analysis may be found in the four cited open-literature references. Material in this report has been abstracted from the original manuscripts and reprints of these references. Each reference is separately outlined.

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1. OVERVIEW OF COMPLETED RESEARCH PUBLICATIONS

Four manuscripts are summarized in the following sections. The paper in Sect. 2 has been accepted for publication in the *Journal of the American Ceramic Society*; the papers in Sects. 3 and 4 have been accepted by the *Journal of Applied Physics* (May 1988); and the paper in Sect. 5 has been published in *Acta Crystallographica* **A42**, 14-19 (1986).

Papers in Sects. 2 and 4 are concerned with the characterization of near-surface structures by X-ray diffraction. The techniques described offer new opportunities for examining the subsurface wear damage in ceramic and metallic materials. Both conventional and synchrotron-generated X-ray sources are potentially useful in performing the analysis. The help of Drs. G. E. Ice and A. Habenschuss on the ORNL beamline (X-14) at the National Synchrotron Light Source is acknowledged.

The paper in Sect. 2 discusses polycrystalline materials and the development of gradients in the amount of microstructural constituents below the surface when subjected to sliding wear. The paper in Sect. 3 addresses the problem of rough-surface X-ray analysis and asserts that, while in principle the proper intensity corrections to characterize roughness could be developed, more conventional topographic methods should be used. The work described in Sect. 4 succeeded for the first time in determining the residual strain gradient in situ in two fully stabilized zirconia samples, which is information of significance for fundamental tribology research. The paper described in Sect. 5 describes a technique for analyzing strains in wear debris particles collected from partially stabilized zirconia sliding wear tests.

In summary, the work outlined here has described new analytical tools for the subsurface analysis of tribomaterials and data to aid in the interpretation of the wear behavior of partially stabilized and fully stabilized zirconia.

2. X-RAY ANALYSIS OF THE NEAR SURFACE PHASE DISTRIBUTION APPLIED TO WEAR ON A PARTIALLY STABILIZED ZIRCONIA DISK

Authors: B. Hwang, C. R. Houska, with G. E. Ice and A. Habenschuss

Status: Accepted for publication in the *Journal of the American Ceramic Society*

Abstract as Submitted by the Authors

"X-ray diffraction methods are described for determining the depth distribution of any phase in a multiphase sample by using either different wavelengths or symmetrical and asymmetrical diffraction optics. The latter provides different X-ray penetration distances with one wavelength. Asymmetrical diffraction optics is obtained by tilting the sample normal toward the incident or diffracted beam and is best carried out with

synchrotron radiation. X-ray intensity ratios from different phases depend on the wavelength, the diffraction optics, and the depth distributions of the phases. The method is demonstrated using symmetrical and asymmetrical diffraction optics and a partially stabilized zirconia (PSZ) sample subjected to a pin on disk wear testing."

Outline

The paper begins with a brief discussion of the cubic, tetragonal, and monoclinic phases of pure zirconia. MgO was used to partially stabilize the material in the current case, thereby producing tetragonal and monoclinic phases dispersed in a matrix of the cubic phase. The authors state that thermal effects during sliding can produce phase changes near the surface. A previous two-wavelength technique was extended to examine three different distribution functions for the phase gradient: linear, exponential, and step. A theory section describes the mathematical form of each distribution function. Using multiple wavelengths or beam paths, one can obtain various probe depths. The amounts of various phases can be estimated for various depths, thereby producing a phase gradient.

A two-beam-path approach is used to calculate the phase distribution on a worn and unworn portion of a PSZ disk specimen. The wear surface was generated at 400°F (204°C) in dry nitrogen at a 2.8-lb (1.3-kg) load on the a 0.25-in.-diam (6.35-mm) pin. Sliding velocity was 1 ft/s (30.48 cm/s). Test duration was 61 h. Figure 4 from the manuscript is reproduced as Fig. 1 in this summary and indicates that the volume fraction of high-temperature (cubic and tetragonal) phases increased as a result of exposure to wear. The gradient in the lower curve is said to be a result of mechanical polishing of the surface.

The paper concludes by noting that the polishing damage did not extend beyond about 2 μm in depth; however, the wear-affected zone was much deeper. Because of the limitations of the technique, data below 4 μm should be treated as semiquantitative only. As a final comment, the authors note that mechanically induced phase transitions as well as thermally induced ones could exist, and that the present analysis could not determine which of these produced the reported results.

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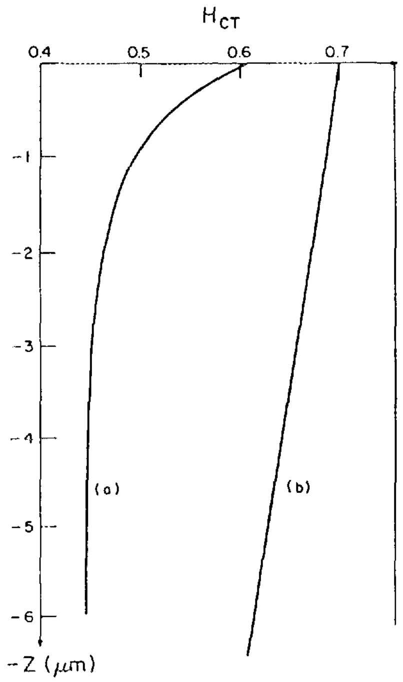

Fig. 1. Volume fraction of high-temperature phases in a polished (a) and worn (b) surface of PSZ (from Hwang et al.).

3. CALCULATION OF X-RAY INTENSITY FROM A ROUGH SAMPLE BASED ON A STATISTICAL MODEL

Authors: B. Hwang and C. R. Houska

Status: Submitted to *Journal of Applied Physics*

Abstract as Submitted by the Authors

"An X-ray intensity correction is developed which begins with a roughness model that is often used to describe real surfaces. This is based upon a normal distribution of surface asperities relative to a mean plane. Pair correlation between absorbing elements along X-ray paths either entering or leaving the sample with respect to the signal producing element is accomplished by means of an exponential auto-correlation function. This allows the degree of roughness to be varied on a local scale to fit specific surfaces using statistical data. Equations are developed to describe X-ray fluorescence and diffraction signals for symmetric and asymmetric beam optics. Theory is compared with experiment using a roughened, fully stabilized zirconia sample."

Outline

The authors begin by noting that the diffracted X-ray intensity of a rough surface is less than that of a flat surface, and that effects of granularity and roughness are similar in the sense that they both produce a distribution of path lengths at each fixed distance below the surface. A normal distribution is used to represent the distribution of asperity heights. For a given layer below the surface, volume elements were designated into groups whose members were at the same distance below the modeled surface. Incident and signal X-rays are coupled by means of an exponential function whose magnitude describes the manner in which a surface excursion loses correlation with increasing distance from its neighbor. The derivation results in a scaled form of the conditional probability function, which is modified to obtain an expression for the average absorption factor for any designated subsurface group of volume elements.

X-ray signal intensities contributed by specific groups are integrated to provide the overall intensities from the surface with the given normal asperity height distribution. The intensity ratio between rough and smooth surfaces is then given. A computer program was used to evaluate this equation for specific cases.

Experimental verification of the analysis was obtained using 8 mol % Y_2O_3 fully stabilized zirconia. Both polished and rough-ground surfaces were used. The authors failed to state the precise conditions under which the rough surface was produced.

The intensity ratio of rough-to-polished surfaces as a function of incident angle is given in Fig. 2 (Fig. 6 in manuscript). The solid line is the calculation, and the points are experimental results. The minimum in the curve would be sharp for a sawtooth 45° slope case; however, for real surfaces, the distribution of surface slopes leads to a less definite minimum. The minimum in Fig. 2 is believed to correspond to an average slope of about 9°. This value was in close agreement with profilometer data for the rough surface. The value for the angle corresponding to the minimum in the given example could be obtained using the arc tangent of the quantity 2.3 times the variance of the height distribution divided by the correlation distance for surface excursion.

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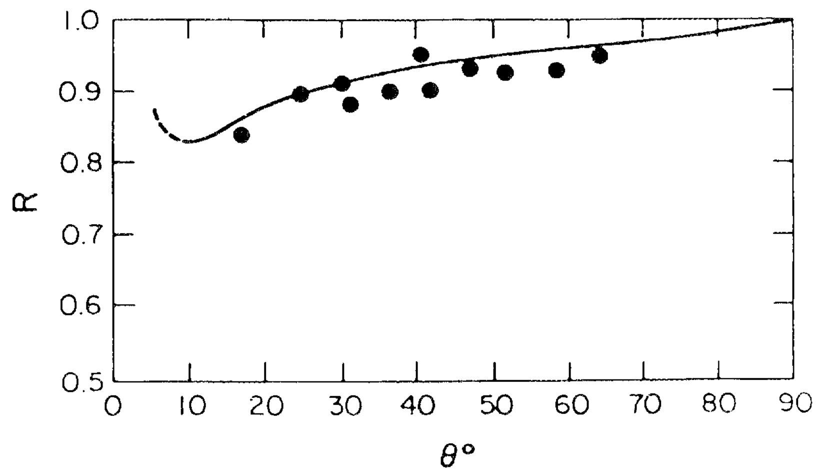

Fig. 2. Comparison of calculated values (solid line) for the intensity ratio of rough-to-polished surfaces with experiment (after Hwang and Houska).

A concluding comment indicated the uncertainties introduced into the analysis by the presence of subsurface residual stresses. As indicated in Sect. 1, Houska cautioned that more traditional methods of roughness determination may be simpler to use and more straightforward to interpret than the X-ray technique.

4. RESIDUAL STRAIN GRADIENTS IN A FULLY STABILIZED ZIRCONIA SAMPLE

Authors: B. Hwang and C. R. Houska, with G. E. Ice and A. Habenschuss

Status: Submitted to *Journal of Applied Physics*

Abstract as Submitted by the Authors

"Polished and severely ground fully stabilized zirconia (FSZ) samples are examined using primarily X-ray diffraction (XRD). The XRD (111) profile reflections from both samples were broadened asymmetrically compared to that of an annealed sample. The asymmetry results from a d-spacing gradient extending from the free surface into the undisturbed

bulk material. There are two possible origins of this depth gradient, i.e., variations in residual strain or chemical composition. The latter is eliminated by means of X-ray photoelectron spectroscopy (XPS) which did not reveal a chemical gradient. D-spacing profiles for both samples are obtained nondestructively using a trial and error fitting procedure. A maximum compressive strain of ~4% is obtained at the surface of the ground sample which decreases gradually to zero at greater depths. The overall compressive zone is ~1-2 μm. A similar but smaller compressive zone is found in the polished sample which is followed by a zone of tension. The maximum compressive strain at the surface is ~5% and the overall zone of residual strain is ~0.1 μm."

Outline

Y_2O_3 (8 mol %) was used to stabilize the zirconia used in this investigation, and the material was completely cubic. The (111) peak profiles of both polished and roughly ground FSZ surfaces were obtained in two ways: (1) by point-counting using Cu K-alpha radiation and symmetrical diffraction optics and (2) by using 2.4797 A synchrotron radiation at the National Synchrotron Light Source (ORNL beamline). Asymmetrical diffraction optics to enhance the low-angle side were used to obtain (111) peak profiles. Specimens were subsequently annealed to study instrumental effects on band broadening.

Results indicated that there was a large strain gradient in the polished surface. The overall strained zone was limited to about 0.1 μm. In contrast, the ground sample's strained zone was about ten times as deep. The 5% strain found at the surface of the ground sample was consistent with that for the PSZ wear debris as discussed in the Sect. 5 summary. Neither polishing nor grinding was found to give significant line broadening in the PSZ.

Figure 3 (Figs. 10 and 11 in manuscript) shows the percent strain vs depth in polished and ground PSZ surfaces, respectively. Note the difference in the depth scale, which demonstrates that the same form for the strain curve was obtained for both polished and ground surfaces but

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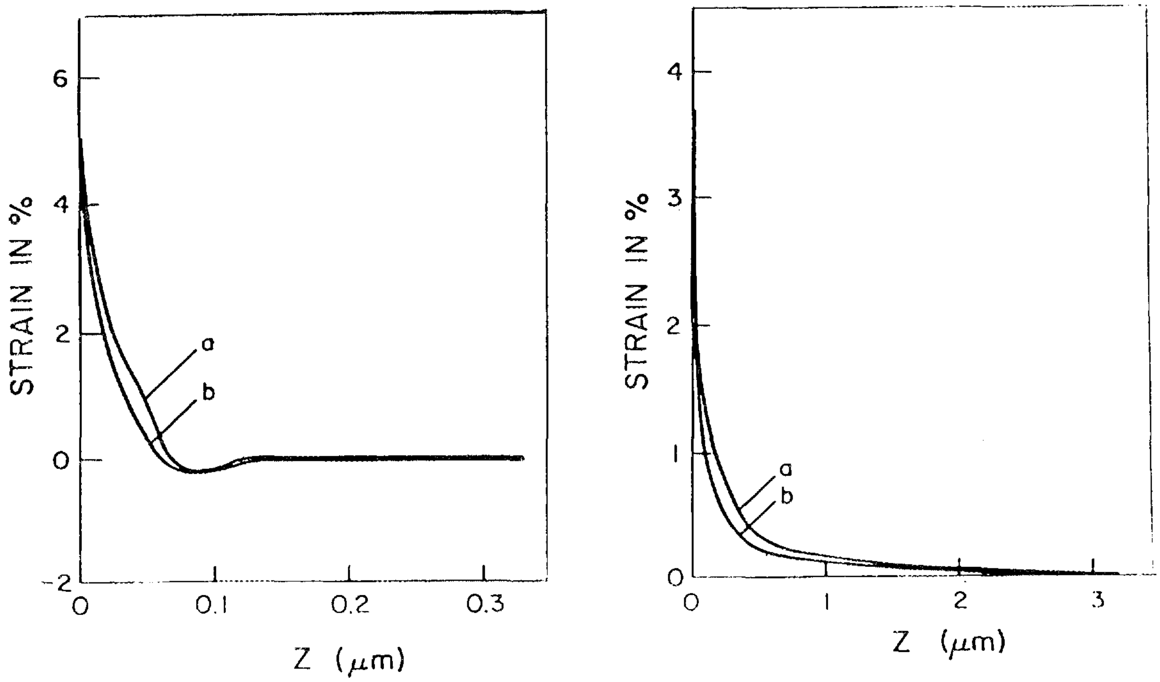

Fig. 3. Strain gradients in polished (left) and roughly ground (right) surfaces of FSZ. Left side: (*a*) symmetrical optics using both Cu K-alpha and synchrotron 2.4797 A radiation, (*b*) asymmetrical optics with synchrotron radiation. Right side: (*a*) symmetrical optics using Cu K-alpha radiation, (*b*) synchrotron radiation of 2.4797 A.

having different ranges of subsurface strains. There appeared to be little effect of using asymmetrical or symmetrical optics on the polished surface.

5. X-RAY DIFFRACTION PROFILES DESCRIBED BY REFINED ANALYTICAL FUNCTIONS

Authors: S. Rao and C. R. Houska

Status: Published in *Acta Crystallographica* A42, 14-19 (1986).

Abstract as Submitted by the Authors

"The line profiles from a sample containing small spherical particles, non-uniform strain and instrumental broadening can be described exactly by

using error functions with complex arguments. Consequently, the development by Houska & Smith [*J. of Appl. Phys.* (1981), 52, 748-754] has been revised in terms of these functions. This calculation has been extended, by the use of error functions with complex arguments, to include a more general distribution of particle size or column heights than that obtained from a single sphere. The latter extension is applied to profiles obtained from a partially stabilized zirconia wear debris. It is found, in this example, that a column-height variation coefficient that is greater than that from a single sphere gives a somewhat better fit of the experimental line profiles. We find that if the single-sphere model is used to fit the profiles the particle size and root-mean-square strain differ by about 12 and 5% respectively."

Outline

The principal investigator's previous work involved the modification of the well-known Warren-Averbach line shape analysis to yield particle size and nonuniform strain information about the particles. This work uses recent developments in computer software to permit the generation of complex error functions to a high degree of precision. The implications for this lie in the ability to extend the existing X-ray analysis to spheres of variable size.

The convolution of two strain distributions is used to describe the state of nonuniform microstrain in the sample. One is due to the interaction of dislocations, and the other is the result of long-range effects between subgrains. The paper describes the instrumental broadening function in detail and applies the analysis to wear debris from a sliding wear test of a PSZ sample. Figure 4 is a reproduction of the authors' Fig. 1 illustrating the theoretical fit and experimental data for 200 and 400 reflections from the debris sample irradiated with Cu K-alpha X rays. It was determined that the magnitude of the strain component present in the PSZ debris was surprisingly close to that expected for cold-worked metals.

This work suggests the potential for using sophisticated X-ray analysis methods to obtain information about the strains sustained by wear debris particles from ceramic sliding wear experiments.

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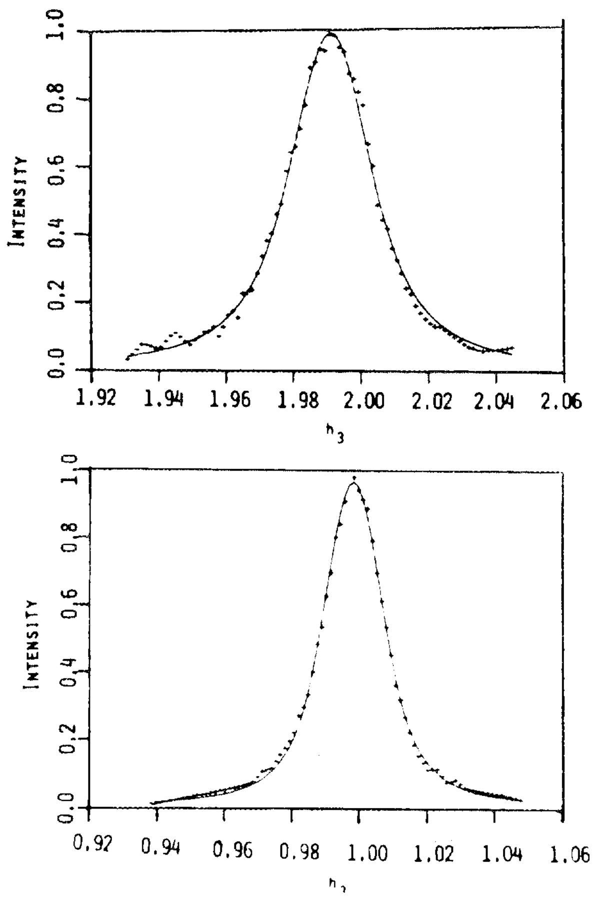

Fig. 4. X-ray line profiles for 200 (top) and 400 (bottom) reflections from PSZ wear debris samples.

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