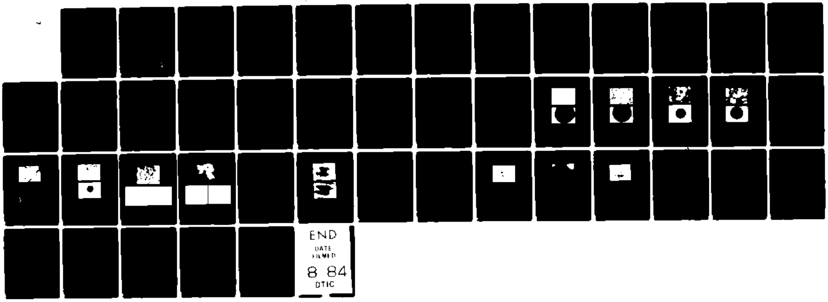
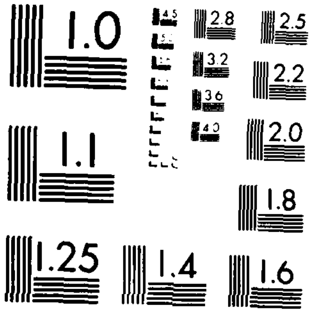
AD-A142 542   STUDY OF MECHANO-CHEMICAL MACHINING OF CERAMICS AND THE   1/1
EFFECT ON THIN FILM BEHAVIOR(U) HONEYWELL INC
BLOOMINGTON MN CORPORATE PHYSICAL SCIENCES CENT..
UNCLASSIFIED   H VORA FEB 84 N00014-83-C-0270   F/G 11/4   NL



END
DATE
FILMED
8 84
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

Technical Report No. 1

Contract N00014-83-C-0270; NR653-002

STUDY OF MECHANO-CHEMICAL MACHINING OF CERAMICS AND THE EFFECT ON THIN FILM BEHAVIOR

H. VORA
HONEYWELL INC.
PHYSICAL SCIENCES CENTER
10701 LYNDALE AVENUE SOUTH
BLOOMINGTON, MINNESOTA 55420

February 1984

Final Technical Report

Prepared for

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

SECURITY CLASSIFICATION OF THIS PAGE (WHEN DATA ENTERED)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
N00014-83-C-0270-1

2. GOV'T ACCESSION NUMBER
AD-A142 542

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (AND SUBTITLE)
Study of Mechano-Chemical Machining of Ceramics and the Effect on Thin Film Behavior.

5. TYPE OF REPORT/PERIOD COVERED
Final Technical Report
1 Feb 1983-31 Dec 1983

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(S)
H. Vora

8. CONTRACT OR GRANT NUMBER(S)
N00014-83-C-0270

9. PERFORMING ORGANIZATIONS NAME/ADDRESS
Honeywell Physical Sciences Center
10701 Lyndale Avenue South
Bloomington, MN 55420

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME/ADDRESS
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

12. REPORT DATE
February 1984

13. NUMBER OF PAGES
40

14. MONITORING AGENCY NAME/ADDRESS (IF DIFFERENT FROM CONT. OFF.)

15. SECURITY CLASSIFICATION (OF THIS REPORT)
Unclassified

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (OF THIS REPORT)
Reproduction in whole or in part is permitted for any purpose by the United States Government.

17. DISTRIBUTION STATEMENT (OF THE ABSTRACT ENTERED IN BLOCK 20, IF DIFFERENT FROM REPORT)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (CONTINUE ON REVERSE SIDE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)
Alumina, Boron Carbide, Ferrite, Fused Silica, Mechano-Chemical Polishing, Silicon, Silicon Carbide, Silicon Nitride, Zirconia.

20. ABSTRACT (CONTINUE ON REVERSE SIDE IF NECESSARY AND IDENTIFY BY BLOCK NUMBER)
Efforts have been made to mechanochemically polish polycrystalline ZrO_2, Mn-Zn ferrite, MgO, Al_2O_3, [illegible], Si_3N_4, SiC and B_4C. Measurements were made of the removal rates obtained by mechanochemically polishing above materials on a polyurethane impregnated polyester lap using a colloidal silica slurry as a polishing medium. These measurements indicate that the colloidal silica slurry polishes oxide ceramics at significantly higher removal rates than non-oxide ceramics. It is shown that a polishing medium consisting of Cr_2O_3 and traces of CrO_3 can mechanochemically polish non-oxide ceramics

HD-168 REV 11/74

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 55 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (WHEN DATA ENTERED) at significantly higher removal rates than the colloidal silica slurry.

Because of the reactive nature of colloidal silica slurries, they are typically used in conjunction with polyurethane impregnated polyester or polyurethane foam laps. Employment of such non-rigid laps yields polished surfaces with orange-peel appearance (in the case of polycrystalline materials), excessive rounding at the edges and with flatness of no better than 1 λ (λ=633nm) per centimeter in the center. Employing rigid linen phenolic laps, we have been able to get mechanochemically polished surfaces with flatness of ~λ/10 per centimeter, a little rounding at the edges and no orange-peel appearance. Peak-to valley surface roughnesses of mechanochemically polished surfaces have been found to vary from material to material over the range 160-1200Å. Electron microscopy analysis of the polishing debris of selected workpiece/abrasive systems indicates that polishing reaction product is a small fraction of the polishing debris and is probably amorphous in nature.

Preface

This report covers work performed during the period February 1 to December 31, 1983 under the Office of Naval Research Contract No. N00014-83-C-0270. The author would like to thank Dr. R.J. Stokes of the National Science Foundation for useful discussion, Mr. Haren Shroff of Magnetic Peripherals, Inc., for providing Mn-Zn ferrite samples, Mr. John Humanensky of the University of Minnesota, for electron microscopy analysis, and Mr. D.J. Sauve, Jr., for technical support.

Table of Contents

Section		Page
1	INTRODUCTION	1
2	EXPERIMENTAL	5
3	RESULTS AND DISCUSSION	7
	3.1 Polishing of Oxide Ceramics Using Colloidal Silica	7
	3.2 Polishing of Non-Oxide Ceramics Using Oxides of Chromium	9
	3.3 Electron Microscopy of Polishing Media and Debris	15
	3.4 Precision of Mechanochemically Polished Surfaces	20
4	CONCLUSIONS	34
	INDEX OF PUBLICATIONS	34
	DISTRIBUTION LIST (BASIC)	36
	DISTRIBUTION LIST B	38

List of Illustrations

Figure Page

1 Removal rates obtained by mechanochemically polishing Si_3N_4 at various pressures using Cr_2O_3 and a mixture of Cr_2O_3 and CrO_3 as polishing media 11

2 Removal rates obtained by mechanochemically polishing SiC at various pressures using Cr_2O_3 and a mixture of Cr_2O_3 and CrO_3 as polishing media 12

3 Removal rates obtained by mechanochemically polishing B_4C at various pressures using Cr_2O_3 and a mixture of Cr_2O_3 and CrO_3 as polishing media 13

4 Removal rates obtained by polishing silicon at various pressures using a colloidal silica slurry and a mixture of Cr_2O_3 and CrO_3 as polishing media 14

5 Transmission electron micrograph and diffraction pattern of colloidal silica 16

6 Transmission electron micrograph and diffraction pattern of debris obtained by polishing Si with colloidal silica 17

7 Transmission electron micrograph and diffraction pattern of Buehler cerium oxide 18

8 Transmission electron micrograph and diffraction pattern of debris obtained by polishing fused silica with Buehler cerium oxide 19

9 Transmission electron micrograph and diffraction pattern of Cr_2O_3 21

10 Transmission electron micrograph and diffraction pattern of debris obtained by polishing Si_3N_4 with Cr_2O_3 22

11 Debris obtained by mechanochemically polishing Si_3N_4 with Cr_2O_3. (A) Scanning electron micrograph, (B) distribution of Si in the debris (C) distribution of Cr in the debris 23

12 Debris obtained by polishing fused silica with cerium oxide. (A) Scanning electron micrograph, (B) distribution of Si in the debris and (C) distribution of Ce in the debris 24

13 Surface figures of mechanochemically polished samples of (A) spinel and (B) zirconium oxides. Samples are approximately 18mm × 25mm in dimensions 26

List of Illustrations (Concluded)

Figure		Page
14	Nomarski micrograph and surface profile of mechanochemically polished ZrO_2	27
15	Nomarski micrograph and surface profile of mechanochemically polished Al_2O_3	28
16	Nomarski micrograph and surface profile of mechanochemically polished $MgO.Al_2O_3$	29
17	Nomarski micrograph and surface profile of mechanochemically polished Mn-Zn ferrite	30
18	Nomarski micrograph and surface profile of mechanochemically polished Si_3N_4	31
19	Nomarski micrograph and surface profile of mechanochemically polished SiC	32
20	Nomarski micrograph and surface profile of mechanochemically polished B_4C	33

List of Tables

Table		Page
1	Removal rates obtained by mechnochemically polishing polycrystalline Al_2O_3 using various polishing media	7
2	Comparison of removal rates obtained by mechanochemically polishing various ceramics using a colloidal silica slurry	8
3	Removal rates (μm/hr) for Si, SiO_2, Si_3N_4, SiC and B_4C obtained by polishing at a pressure of 10 psi using various polishing media	10
4	Analysis of the diffraction patterns of Buehler CeO_2 and the debris obtained by polishing fused silica with Buehler CeO_2	20

The reverse of this page is blank.

Section 1
Introduction

A major fraction of ceramics in industrial use today is in polycrystalline form, partly because polycrystalline ceramics are less expensive than single-crystal ceramics and partly because large single crystals of many ceramics are difficult to grow. The applications of ceramics in optics and electronics have been growing rapidly in recent years. In some of these applications, polycrystalline ceramics possessing damage-free surfaces that are both smooth and flat are required.

In the conventional surface finishing approach in which abrasives with hardnesses greater than that of the workpiece are used to remove material from the workpiece, the flatness is achieved by employing flat laps (such as cast iron or tin) and the required smoothness is achieved by polishing the workpiece with abrasives of successively finer grit size. This approach generally produces damaged surfaces consisting of fine scratches and a thin damaged layer.

A thin damaged layer from a conventionally polished material can be removed in a number of ways, for example, by chemical polishing or by electropolishing. The main disadvantages associated with these methods of damage removal are formation of deep steps at the grain boundaries, because of the anisotropy in the material removal rates associated with the grains of different orientation, and the flatness degradation.

In an effort to produce damage-free surfaces possessing a higher degree of flatness and smoothness than can be achieved by chemical or electropolishing, the technique of mechanochemical polishing has been in use for the last several years. The mechanochemical polishing technique is very similar to the conventional polishing technique except that the emphasis in the former technique is on removing material from the workpiece through a chemical reaction between the workpiece and the polishing medium. This chemical reaction is activated by application of pressure during polishing, typically in the $7 \times 10^3 - 7 \times 10^4$ N/m^2 (1-10 psi) range.

A well known example of mechanochemical polishing is the surface finishing of single-crystal silicon wafers using an alkaline colloidal silica slurry for electronic applications. A colloidal silica slurry is a stable dispersion of very fine (40-800Å) sized SiO_2 particles in water. The dispersion is stable over a very long period of time if the pH of the slurry is adjusted to a value in the range of 8.0-11.5. A colloidal silica slurry with pH of 11 is frequently used for polishing silicon wafers.

Chemical compositions of many commercially available colloidal silica slurries are proprietary, and one can only postulate the mechanism by which they remove material from silicon. Based on the work of Karaki et al.[1] this mechanism appears to be the

---

[1] T. Karaki, S. Miyake and J. Watanabe, Bull. Japan Soc. of Prec. Engg. *15*, 14 (1981).

dissolution of silicon in the alkaline slurry. Solubility of silicon in an alkaline solution is significant at room temperature and increases rapidly with increasing temperature. The action of rubbing the silicon surface against the lap surface (typical lap material being polyurethane impregnated polyester) is the origin of heat in the mechanochemical polishing process. The amount of heat generated (and hence the silicon removal rate) increases as the pressure applied to the silicon workpiece increases, and for a given pressure, increases very significantly if the alkaline polishing medium contains fine solid particles (such as colloidal SiO_2 particles).

Because of the reactive nature of colloidal silica slurries, difficulties are encountered in using them in conjunction with laps such as pitch, metal and beeswax, which have been used traditionally to obtain flat surfaces. The colloidal silica slurries are typically used in conjunction with polyurethane impregnated polyester or similar lap materials. The main disadvantages associated with the use of such non-rigid laps are excessive rounding at the edges of the workpiece, flatness restriction of approximately 1 λ (λ = 633nm) per centimeter in the center of the workpiece, and orange-peel appearance in the case of polycrystalline workpiece.

In contrast to the liquid-solid type of chemical reaction which appears to be operative in the case of colloidal silica polishing of silicon, there is another form of mechanochemical polishing in which the emphasis is on material removal through chemical reaction between two solids, the workpiece and a soft abrasive. These chemical reactions are also promoted by an application of pressure in the range of $7 \times 10^3 - 7 \times 10^4$ N/m^2 (1-10 psi) during polishing and often by performing the mechanochemical polishing dry, that is by employing a loose powder of soft abrasive as the polishing medium as compared to wet polishing in which the slurry of an abrasive in liquid (usually water) is used as a polishing medium. Since the abrasive used in this form of mechanochemical polishing is softer than the workpiece, it is not likely to introduce scratches and a damaged layer in the workpiece, at least not to the same extent as a harder abrasive would. In an earlier study of this form of mechanochemical polishing by Yasunaga et al.[2] it has been shown that soft abrasives like $CaCO_3$ (or $BaCO_3$) and SiO_2 can be used to obtain scratch-free and damage-free silicon and sapphire surfaces, respectively. If the workpiece and the selected soft abrasive are compatible with a rigid lap (such as metal or glass), then this form of mechanochemical polishing carries a potential for yielding surfaces that are not only scratch-free and damage-free but also flat. It has been shown by Yasunaga et al.[3] that damage-free and flat sapphire surfaces can be obtained by mechanochemically polishing on a flat glass lap using fine SiO_2 particles as soft abrasive.

In an effort to develop basic understanding of the usefulness and limitations of colloidal silica as a mechanochemical polishing medium for various ceramics and of

---

[2] N. Yasunaga, N. Tarumi, A. Obara and O. Imananka, in The Science of Ceramic Machining and Surface Finishing II, B.J. Hockey and R.W. Rice, editors. National Bureau of Standards Special Publication 562, 1979, p. 117.

[3] N. Yasunaga and O. Imananka, Technocrat *8*, 15 (1975).

Yasunaga's approach, attempts have been made to mechanochemically polish several oxide and non-oxide ceramics using these approaches. All the materials selected in this work were polycrystalline for the reasons stated earlier. Removal rates that can be achieved by mechanochemically polishing various ceramics have been measured as well as the flatness and surface roughness of mechanochemically polished surfaces because of the lack of such information in the literature. In addition, efforts have been made to analyze the debris of mechanochemical polishing using the technique of transmission electron microscopy.

Section 2
Experimental

Polycrystalline ceramics used in the present work were obtained from the following sources: Al_2O_3 (Coors ADS 997), Coors Porcelain Co., Golden, Colorado; Mn-Zn ferrite, Magnetic Peripherals, Inc., Bloomington, Minnesota; Si_3N_4 (Wesgo SNW-100), GTE Products Corporation, Belmont, California; $MgO.Al_2O_3$ (Ceralloy 12-138), partially stabilized ZrO_2 (ZrO_2 + 12% Y_2O_3, Ceralloy 3982), SiC (Ceralloy 1461G), and B_4C (Ceralloy 546), Ceradyne, Inc., Santa Ana, California.

All polishing experiments were conducted on a Strausbaugh polishing machine, model 6Y-1. Stock removal rates were determined from the measured weight loss of the workpiece after polishing for a known period of time using the following parameters: lap diameter, 10 cm; lap RPM, 80; stroke frequency, 60 cpm; and polishing pressures in the range of $7 \times 10^3 - 7 \times 10^4$ N/m² (1-10 psi). Laps were completely covered with the abrasive and the slurry of the abrasive in water was sprayed on the periphery of the lap periodically. With this procedure, the mechanochemical polishing occurred in the wet mode when the sample holder was at the periphery of the lap and in the dry mode when it was away from the periphery. This procedure was adopted because of the observations of a reaction between the sample and the lap and of the rapid degradation of lap when the mechanochemical polishing was performed strictly in dry mode over an extended period of time.

Colloidal silica slurries of three different types were used in this work, Nalco 2350, Nalco 2360, and Nalco 1034A, all marketed by Nalco Chemical Company, Oak Brook, Illinois. Nalco 2350 has a pH of 11 and contains 50% of 500-700Å SiO_2; Nalco 2360 has a pH of 8.5 and also contains 50% of 500-700Å SiO_2; and Nalco 1034 A has a pH of 3.1 and contains 35% of 160-220Å SiO2. A dilution ratio of 1:10 (1 part colloidal silica slurry and 10 part of deionized water) was used typically for mechanochemical polishing.

The reverse of this page is blank.

Section 3
Results and Discussion

3.1 POLISHING OF OXIDE CERAMICS USING COLLOIDAL SILICA

Because of the technical importance of polycrystalline Al_2O_3 as a substrate material for electronics packaging, a significant fraction of our efforts had concentrated on mechanochemical polishing of Al_2O_3. Based on the earlier work of Gutsche and Moody[4] on colloidal silica polishing of sapphire crystal of $(1\bar{1}02)$ orientation and of Yasunaga et al. [2,3] on dry mechanochemical polishing of sapphire crystals of various orientations using fine SiO_2 particles as soft abrasive, we chose to concentrate our efforts on these two polishing media.

Measurements were made in the present work of the removal rates that can be obtained by mechanochemically polishing Coors ADS 997 Al_2O_3 at a pressure of 3.5×10^4 N/m^2 (5 psi) on a polyurethane impregnated polyester lap using the following polishing media: (1) 1 molar solution of NaOH in water, (2) loose SiO_2 particles 70Å in diameter, (3) a mixture of 70Å SiO_2 particles and 1 molar solution of NaOH in water, (4) Nalco 2350 colloidal silica slurry and (5) Nalco 2360 colloidal silica slurry. The measured removal rates are listed in Table 1.

Table 1. Removal rates obtained by mechanochemically polishing polycrystalline Al_2O_3 using various polishing media.

Polishing Medium	Remcval Rate, μm/hr
1 molar soln of NaOH in water	0.1
70ÅSiO_2	1.2
1 molar soln of NaOH in water + 70Å SiO_2	1.0
Nalco 2350 (pH = 11.0, dilution ratio 1:10)	1.4
Nalco 2360 (pH = 8.5, dilution ratio 1:10)	1.8

An important reason for choosing various polishing media listed in Table 1 was to determine if the solubility of Al_2O_3 ceramic in an alkaline solution is significant at or moderately above room temperature. If it is, then increasing the alkalinity of the polishing medium could provide a means to increase the removal rate for Al_2O_3. Apparently, the solubility of Al_2O_3 in an alkaline solution is not significant at temperatures typically encountered in polishing, of the order of 100°C.[1] Because the removal rate obtained by mechanochemically polishing Al_2O_3 with 1 molar solution of NaOH in water is very low, 0.1μm/hr, and addition of alkaline solution to 70Å SiO_2 does not increase the removal rate that can be obtained by polishing Al_2O_3 alone with 70Å SiO_2.

---

[4] H.W. Gutsche and J.W. Moody, J. Elec. Chem. Soc. *125*, 136 (1978).

It is seen in Table 1 that Nalco 2360 colloidal silica slurry with pH of 8.5 polishes Al_2O_3 at a slightly higher rate than Nalco 2350 colloidal silica slurry with pH of 11.0. This is in agreement with the earlier observation of Gutsche and Moody[4] regarding the influence of pH of colloidal silica slurries on mechanochemical polishing rates for sapphire of $(1\bar{1}02)$ orientation; although the removal rates reported by Gutsche and Moody are significantly (about a factor of 10) higher than those listed in Table 1 for polycrystalline Al_2O_3. This could be due to the possibility that the colloidal silica polishes sapphire crystals of different orientations at different rates, and for some orientations the rates are much lower than the measured rate for sapphire of $(1\bar{1}02)$ orientation. (Such an anisotropy has been observed by Yasunaga et al.[2] in their study of dry mechanochemical polishing of sapphire with SiO_2 particles, and by Namba and Tsuwa[5] in their study of float polishing of sapphire using a slurry of 70Å SiO_2 particles in water.) The presence of such grains of unfavorable orientations is expected in polycrystalline Al_2O_3 and can contribute to the observed discrepancy in the removal rates.

The removal rate in mechanochemical polishing generally increases with increasing pressure. For Coors ADS 997 Al_2O_3, an increase in polishing pressure from 3.5×10^4 N/m^2 (5 psi) to 7.0×10^4 N/m^2 (10 psi) increased the removal rate by a factor of 2 to the value of ~4μm/hr when Nalco 2360 colloidal silica slurry was used as the polishing medium. The removal rates obtained by mechanochemically polishing other ceramics using the same slurry under identical polishing conditions were measured. The measured rates are compared in Table 2, where it is seen that the colloidal silica slurry polishes oxide ceramics at significantly higher removal rates than the non-oxide ceramics. The rates are observed to vary in the range of 3-7μm/hr for oxide ceramics and in the range of 0.5-1.3μm/hr for non-oxide ceramics.

Table 2. Comparison of removal rates obtained by mechanochemically polishing various ceramics using a colloidal silica slurry.

Workpiece	Removal rate, μm/hr
$MgO.Al_2O_3$	7.0
Mn-Zn ferrite	4.0
Al_2O_3	4.0
ZrO_2	3.0
Si_3N_4	1.3
B_4C	0.6
SiC	0.5

As noted earlier, alkaline colloidal silica slurries with pH in the range of 8.0-11.0 are stable over a long period of time. An acidic colloidal silica slurry with pH = 3.1 is available commercially (Nalco 1034A) and possesses a fair degree of stability. Efforts were made to mechanochemically polish Mn-Zn ferrite using this slurry to determine if it would yield a higher removal rate than 4μm/hr, obtained using alkaline Nalco

---

[5] Y. Namba and H. Tsuwa, Annals of the CIRP *27*, 511 (1978).

2360 colloidal silica slurry with pH = 8.5 (Table 2). It has been reported by Namba and Tsuwa[6] that an acidic solution can chemically polish Mn-Zn ferrite at a significantly higher rate than an alkaline solution. Nalco 1034A colloidal silica slurry with a dilution ratio of 1:6 was found to yield a removal rate of $\sim 8\mu m/hr$, about a factor of two higher than that measured using Nalco 2360 colloidal silica slurry (Table 2).

3.2 POLISHING OF NON-OXIDE CERAMICS USING OXIDES OF CHROMIUM

Data shown in Table 2 indicate that the colloidal silica slurry polishes oxide ceramics at significantly higher removal rates than non-oxide ceramics. Because of this, the efforts were made to determine if the removal rates for non-oxide ceramics can be increased by addition of hydrogen peroxide to colloidal silica slurry. Addition of hydrogen peroxide, which is a well-known oxidizer, has been shown to increase the removal rates for many semiconductors, such as Ge and GaAs,[7] apparently by promoting the oxidation of these semiconductors during polishing. In the case of non-oxide ceramics, significant increases in the removal rates were not obtained upon addition of up to 10 volume percent of hydrogen peroxide to the colloidal silica slurry. Because of this, the efforts were then concentrated on Yasunaga's approach to get high removal rates for non-oxide ceramics.

The results of our preliminary efforts to mechanochemically polish ceramics using several soft abrasives have been reported earlier.[8] Briefly, samples of both oxide and non-oxide ceramics were initially lapped conventionally on a brass lap using $15\mu m$ diamond paste and attempts were made to mechanochemically polish them using a variety of soft abrasives. Several soft abrasives were observed to remove scratches from the conventionally polished surfaces of both oxide and non-oxide ceramics.

In the present work, efforts were made to identify soft abrasives with potentials for yielding higher removal rates than those which can be achieved by using colloidal silica slurry as a polishing medium (Table 2). For this purpose, Knoop indentations were made on both oxide and non-oxide ceramic samples. Decreases in size of these indentations were measured after polishing for a period of 1 hr to determine the removal rates. Soft abrasives included in this study were MgO, NiO, Cr_2O_3, Fe_2O_3, Fe_3O_4, and $SrCO_3$. For oxide ceramics, these abrasives did not yield higher removal rates than colloidal silica slurry (Table 2). In the case of non-oxide ceramics, Cr_2O_3 for SiC, B_4C and Si_3N_4 and Fe_2O_3 for Si_3N_4 were found to yield higher removal rates than colloidal silica slurry; the measured removal rates for other soft abrasives were in the range of $0.3\text{-}0.6\mu m/hr$. The results of efforts to mechanochemically polish Si_3N_4 with Fe_2O_3 were reported earlier;[8] the results of efforts to mechanochemically polish Si_3N_4, SiC and B_4C using Cr_2O_3 abrasive are reported below.

---

[6] Y. Namba and H. Tsuwa, Annals of the CIRP *28*, 425 (1979).

[7] G.W. Fynn and W.J.A. Powell, The Cutting and Polishing of Electro-Optics Materials (New York: John Wiley & Sons) p. 207

[8] H. Vora and R.J. Stokes, "Study of Mechanochemical Machining of Ceramics and the Effect on Thin Film Behavior," Final Technical Report #N00014-80-C-0437-2, Contract N00014-80-C-0437, January 1983.

In an effort to gain better understanding of the mechanism of material removal in mechanochemical polishing, two more workpiece materials, single-crystal silicon of (100) orientation and fused silica were included in the present study. In addition, attempts were made to see if the rates at which Cr_2O_3 polishes various materials can be increased by addition of CrO_3 to it. Cr_2O_3, like jeweller's rouge (Fe_2O_3) or CeO_2, is not a very reactive polishing medium. CrO_3, on the other hand, is a very strong oxidizer and rapidly degrades many lap materials, including polyurethane impregnated polyester, when used alone. The lap degradation can be controlled to a great extent by mixing traces of CrO_3 with Cr_2O_3 and using the resulting mixture for polishing, rather than using CrO_3 alone as a polishing medium.

If the inability of non-oxide ceramics to oxidize rapidly enough during mechanochemical polishing restricts their removal rates, and if CrO_3 is able to promote oxidation of non-oxide ceramics during mechanochemical polishing, one would expect to see an increase in removal rates for non-oxide ceramics upon addition of CrO_3 to Cr_2O_3.

Removal rates obtained by mechanochemically polishing Si_3N_4, SiC and B_4C at various pressures in the range of $7 \times 10^3 - 7 \times 10^4$ N/m² (1-10 psi) using both Cr_2O_3 and a mixture of CrO_3 and Cr_2O_3 as polishing media are plotted in Figures 1 through 3, respectively. For the three non-oxide ceramics, removal rates are observed to increase with increasing polishing pressure, and at given pressure, the mixture of CrO_3 and Cr_2O_3 is observed to yield higher removal rate than Cr_2O_3.

Figure 4 illustrates the effect of polishing pressure on the removal rates obtained by polishing silicon single crystal with colloidal silica slurry (Nalco 2360, pH = 11, dilution ratio 1:10) and a mixture of Cr_2O_3 and CrO_3.

Compared in Table 3 are the removal rates obtained by polishing Si, SiO_2, Si_3N_4, SiC and B_4C at a pressure of 7×10^4 N/m² (10 psi) using Cr_2O_3, mixture of Cr_2O_3 and CrO_3, and colloidal silica as polishing media. It is seen that the mixture of CrO_3 and Cr_2O_3 mechanochemically polishes non-oxide ceramics at significantly higher rates than the slurry of colloidal silica. The measured rate is higher by a factor of 14 for Si_3N_4, 7 for SiC and 6 for B_4C.

Table 3. Removal rates (μm/hr) for Si, SiO_2, Si_3N_4, SiC and B_4C obtained by polishing at a pressure of 10 psi using various polishing media.

Workpiece	Polishing Medium		
	Cr_2O_3	Cr_2O_3 + CrO_3	Colloidal Silica
Si	—	31.0	31.0
SiO_2	14.0	22.0	4.0
Si_3N_4	7.0	18.0	1.3
SiC	1.2	4.0	0.6
B_4C	1.3	3.0	0.5

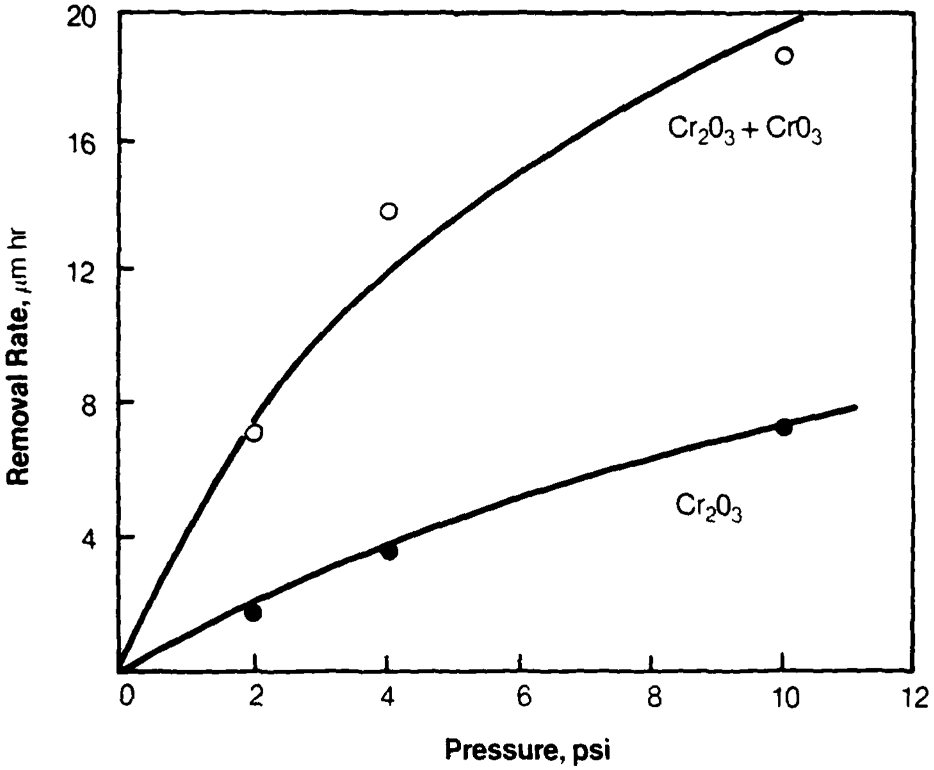


Figure 1. Removal rates obtained by mechanochemically polishing Si_3N_4 at various pressures using Cr_2O_3 and a mixture of Cr_2O_3 and CrO_3 as polishing media

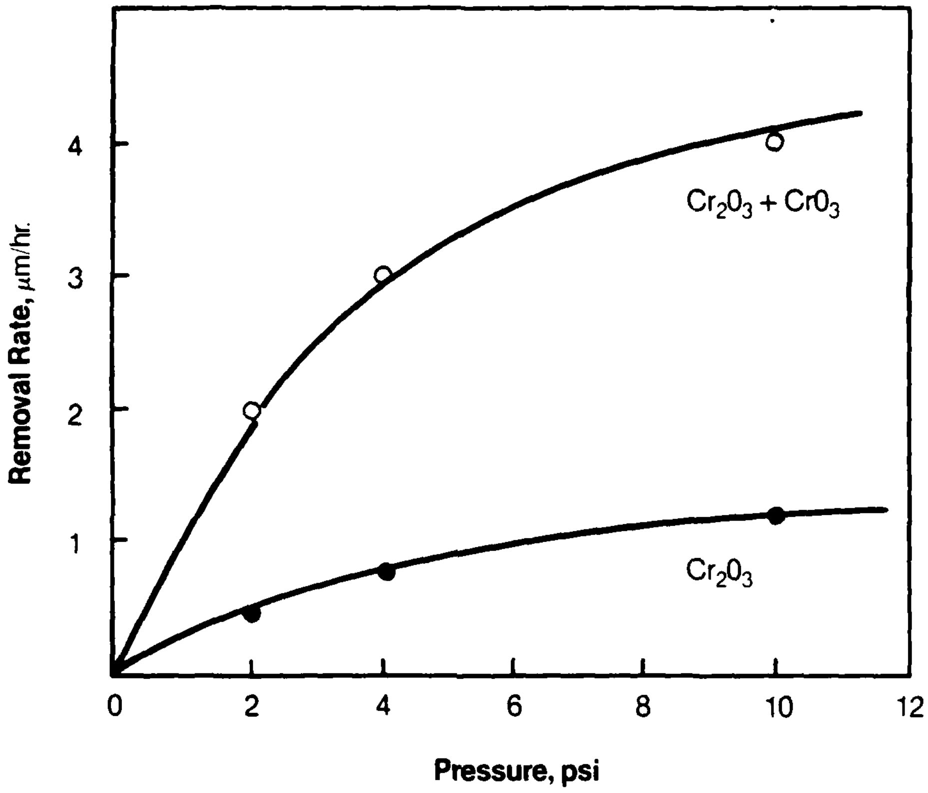


Figure 2. Removal rates obtained by mechanochemically polishing SiC at various pressures using Cr_2O_3 and a mixture of Cr_2O_3 and CrO_3 as polishing media

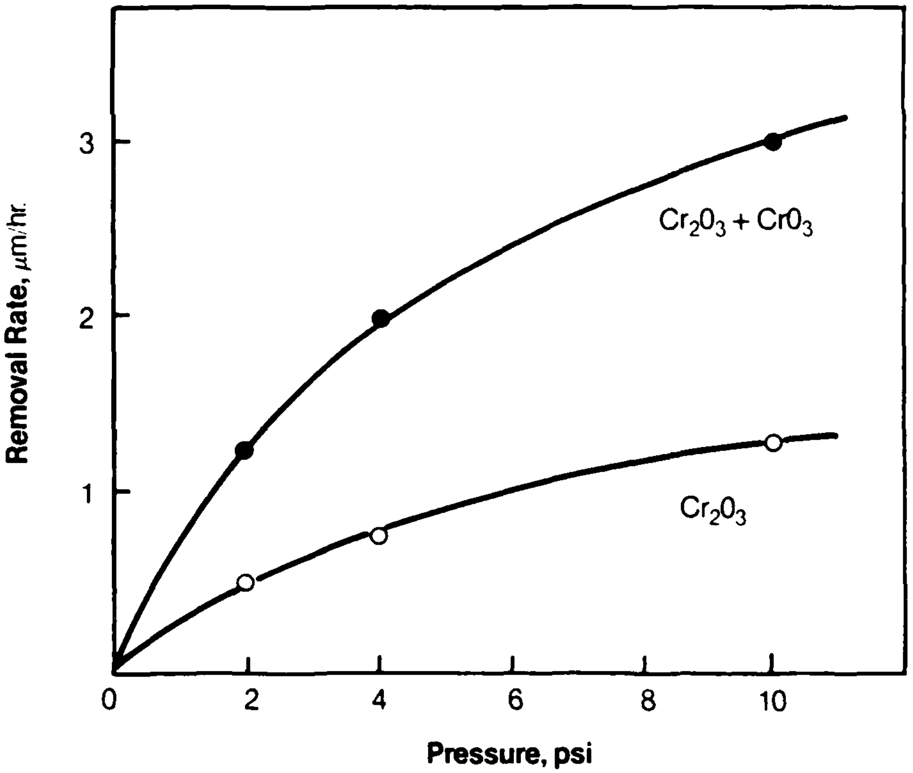


Figure 3. Removal rates obtained by mechanochemically polishing B_4C at various pressures using Cr_2O_3 and a mixture of Cr_2O_3 and CrO_3 as polishing media

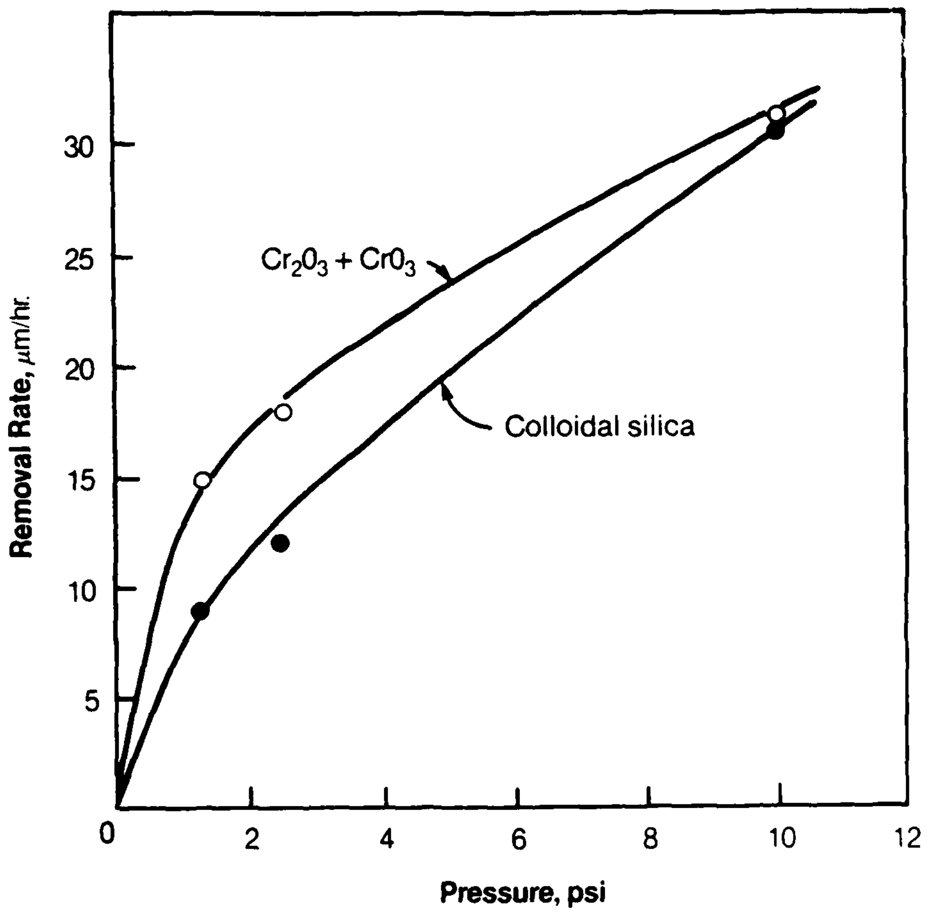


Figure 4. Removal rates obtained by polishing silicon at various pressures using a colloidal silica slurry and a mixture of Cr_2O_3 and CrO_3 as polishing media

An important reason for including fused silica in the present work was to see if the material removal in the cases of Si_3N_4 and SiC occurs in two steps, oxidation of the workpiece surface and the subsequent removal of the oxide layer by the abrasive (Cr_2O_3). If this is the case, one would expect Cr_2O_3 to polish fused silica at a higher rate than Si_3N_4 and SiC because fused silica is in an oxide form to start with, and an addition of CrO_3 to Cr_2O_3 to increase the removal rates for Si_3N_4 and SiC. Both these effects were observed as shown in Table 3.

What is not clear, however, is the observed increase in the removal rate for fused silica upon addition of CrO_3 to Cr_2O_3. If the only role played by CrO_3 is to promote the oxidation of the workpiece surface, this increase is not expected. It should be mentioned here that the polishing of SiC and Si_3N_4 with a mixture of Cr_2O_3 and CrO_3 constitutes mechanochemical polishing because no scratches were observed on the polished surfaces of these materials, whereas polishing of fused silica with this mixture is mechanical in nature to a certain extent as scratches were observed on the polished surface of fused silica. The reported Mohs hardness of the fused silica which is in the range of 5.5-6.5 is less than the Mohs hardness of 7 for Cr_2O_3. Mohs hardness of Si is also 7. Its polishing with a mixture of Cr_2O_3 and CrO_3 has appeared to be mechanochemical in nature. The polished surface of Si had mirror finish and showed no scratches.

3.3 ELECTRON MICROSCOPY OF POLISHING MEDIA AND DEBRIS

If the reaction product of conventional or mechanochemical polishing is crystalline, it may be possible to identify it through electron diffraction analysis.

In the present work, three polishing media were examined in a transmission electron microscope. They were: Nalco 2350 colloidal silica, Buehler cerium oxide (Mirometi), and Fisher chromium oxide. Also examined were the debris obtained by polishing silicon with Nalco 2350 colloidal silica, fused silica with Buehler CeO_2, and Si_3N_4 with chromium oxide.

The transmission electron micrograph and the diffraction pattern of colloidal silica are shown in Figure 5. Corresponding micrograph and the diffraction pattern of the debris obtained by polishing silicon with colloidal silica are shown in Figure 6. The diffraction patterns indicate that both polishing medium and the debris are amorphous in nature.

The transmission electron micrograph and the diffraction pattern of Buehler cerium oxide and the debris obtained by polishing fused silica with this polishing compound are shown in Figures 7 and 8, respectively. The d-spacings of the diffraction rings seen in Figures 7 and 8 are tabulated in Table 4, where they are compared with the reported d-spacings of cerium oxide (CeO_2). It is seen that the Buehler CeO_2 contains some unidentified compound in addition to cerium oxide. Since all the diffraction rings observed in the diffraction pattern of the polishing debris can be assigned to cerium oxide polishing compound, it is concluded that cerium oxide removes material from fused silica in an amorphous form which could be pure SiO_2 or some compound of SiO_2 and CeO_2.

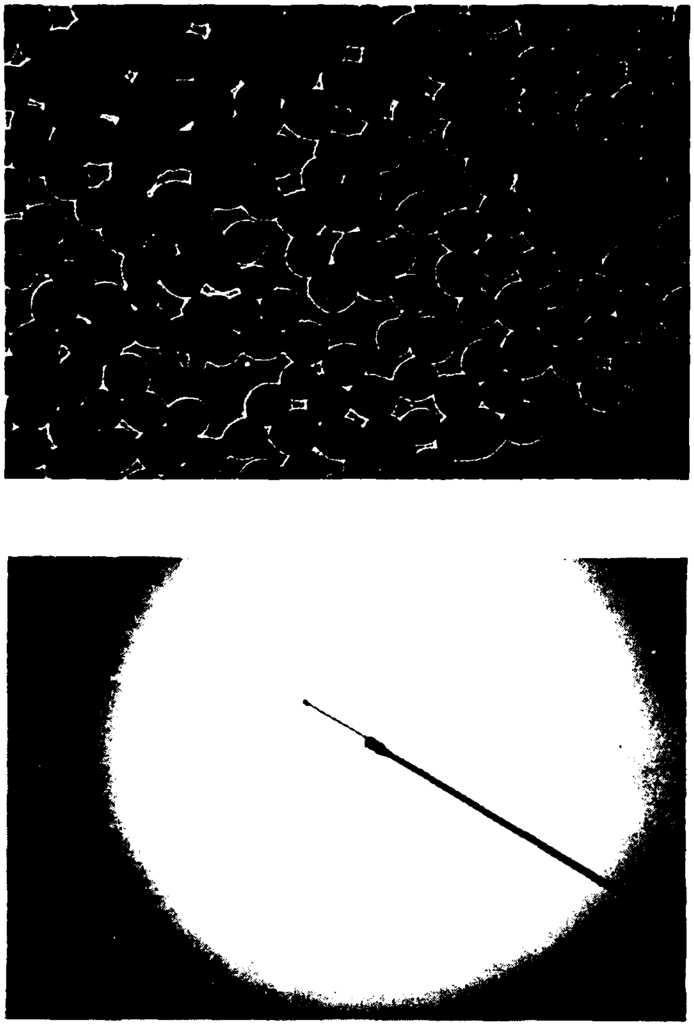


Figure 5. Transmission electron micrograph and diffraction pattern of colloidal silica

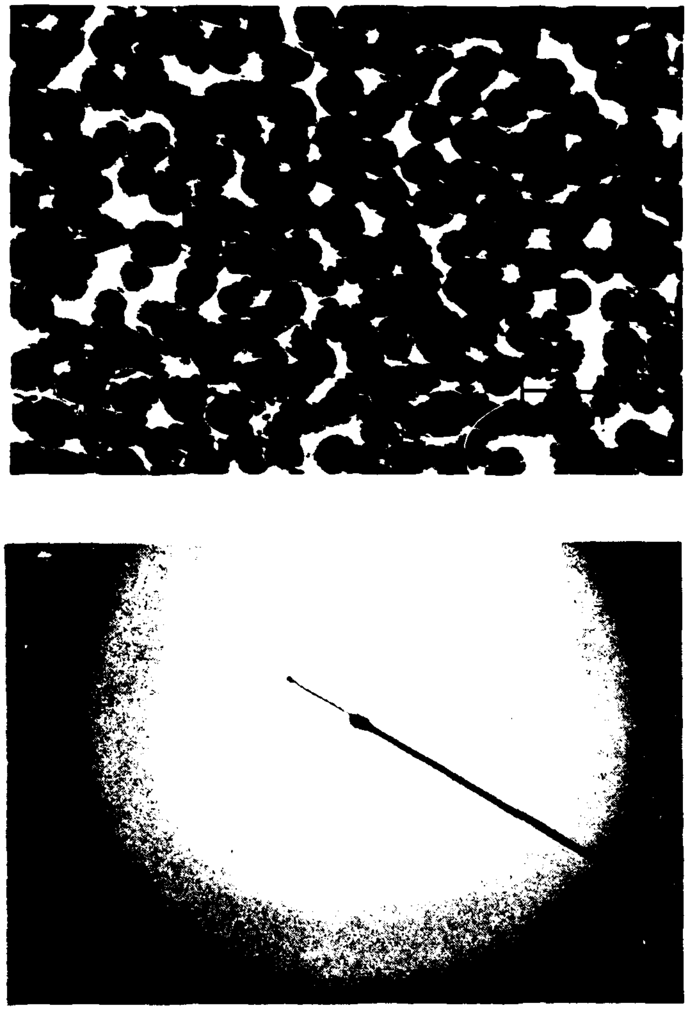


Figure 6. Transmission electron micrograph and diffraction pattern of debris obtained by polishing Si with colloidal silica

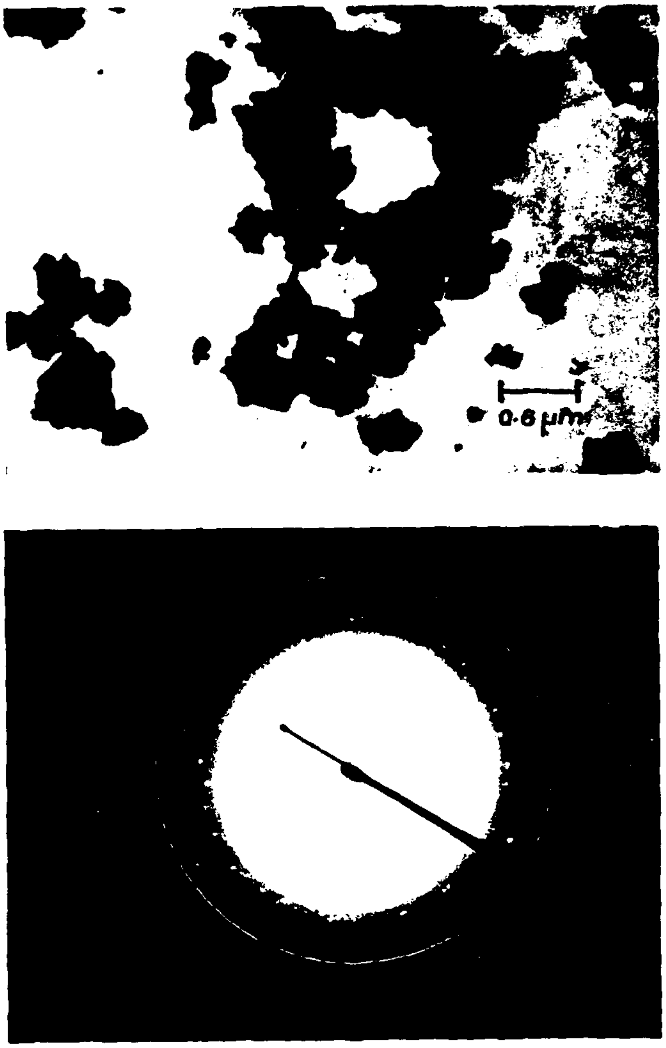


Figure 7. *Transmission electron* micrograph and diffraction pattern of Buehler cerium oxide

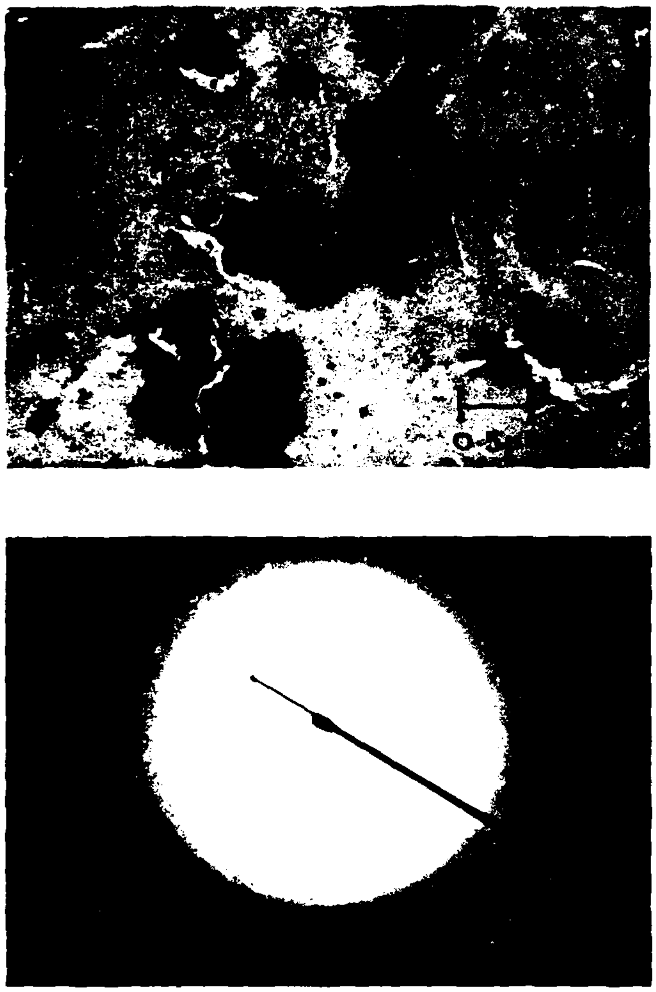


Figure 8. Transmission electron micrograph and diffraction pattern of debris obtained by polishing fused silica with Buehler cerium oxide

The transmission electron micrograph and diffraction pattern of Cr_2O_3 and the debris obtained by polishing Si_3N_4 with Cr_2O_3 are shown in Figures 9 and 10, respectively. We were able to attribute all the diffraction rings observed in the diffraction patterns of the polishing compound and the debris to Cr_2O_3, suggesting the possibility that the reaction product of Cr_2O_3 and Si_3N_4 is also amorphous in nature.

Scanning electron micrograph of the debris obtained by polishing Si_3N_4 with Cr_2O_3 is shown in Figure 11(a). The distributions of Si and Cr in this debris are shown in Figures 11(b) and 11(c), respectively. Scanning electron micrograph of the debris obtained by polishing fused silica with CeO_2 is shown in Figure 12(a). The distributions of Si and Ce in this debris are shown in Figure 12(b) and 12(c), respectively. These data indicate that the reaction product of polishing is a small fraction of polishing debris.

Table 4. Analysis of the diffraction patterns of Buehler CeO_2 and the debris obtained by polishing fused silica with Buehler CeO_2.

Measured d-spacings,Å		Reported d-spacings of CeO_2, Å
Buehler CeO_2	Polishing debris	
3.15	3.15	3.12
2.70	2.72	2.71
2.28	2.25	—
1.93	1.93	1.91
1.72	1.72	—
1.67	1.65	1.63
1.52	1.51	1.56
1.33		1.33
1.26		1.24

In an earlier study of the reaction product of mechanochemical polishing of $Al_2O_3$with SiO_2, Yasunaga et al.[2] have found it to be amorphous in nature. They were able to crystallize it by heating and identifying it as mullite. Experiments of this nature will be useful in identification of the reaction product of mechanochemical polishing.

3.4 PRECISION OF MECHANOCHEMICALLY POLISHED SURFACES

Precision in the context of this work refers to the flatness and surface roughness of mechanochemically polished surfaces. Because of the need to use a chemically reactive polishing medium and to apply high pressures in mechanochemical polishing, difficulties are encountered in finding a compatible lap material. Laps such as polyurethane impregnated polyester or polyurethane foam are frequently employed for mechanochemical polishing of amorphous or monocrystalline, single-phase materials. Employment of such non-rigid laps for mechanochemical polishing yields polished surfaces with orange-peel appearance (in the case of polycrystalline materials), showing excessive rounding at the edges and with flatness of no better than 1 λ (λ = 633nm) per centimeter in the center. Efforts were made in the present work to see if these difficulties can be overcome by employing machinable plastics as laps for mechanochemical polishing.

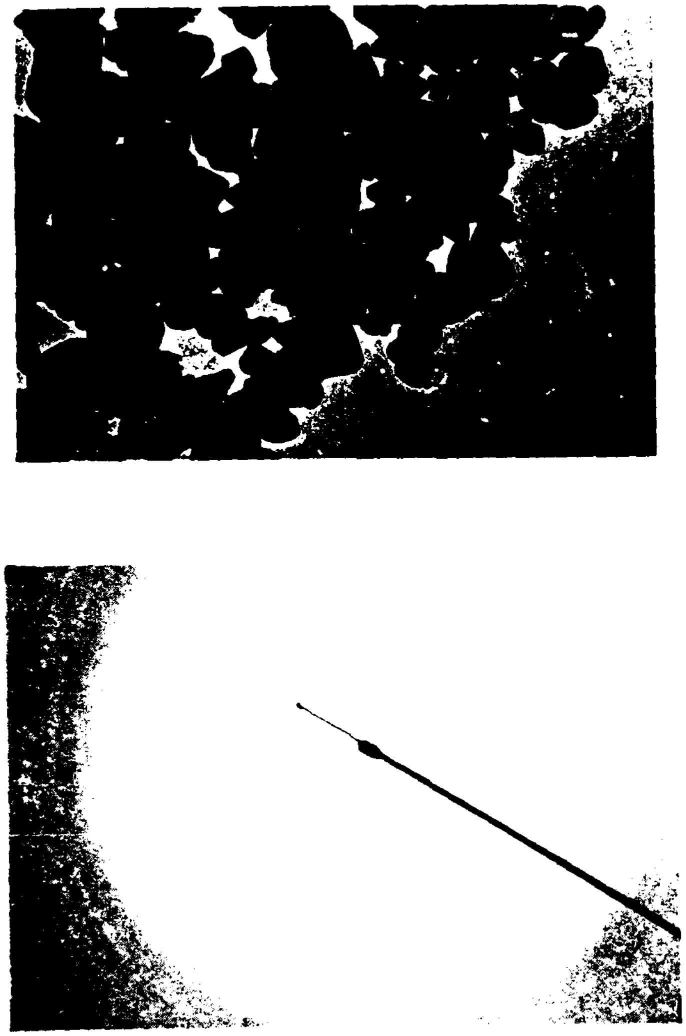


Figure 9. Transmission electron micrograph and diffraction pattern of Cr_2O_3

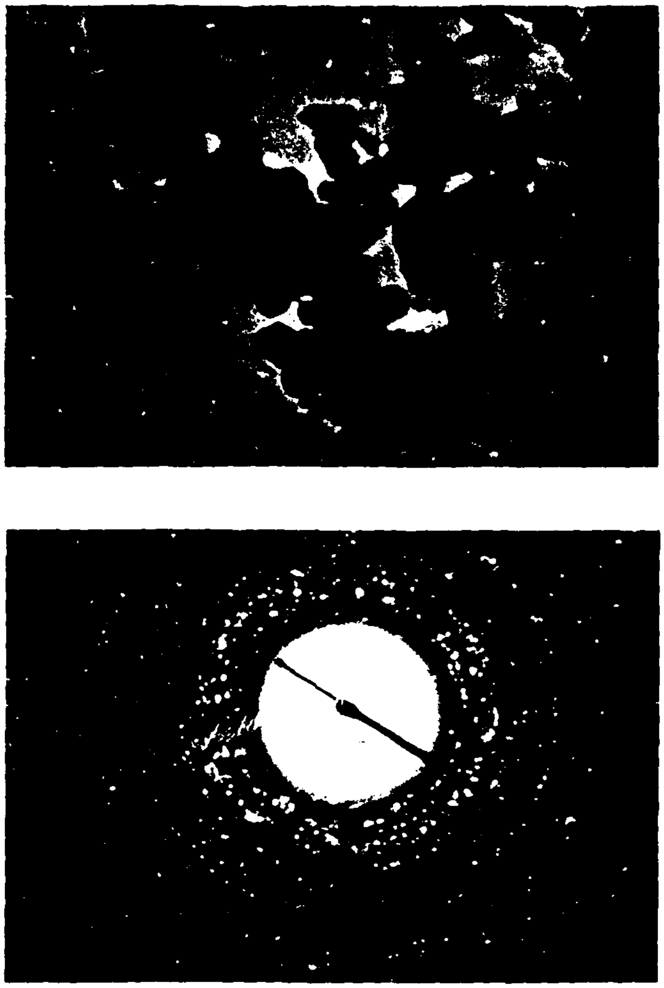


Figure 10. Transmission electron micrograph and diffraction pattern of debris obtained by polishing Si_3N_4 with Cr_2O_3

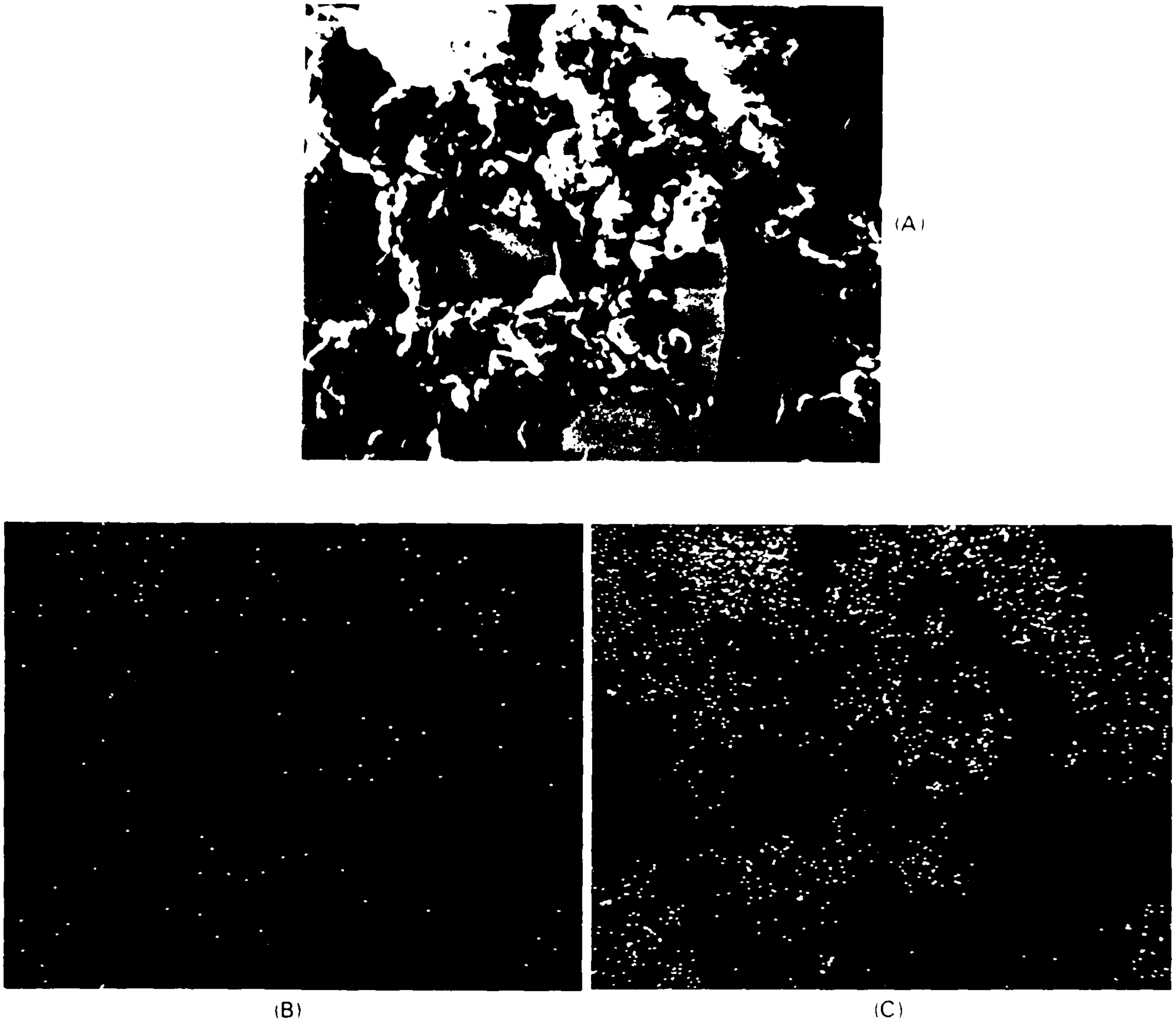


Figure 11. Debris obtained by mechanochemically polishing Si_3N_4 with Cr_2O_3. (A) Scanning electron micrograph, (B) distribution of Si in the debris (C) distribution of Cr in the debris

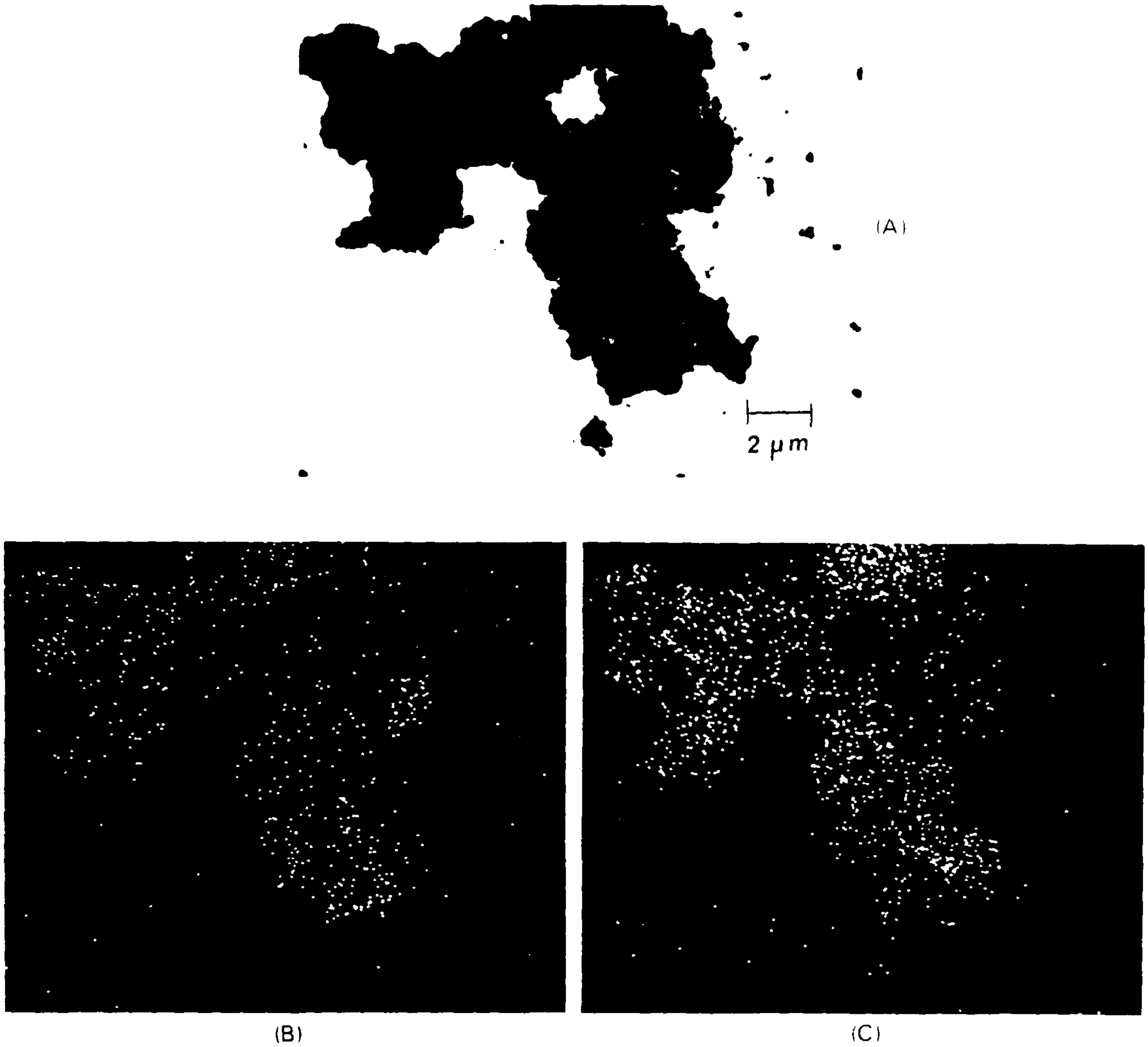


Figure 12. Debris obtained by polishing fused silica with cerium oxide. (A) Scanning electron micrograph, (B) distribution of Si in the debris and (C) distribution of Ce in the debris

Machined laps of plastics such as linen phenolic, Teflon, bts, polyethylene and pvc were used for mechanochemical polishing. Except for linen phenolic, these plastics were found unsuitable for mechanochemical polishing because of the difficulties encountered in milling or grinding them to a high degree of flatness as well as due to their inability to withstand pressures on the order of 7×10^4 N/m^2 (10 psi) applied during mechanochemical polishing.

Using milled linen phenolic laps, we have been able to obtain flatness of $\lambda/10$ ($\lambda = 633$ nm) per centimeter of the polished surface. Surface figures of mechanochemically polished samples of ZrO_2 and spinel are shown in Figure 13. A colloidal silica slurry was used as a mechanochemical polishing medium for these materials.

Anisotropy in the material removal rates associated with grains of different orientations introduces steps at the grain boundaries in polycrystalline materials. Steps are also introduced at the phase boundaries in polyphase materials. This phenomenon limits the maximum smoothness that can be achieved by mechanochemically polishing single-phase and multiphase polycrystalline materials. In an effort to determine what these limitations are, surface profiles of mechanochemically polished surfaces of ZrO_2, Al_2O_3, $MgO.Al_2O_3$, Mn-Zn ferrite, B_4C, SiC and Si_3N_4 were measured using a Talystep profilometer. All these materials were polished on a linen phenolic lap. The polishing media were colloidal silica slurries for all oxide ceramics, Cr_2O_3 for B_4C and SiC, and Fe_2O_3 for Si_3N_4. The surface profiles, along with the corresponding Nomarski micrographs, of the mechanochemically polished surfaces of various materials are shown in Figures 14-20. It is seen that the peak-to-valley roughness varies from material-to-material over the range of 160Å for spinel to 1300Å for partially stabilized ZrO_2.

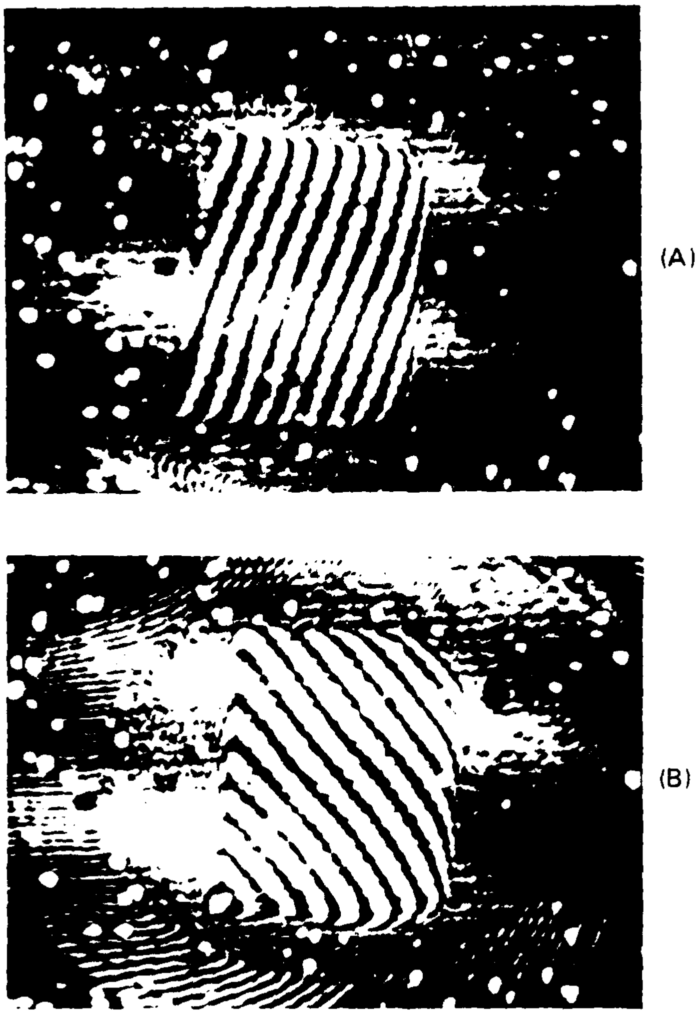


Figure 13. Surface figures of mechanochemically polished samples of (A) spinel and (B) zirconium oxides. Samples are approximately 18mm × 25mm in dimensions

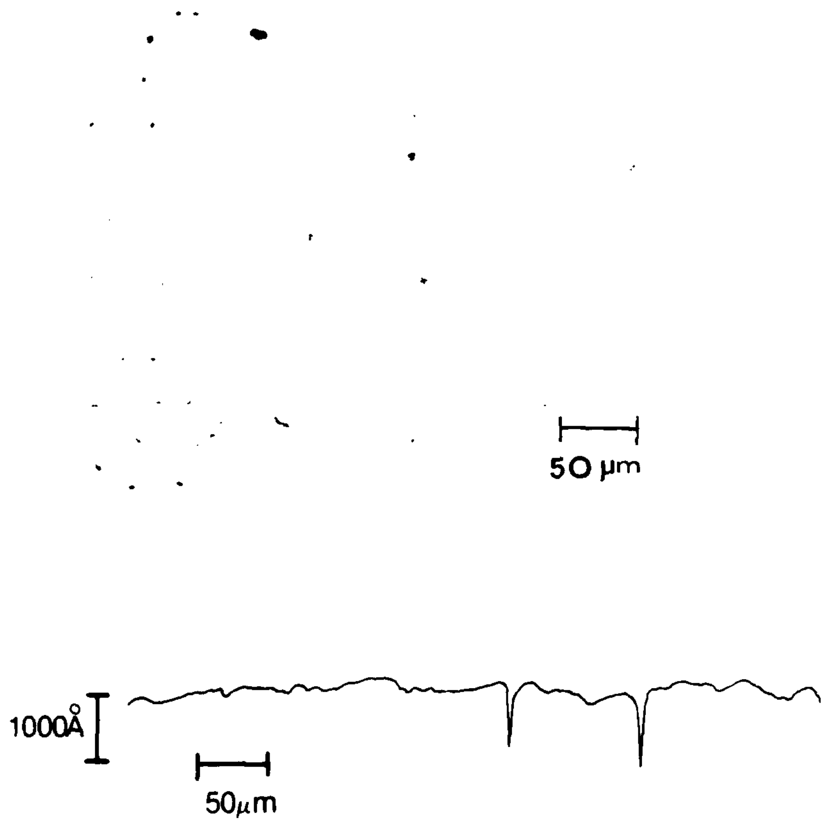


Figure 14. Nomarski micrograph and surface profile of mechanochemically polished ZrO_2

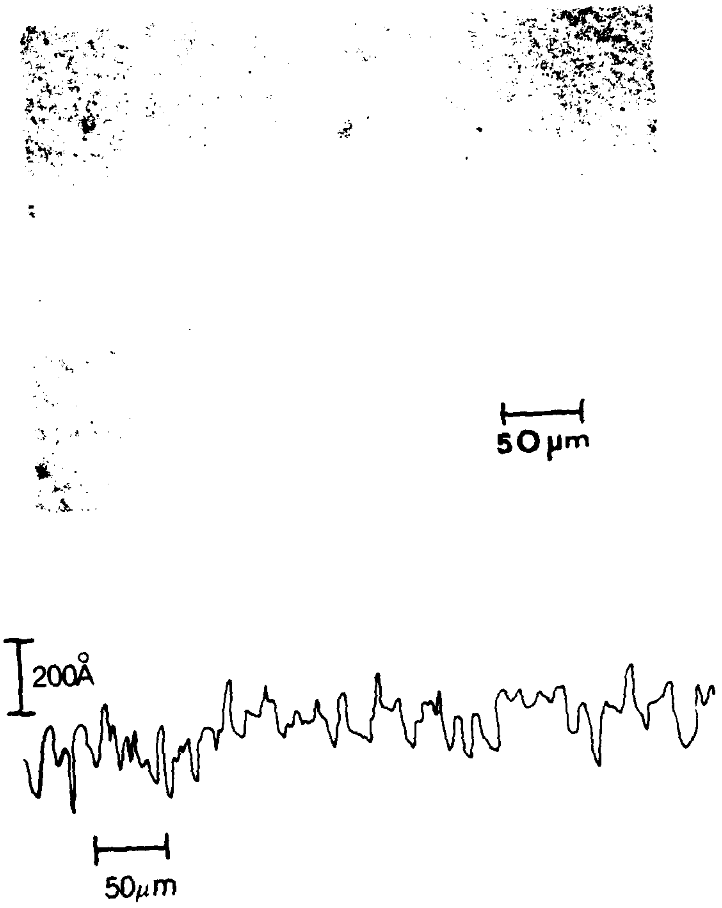


Figure 15. Nomarski micrograph and surface profile of mechanochemically polished Al_2O_3

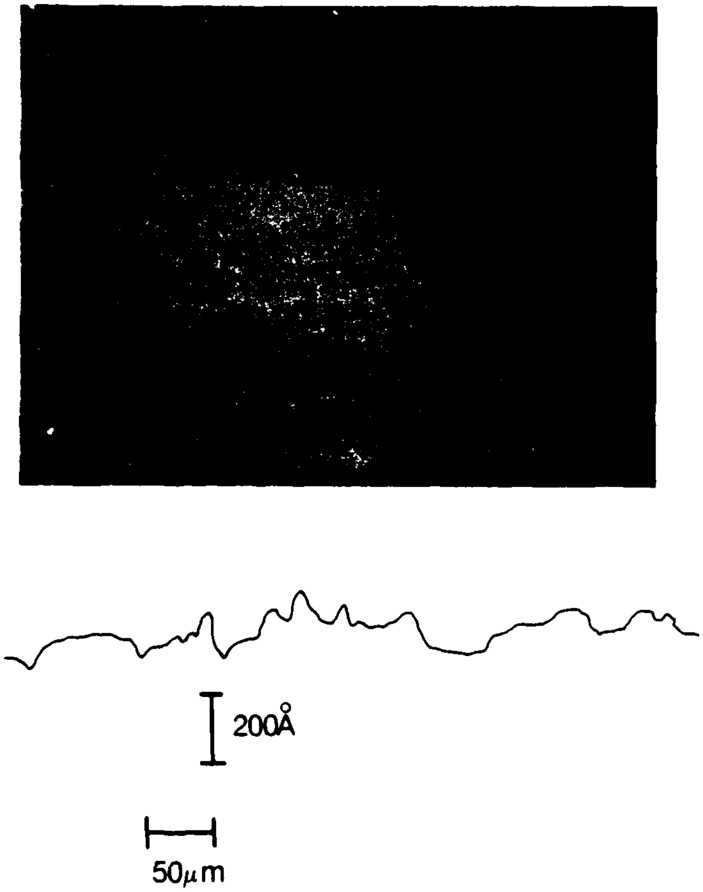


Figure 16. Nomarski micrograph and surface profile of mechanochemically polished $MgO.Al_2O_3$

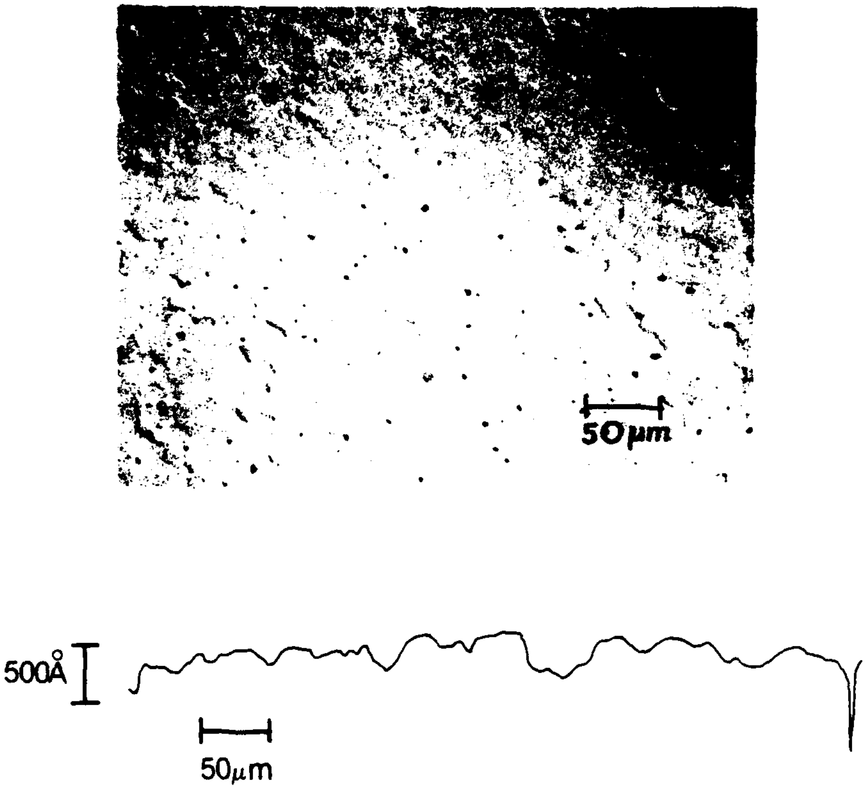


Figure 17. Nomarski micrograph and surface profile of mechanochemically polished Mn-Zn ferrite

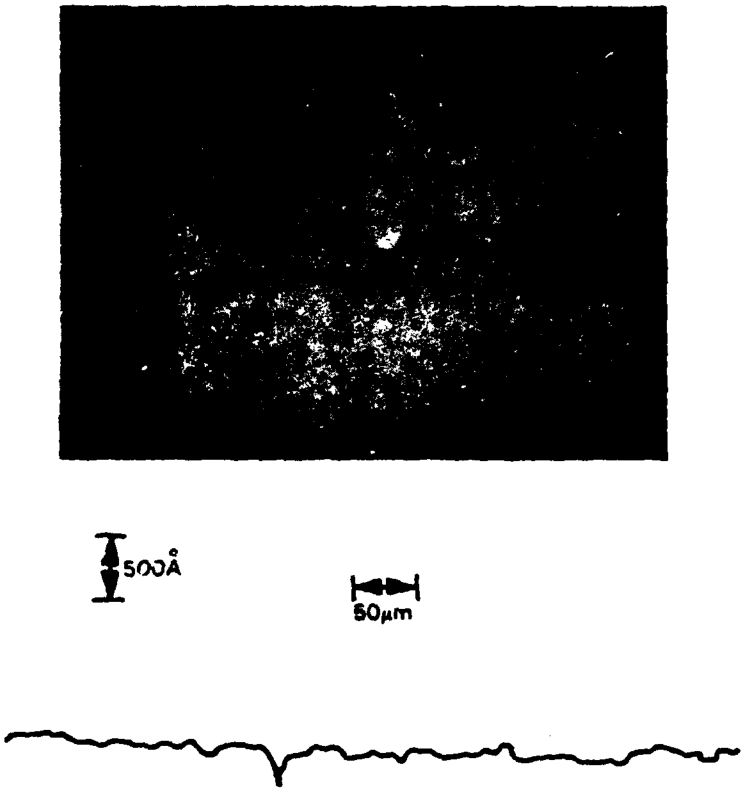


Figure 18. Nomarski micrograph and surface profile of mechanochemically polished Si_3N_4

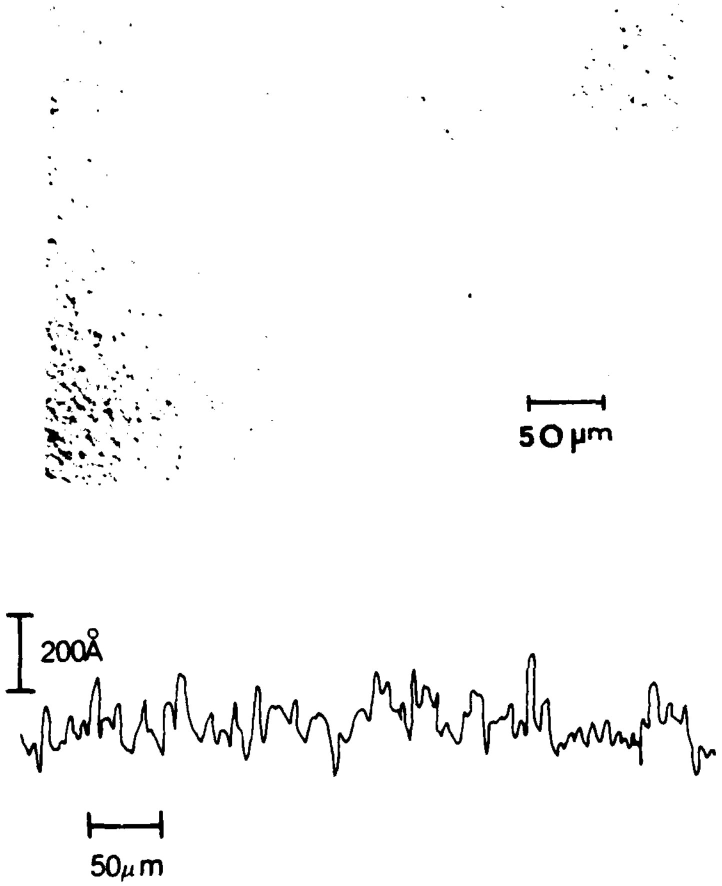


Figure 19. Nomarski micrograph and surface profile of mechanochemically polished SiC

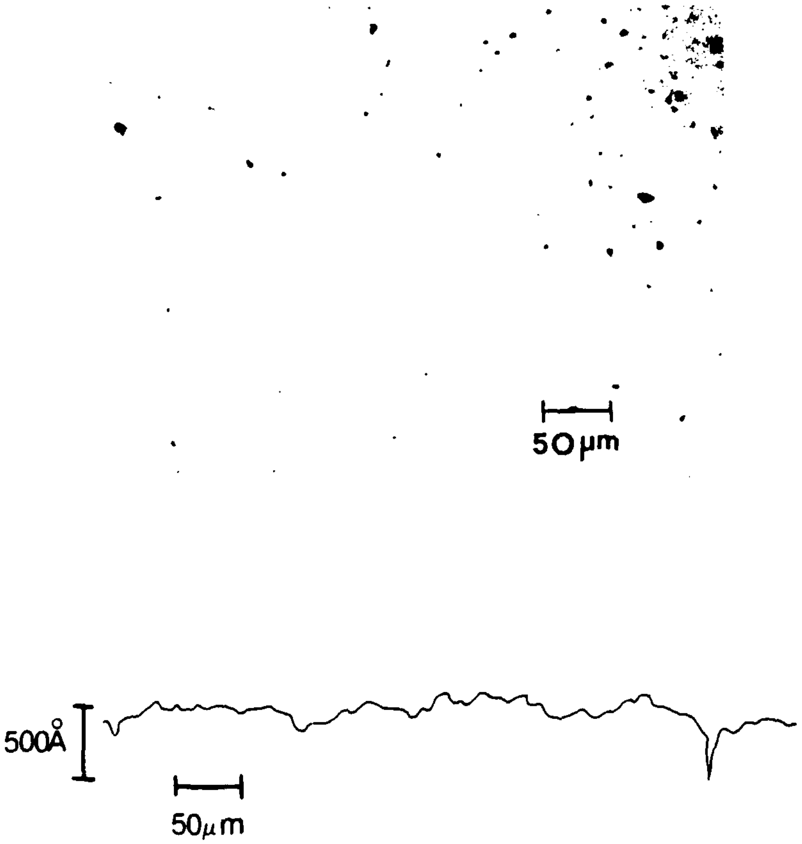


Figure 20. Nomarski micrograph and surface profile of mechanochemically polished B_4C

Section 4
Conclusions

Our study of mechanochemical polishing of ceramics indicates that soft abrasives which mechanochemically polish hard ceramics can be found with little difficulty, but that a limitation of low removal rates, in the range of 0.3-0.6 μm/hr, is associated with most of them. Oxide ceramics can be polished at significantly higher removal rates, in the range of 4-8μm/hr, by employing colloidal slurry as a mechanochemical polishing medium.

A limitation of low removal rates, in the range of 0.5-1.3μm/hr, is associated with colloidal silica slurry when used as a mechanochemical polishing medium for non-oxide ceramics. Significantly higher removal rates can be achieved by employing oxides of chromium as mechanochemical polishing media for non-oxide ceramics. The measured removal rates are as high as 16μm/hr for Si_3N_4, 6μm/hr for B_4C and 5μm/hr for SiC.

Mechanochemically polished surfaces with flatness of $\sim\lambda/10$ ($\lambda = 633$nm) per centimeter can be achieved by using machined linen phenolic lap. This is adequate for substrate applications of ceramics in electronics packaging as well as for application of Mn-Zn ferrite in manufacturing of high-performance magnetic recording heads. Since in many applications in optics flatness of better than $\lambda/20$ per centimeter is required, a need exists for additional work in this area.

Anisotropy in the material removal rates associated with grains of different orientations or with different phases restricts the maximum smoothness that can be achieved by mechanochemically polishing polycrystalline ceramics. The measured peak-to-valley surface roughness has been found to vary over the range of 160-1200 Å for the polycrystalline ceramics used in this work.

Electron microscopy analysis of the debris obtained by polishing Si_3N_4 with Cr_2O_3, Si with colloidal silica, and fused silica with cerium oxide suggest the possibility that the reaction products of polishing in these three cases are amorphous in nature.

Index of Publications

1 H. Vora, "Study of Mechanochemical Machining of Ceramics and the Effect on Thin Film Behavior," Final Technical Report #N00014-83-C-0270; NR653-002; February 1984.

Distribution List (Basic)
(Technical and Summary Reports, November 1979)

Organization	Copies
Defense Documentation Center Cameron Station Alexandria, VA 22314	12
Office of Naval Research Department of the Navy 800 N. Quincy Street Arlington, VA 22217 ATTN: Code 471	1
Code 470	1
Commanding Officer Office of Naval Research Branch Office Building 114, Section D 666 Summer Street Boston, MA 02210	1
Commanding Officer Office of Naval Research Branch Office 536 South Clark Street Chicago, IL 60605	1
Office of Naval Research San Francisco Area Office One Hallidie Plaza Suite 601 San Francisco, CA 94102	1
Naval Research Laboratory Washington, DC 20375 ATTN: Codes 6000	1
6100	1
6300	1
2627	1
Naval Air Development Center Code 606 Warminster, PA 18974 ATTN: Mr. F.S. Williams	1
Naval Air Propulsion Test Center Trenton, NJ 08628 ATTN: Library	1
Naval Construction Batallion Civil Engineering Laboratory Port Hueneme, CA 93043 ATTN: Materials Division	1
Naval Electronics Laboratory San Diego, CA 92152 ATTN: Electron Materials Sciences Division	1
Naval Missile Center Materials Consultant Code 3312-1 Point Mugu, CA 92041	1
Commanding Officer Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910 ATTN: Library	1
Commander David W. Taylor, Naval Ship Research and Development Center Bethesda, MD 20084	1
Naval Oceans Systems Center San Diego, CA 92132 ATTN: Library	1
Naval Underwater Systems Center Newport, RI 02840 ATTN: Library	1
Naval Postgraduate School Monterey, CA 93940 ATTN: Mechanical Engineering Department	1
Naval Weapons Center China Lake, CA 93555 ATTN: Library	1
Naval Air Systems Command Washington, DC 20360 ATTN: 53031	1
52032	1

Organization	Copies
Naval Sea Systems Command Washington, DC 20362 ATTN: Code 05R	1
Naval Facilities Engineering Command Alexandria, VA 22331 ATTN: Code 03	1
Scientific Advisor Commandant of the Marine Corps Washington, DC 20380 ATTN: Code AX	1
Army Research Office P.O. Box 12211 Triangle Park, NC 27709 ATTN: Metallurgy & Ceramics Program	1
Army Materials and Mechanics Research Center Watertown, MA 02172 ATTN: Research Programs Office	1
Air Force Office of Scientific Research/NE Building 410 Bolling Air Force Base Washington, DC 20332 ATTN: Chemical Science Directorate	1
Electronics & Materials Sciences Directorate	1
Air Force Materials Laboratory Wright-Patterson AFB Dayton, OH 45433	1
Library Building 50, Room 134 Lawrence Radiation Laboratory Berkeley, CA	1
NASA Headquarters Washington, DC 20546 ATTN: Code RRM	1
NASA Lewis Research Center 21000 Brookpark Road Cleveland, OH 44135 ATTN: Library	1
National Bureau of Standards Washington DC 20234 ATTN: Metals Science and Standards Division	1
Ceramics Glass and Solid State Science Division	1
Fracture and Deformation Division	1
Director Applied Physics Laboratory University of Washington 1013 Northeast Fortieth Street Seattle, WA 98105	1
Defense Metals and Ceramics Information Center Battelle Memorial Institute 505 King Avenue Columbus, OH 43201	1
Metals and Ceramics Division Oak Ridge National Laboratory P.O. Box X Oak Ridge, TN 37380	1
Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, NM 87544 ATTN: Report Librarian	1
Argonne National Laboratory Metallurgy Division P.O. Box 229 Lemont, IL 60439	1
Brookhaven National Laboratory Technical Information Division Upton, Long Island New York 11973 ATTN: Research Laboratory	1
Office of Naval Research Branch Office 1030 East Green Street Pasadena, CA 91106	1

Distribution List B (Supplementary)
(Fracture Mechanics and Erosion Processes)

Dr. W.F. Adler
Effects Technology, Inc.
5383 Hollister Avenue
Santa Barbara, CA 92105

Dr. G. Denman, Code LPJ
AFML, Wright-Patterson AFB
Dayton, OH 45433

Professor R. Bradt, Ceramics Section
Materials Science Department
Pennsylvania State University
University Park, PA 16802

Dr. S.A. Bortz
IITRI
10 W. 5th Street
Chicago, IL 60616

Mr. E. Fisher
Ford Motor Company
Dearborn, MI 48121

Dr. W.G.D. Frederick
AFML, Wright-Patterson AFB
Dayton, Ohio 45433

Dr. P. Gielisse
University of Rhode Island
Kingston, RI 02881

Dr. M.E. Gulden
International Harvester
Solar Division
2200 Pacific Highway
San Diego, CA 92138

Dr. D.P.H. Hasselman
Virginia Polytechnic Institute
Department of Materials Engineering
Blacksburg, VA 24061

Dr. L.L. Hench
Department of Metallurgy
University of Florida
Gainesville, FL 32611

Dr. A.H. Heuer
Case Western Reserve University
University Circle
Cleveland, OH 44106

Mr. G. Hayes
Naval Weapons Center
China Lake, CA 93555

Dr. P. Jorgensen
Stanford Research Institute
Poulter Laboratory
Menlo Park, CA 94025

Dr. R.N. Katz
Army Materials and Mechanics Research
Center
Watertown, MA 02171

Dr. H. Kirchner
Ceramic Finishing Company
P.O. Box 498
State College, PA 16801

Dr. B. Koepke
Honeywell Inc.
Systems and Research Center
2600 Ridgway Parkway
P.O. Box 312
Minneapolis, MN 55440

Mr. Frank Koubek
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, MD 20910

r R. Jaffee
Electric Power Resources Institute
Palo Alto, CA

Dr. J. Ritter
University of Massachusetts
Department of Mechanical Engineering
Amherst, MA 01002

Dr. P. Land
AFML, Wright-Patterson AFB
Dayton, Ohio 45433

Dr. F.F. Lange
Rockwell International
P.O. Box 1085
1049 Camino Dos Rios
Thousand Oaks, CA 91360

Dr. J. Lankford
Southwest Research Institute
8500 Culebra Road
San Antonio, TX 78284

Dr. N. Macmillan
Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802

Mr. F. Markarian
Naval Weapons Center
China Lake, CA 93555

Dr. K.D. McHenry
Honeywell Inc.
Ceramics Center
1885 Douglas Drive
Golden Valley, MN 55422

Dr. N. Perrone, Code 474
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Dr. R.A. Queeney
126 Hammon Building
Pennsylvania State University
University Park, PA 16802

Mr. R. Rice
Naval Research Laboratory
Code 6360
Washington, DC 20375

Dr. D. Richardson
AiResearch Manufacturing Company
4023 36th Street
P.O. Box 5217
Phoenix, AZ 85010

Dr. Rustum Roy
Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802

Dr. R. Ruh
AFML, Wright-Patterson AFB
Dayton, OH 45433

Norton Company
Industrial Ceramics Division
Worcester, MA 01606
ATTN: Library

Dr. J.H. Rosolowski
G.E. Company, R&D Center
P.O. Box 8
Schenectady, NY 02301

State University of New York
College of Ceramics
Alfred University
Alfred, NY 14802
ATTN: Library

State University of New York
Alfred University
Materials Science Division
Alfred, NY 14802

Dr. N. Tallan
AFML, Wright-Patterson AFB
Dayton, OH 45433

Mr. K. Letson
Redstone Arsenal
Huntsville, AL 35809

Charles Lewis
EBI Company, Inc.
91 Tolland Street
East Hartford, CT 06108

Dr. D.A. Shockey
Stanford Research Institute
Poulter Laboratory
Menlo Park, CA 94025

Dr. G. Sines
University of California at Los Angeles
Los Angeles, CA 90024

Mr. J.D. Walton
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, GA 30332

Mr. L.B. Weckesser
Applied Physics Laboratory
Johns Hopkins Road
Laurel, MD 20810

Dr. S.M. Widerhorn
Inorganic Materials Division
National Bureau of Standards
Washington, DC 20234

Dr. Paul D. Wilcox
Sandia Laboratories
Division 2521
Albuquerque, NM 87115

Dr. R.E. Tressler
Ceramic Science Section
226 Steidle Building
Pennsylvania State University
University Park, PA 16802

Dr. T. Vasilos
AVCO Research & Advanced Development
Division
201 Lowell Street
Wilmington, MA 01887

Dr. Eugene A. Larson, President
Blue River Laboratories
P.O. Box 442
Lewiston, PA 17044

Mr. G. Schmitt
AFML, Wright-Patterson AFB
Dayton, OH 45433

Dr. M. Rosenblatt
California Research and Technology
6269 Variel Avenue, Suite 200
Woodland Hills, CA 91364

Dr. A.G. Evans
University of California
Berkeley, CA 94720

Mr. D. Cassidy
Ford Motor Company
P.O. Box 1603
Dearborn, MI 48121

Dr. J. Brennan
United Technologies Corporation
United Technologies Research Center
East Hartford, CT 06108

Professor M. Tomozawa
Rensselaer Polytechnic Institute
Department of Materials Engineering
Troy, NY 12181

Murli H. Manghnani
Hawaii Institute of Geophysics
University of Hawaii
Honolulu, Hawaii 96822 U.S.A.