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PROPERTIES OF YTTRIA-TETRAGONAL ZIRCONIA POLYCRYSTAL (Y-TZP) MATERIALS AFTER LONG-TERM EXPOSURE TO ELEVATED TEMPERATURES

JEFFREY J. SWAB

March 1989

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ABSTRACT

Due to an unusual combination of high strength and toughness, tetragonal zirconia polycrystal (TZP) materials are candidates for use in advanced heat engines. The properties of these materials stem from the stress-assisted transformation of metastable tetragonal zirconia particles. However, after long times at elevated temperatures, this class of materials is susceptible to properties degradation due to the undesirable transformation of tetragonal zirconia to monoclinic zirconia upon cooling. Accordingly, a task was initiated to examine the extent and magnitude of this phenomenon's effect on the properties.

Seven commercially available yttria-tetragonal zirconia polycrystal (Y-TZP) materials were evaluated. Room temperature properties were measured before and after heat treatments at 1000°C. Microstructure and phase stability were also examined. In all but one case, the Y-TZPs showed very little change in room temperature properties after long times at this temperature. Results show that the use of pressure-assisted processing greatly improves the strength by reducing porosity and keeping the grain size extremely fine, but this reduces the toughness because finer grains are more difficult to transform.

→ Key words. →

In addition, a small amount of cubic zirconia appears to enhance the toughness of fine-grained Y-TZP while maintaining good strength. During processing, a small amount of cubic zirconia is formed and allowed to grow. This creates regions poor in yttria which can transform spontaneously in the presence of a crack-tip stress field.

CONTENTS

RESULTS

FOREWORD

The work described herein is part of the Characterization of Transformation-Toughened Ceramics Program which is a subtask of the Department of Energy (DoE) sponsored, Oak Ridge National Laboratory (ORNL) monitored, Ceramic Technology for Advanced Heat Engines Project (Interagency Agreement No. DE-AI05-840R21411). The purpose of this subtask is to examine commercial and experimental transformation-toughened ceramics for possible application in advanced heat engines.

The approach is two-fold: a) to determine the effects of long-term/elevated temperature exposure on microstructure, phase stability, and room temperarature properties, and b) to examine the high temperature performance of the most promising materials from a) using stepped-temperature stress-rupture and stress-rupture tests. This report summarizes the results of part a).

INTRODUCTION

A variety of structural ceramics are being considered for use in advanced diesel engines. Currently, silicon nitride, silicon carbide, zirconia, and ceramic composites (e.g., zirconia-toughened alumina) are being considered for monolithic applications. In addition, zirconia is being examined as a possible thermal barrier coating. These materials possess some properties which are comparable to those desired of materials for use in advanced heat engines, as described in Table 1.

Table 1. DESIRED MATERIAL PROPERTIES FOR AN ADVANCED HEAT ENGINE APPLICATION (Ref. 1)

Temperature Limit, °F/ °C	> 1800/982
Fracture Toughness, MPa*m$^{1/2}$	> 8.0
Flexure Strength, MPa	> 800
Thermal Conductivity, Cal/cm-sec-°C	< 0.01
Thermal Shock Resistance, T °C	> 500
Thermal Expansion x 10^{-6}/ °C	> 10
Weibull Modulus	> 18
Time, Exposure, Hours	> 1000

The potential benefits of incorporating these ceramics into advanced heat engines include improved fuel economy, significantly higher performance, and reduced dependence on scarce materials.

One broad class of materials, transformation-toughened zirconias (TTZ), has been extensively examined for advanced heat engines. This particular class of materials possesses a very low thermal conductivity and an unusual combination of high strength and fracture toughness at room temperature. The material's unusual mechanical properties stem from a

1. KAMO, R., and BRYZIK, W. *Cummins/TACOM Advanced Adiabatic Engine.* SAE Paper 840428. Adiabatic Engines: World Wide Review SP-571, SAE International Congress and Exposition, Detroit, MI, 1984, p. 21-34.

stress-assisted "martensitic" phase transformation of a metastable tetragonal (t) phase to the stable monoclinic (m) phase; hence the name "transformation toughening."[2]

The mechanisms of this toughening are believed to include one or more of the following:

- deflection of the crack tip
- microcracking which leads to crack branching and an increase in the energy required for continued crack growth
- absorption of the crack tip energy by the phase transformation ($t \longrightarrow m$)[3] .

Pure zirconia exhibits three distinct polymorphs according to the following transformations:

$$\text{Monoclinic} \underset{1150^{\circ}C}{\overset{950^{\circ}C}{\rightleftarrows}} \text{Tetragonal} \xleftarrow{2370^{\circ}C} \text{Cubic} \xleftarrow{2680^{\circ}C} \text{Liquid.}^{2}$$

In order to achieve some degree of transformation toughening, a stabilizer (typically CaO, MgO, Y_2O_3, or CeO_2) must be added. The addition of one of these stabilizers lowers the $t \longrightarrow m$ chemical driving force and thus the $t \longrightarrow m$ transformation temperature, enabling the t-phase to be retained in a metastable state upon cooling to room temperature. With these additions, new phases have also been identified. These include a high pressure orthorhombic phase,[4] (which has been identified in CaO-stabilized cubic zirconia), a rhombohedral phase,[5-7] and a nontransformable t'-phase[8,9] (in Y_2O_3-stabilized zirconia).

The addition of various stabilizers results in one of two types of TTZs: a) partially stabilized zirconia (PSZ) or b) tetragonal zirconia polycrystalline (TZP) materials. Although both PSZ and TZP are, in fact, "partially stabilized," their microstructure and stabilizers are quite different.

PSZ

This material is most commonly stabilized by MgO or CaO. The microstructure consists of small ($\sim 0.5\ \mu m$) coherent precipitates of metastable t-ZrO_2 in a large-grained (50-75 μm) cubic (c) ZrO_2 matrix. This material is obtained by annealing in the two-phase (t+c) field. Toughening results when the tetragonal precipitates transform to the stable monoclinic phase at the crack tip as the crack propagates through the material.

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[2] RÜHLE, M., and HEUER, A. H. *Phase Transformation in ZrO_2-Containing Ceramics: II, The Martensitic Reaction in t-ZrO_2.* Advances in Ceramics, v. 12, Science and Technology of Zirconia, N. Claussen, M. Rühle, and A. H. Heuer, ed., The American Ceramic Society, Columbus, OH, 1984, p. 14-32.

[3] LARSEN, D. C., and ADAMS, J. W. *Long-Term Stability and Properties of Zirconia Ceramics for Heavy Duty Diesel Engine Components.* Prepared for NASA-Lewis Research Center, for U.S. Department of Energy under Contract DEN 3-305 NASA CR-174943, September 1985.

[4] DEVI, S. R. U., MING, L. C., and MANGHANANI, M. H. *Structural Transformation in Cubic Zirconia.* J. Am. Ceram. Soc., v. 70, no. 9, 1987, p. C218-C219.

[5] HASEGAWA, H. *Rhombohedral Phase Produced in Abraded Surfaces of Partially Stabilized Zirconia (PSZ).* J. Mat. Sci. Lett., v. 2, 1983, p. 91-93.

[6] SAKUMA, T., YOSHIZAWA, Y. I., and SATO, H. *The Rhombohedral Phase Produced in Partially-Stabilized Zirconia.* J. Mat. Sci. Lett., v. 4, 1985, p. 29-30.

[7] KITANO, Y., MORI, Y., and ISHITANI, A. *Rhombohedral Phase in Y_2O_3-Partially-Stabilized ZrO_2.* J. Am. Ceram. Soc., v. 71, no. 1, 1988, p. C34-C36.

[8] MILLER, R. A., SMIALEK, J. L., and GARLICK, R. G. *Phase Stability in Plasma-Sprayed Partially Stabilized Zirconia-Yttria.* Advances in Ceramics, v. 3, Science and Technology of Zirconia, A. H. Heuer and L. W. Hobbs, ed., The American Ceramic Society, Columbus, OH, 1981, p. 241-253.

[9] LANTERI, V., HEUER, A. H., and MITCHELL, T. E. *Tetragonal Phase in the System ZrO_2-Y_2O_3.* Advances in Ceramics, v. 12, Science and Technology of Zirconia II, N. Claussen, M. Rühle, and A. H. Heuer, ed., The American Ceramic Society, Columbus, OH, 1984, p. 118-130.

TZP

These materials are stabilized by Y_2O_3 or CeO_2. Because the solubility of these oxides in zirconia is much greater than that of MgO or CaO, it enables greater stability of t-ZrO_2 grains against the t $\longrightarrow$ m transformation, allowing the production of a 100% t-ZrO_2 material. The t-ZrO_2 grains are faceted and fine grained ($\sim$2 μm or less). Rühle and Heuer[2] have indicated that autocatalytic nucleation is important in these materials to enhance toughening. That is, the stress created by a t-ZrO_2 grain which transforms is transferred to neighboring grains causing further transformation, thus forming a discrete area of monoclinic grains around the crack tip.

For both types of TTZs, Lange[10] has determined that for a given temperature there is a critical grain size needed to prevent the spontaneous t $\longrightarrow$ m transformation during cooling. If the t-zirconia grains are below this critical size, the thermodynamic free energy for transformation is higher and few grains transform. However, when grains are above this critical size, the thermodynamic free energy decreases and the t-zirconia grains can transform spontaneously. This is important when considering TTZs for advanced heat engines, because the typical engine operating temperature is $\sim$1000°C. This temperature is in the range where grain growth can occur and the t-ZrO_2 phase is stable. As a result, mechanical properties, such as strength and toughness, can decrease due to the increase in grain size and stability of the t-phase.

Due to this potential degradation of mechanical properties at engine operating temperature, research has been done to evaluate the long-term stability of Mg-PSZ,[3,11,12] Y-TZP,[3,11,13] and Ce-TZP.[14,15] This report summarizes the results of an effort to evaluate commercially available Y-TZP materials for long-term stability at typical engine operating temperatures.

EXPERIMENTAL PROCEDURE

Billets of Y-TZP materials were obtained from a variety of manufacturers as illustrated in Table 2. Type "B" bars (3 by 4 by 50 mm) were machined from these billets according to MIL-STD-1942. Due to material limitations, the AC Sparkplug TZP-110 was machined into "A" bars (1.5 by 2 by 30 mm) according to the same standard. The bulk density of each bar was determined by measuring the mass and geometry, and a pulse-echo ultrasonic technique was used to determine the modulus of elasticity (MOE). Bars from each manufacturer were then randomly divided into three lots of 40, with each lot undergoing one of the following heat treatments:

0 hr at 1000°C (as-received)
100 hr at 1000°C
500 hr at 1000°C.

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[10] LANGE, F. F. *Transformation Toughening - Part I - Size Effects Associated with the Thermodynamics of Constrained Transformations.* J. Mat. Sci., no. 17, 1982, p. 225-234.

[11] SCHIOLER, L. J. *Effect of Time and Temperature on Transformation Toughened Zirconias.* U.S. Army Materials Technology Laboratory, MTL TR 87-29, prepared for Oak Ridge National Laboratory for U.S. Department of Energy under Interagency Agreement DE-AI05-840R-21411, June 1987.

[12] FERBER, M. K., and HINE, T. *Time-Dependent Mechanical Behavior of Partially Stabilized Zirconia for Diesel Engine Applications.* ORNL/Sub/85-27416/1, prepared for Oak Ridge National Laboratory for U.S. Department of Energy under Contract DE-AC05-840R21400, July 1988.

[13] MASAKI, T. *Mechanical Properties of Y_2O_3-Stabilized Tetragonal Polycrystals after Aging at High Temperatures.* J. Am. Ceram. Soc., v. 69, no. 7, 1986, p. 519-522.

[14] TSUKMA, K. *Mechanical Properties and Thermal Stability of CeO_2 Containing Tetragonal Zirconia Polycrystals.* Am. Ceram. Soc. Bull., v. 65, no. 10, 1986, p. 1386-1389.

[15] TSUKUMA, K., and SHIMADA, M. *Strength, Fracture Toughness and Vickers Hardness of CeO_2-Stabilized Tetragonal ZrO_2 Polycrystals (Ce-TZP).* J. Mat. Sci., v. 20, 1985, p. 1178-1184.

Table 2. EVALUATED MATERIALS

	Code	Manufacturer	Material	Process	%Y_2O_3
Japanese					
	KY	Kyocera	Z-201	Sintered	2.8
	TOSH	Toshiba	TASZIC	Sintered	2-3
	HIT	Hitachi	1985	Hot-Pressed (?)	2.0
	NGk	NGK Locke	Z-191	Sintered	3.0
	KS	Koransha	1986	Sintered	3.0
	KH	Koransha	1986	HIP'ed	3.0
Domestic					
	AC	AC Sparkplug	TZP-110	Sintered	2.6

Heat treatments were done in air, at laboratory ambient humidity (40-60%), in an unstressed condition with the bars on silicon carbide knife edges to assure uniform thermal treatment. The knife edges supported the bars well outside the test area, assuring no effect on the mechanical property evaluation. The density and MOE were again measured after each thermal treatment. Thirty bars were then broken at room temperature with 4-point bending, according to MIL-STD-1942, with inner and outer spans of 20 mm and 40 mm, respectively, and a crosshead speed of 0.5 mm/min. (For the type "A" bars, spans of 10 mm and 20 mm were used.) The characteristic strength of the flexure specimen was then calculated for the bar. This value was not corrected for volume and surface effects. Weibull slopes were obtained by interpreting the strength data with a simple least-squares curve fit in a standard Weibull two-parameter plot. The fracture surface of each bar was examined optically using a low magnification microscope in an attempt to determine the cause of failure. In many cases, a scanning electron microscope (SEM) was needed to improve the chances of determining the flaw type.

The "effective" fracture toughness (K_c) was measured on the remaining 10 bars via the Vickers indentation-strength technique outline in Ref. 16 using various indentation loads on military standard "B" bars only. Prior to indentation, all bars were polished to a finish of 2-microinch RMS or better on one of their 4 mm by 50 mm faces. The polishing was necessary to remove any existing machining damage. The bars were broken using 4-point bending immediately after indentation to minimize any environmental effects. Bars were examined after failure to insure that the break had occurred at the indent. (Those that did not fail at the indent were excluded from K_c calculations.)

The linear intercept method[17] was used to determine the average grain size. This method was applied to SEM micrographs of specimens which were thermally etched at 1450°C for 15 minutes. A transmission electron microscope (TEM) was employed to analyze any grain-boundary phase that may be present in the material. Pieces of fractured bend bars were prepared by ion milling for examination in the TEM. This analysis could not be completed on the military standard "A" bars because the small size made ion milling impossible.

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16. CHANTIKUL, P., ANTIS, G. R., LAWN, B. R., and MARSHALL, D. B. *A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness: II, Strength Method.* J. Am. Ceram. Soc., v. 64, no. 9, 1981, p. 539-543.
17. MENDELSON, M. I. *Average Grain Size in Polycrystalline Ceramics.* J. Am. Ceram. Soc., v. 52, no. 8, 1969, p. 443-446.

The zirconia phases present were determined using X-ray diffraction with CuKα radiation over an angular range of 25° to 40° 2θ. The surface volume fraction of monoclinic and the fraction of tetragonal-plus-cubic zirconia was calculated using the equations and constants in Ref. 11, which take into account the difficulty in deconvoluting the tetragonal (101) and cubic (111) peaks. These equation are:

$$V_{t+c} = \frac{1}{1+[(I_m/R_m)\,(R_{t+c}/I_{t+c})]}$$

and

$$V_m = 1 - V_{t+c}$$

where:

V_{t+c} = volume fraction of tetragonal plus cubic zirconia
V_m = volume fraction of the monoclinic (111) plus (11T) peaks
I_m = sum of the monoclinic (111) and (11T) integrated intensities
I_{t+c} = sum of the tetragonal plus cubic integrated intensities
R_{t+c} = sum of the tetragonal and cubic calculated intensities = 388.27
R_m = sum of the monoclinic (111) and (11T) calculated intensities = 227.02.

These volume fractions were obtained from as-machined, heat-treated specimens and from the fracture surface of related specimens used in toughness testing. Deconvolution of the high-angle tetragonal and cubic peaks and the calculation of their integrated intensities was completed via computer analysis.[18] The data was collected using a step scan made with incremental steps of 0.05° = 2θ and a count time of 10 seconds over the 2θ = 70° to 76° region. Using these peaks and their respective integrated intensities allowed for the determination of the relative amount of each phase.* Hardness was measured by Knoop indentation with a 300g load on specimens which were polished on a lead lap using 6 μm to 12 μm diamond paste.

RESULTS

Strength and Toughness

Figures 1 and 2 suggest that the seven Y-TZP materials may be divided into three general groups according to their mechanical properties (as defined in Table 1) and ability to retain these properties after heat treatments at 1000°C. The three groups are:

Group I: TZPs with excellent as-received strength and strength retention, but poor effective fracture toughness,

Group II: TZPs with good as-received strength, excellent strength retention, and good effective fracture toughness, and

Group III: TZPs with good as-received strength but poor strength retention, and good effective fracture toughness.

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*Special thanks to Prof. Gary Leatherman and James Marra at Worcester Polytechnic Institute for this analysis.

[18] DOUGLAS, C. *Quantitative Phase Analysis of Partially Stabilized Zirconia by X-ray Diffraction.* Masters Thesis, Worcestor Polytechnic Institute, Worcestor, MA, September 1987.

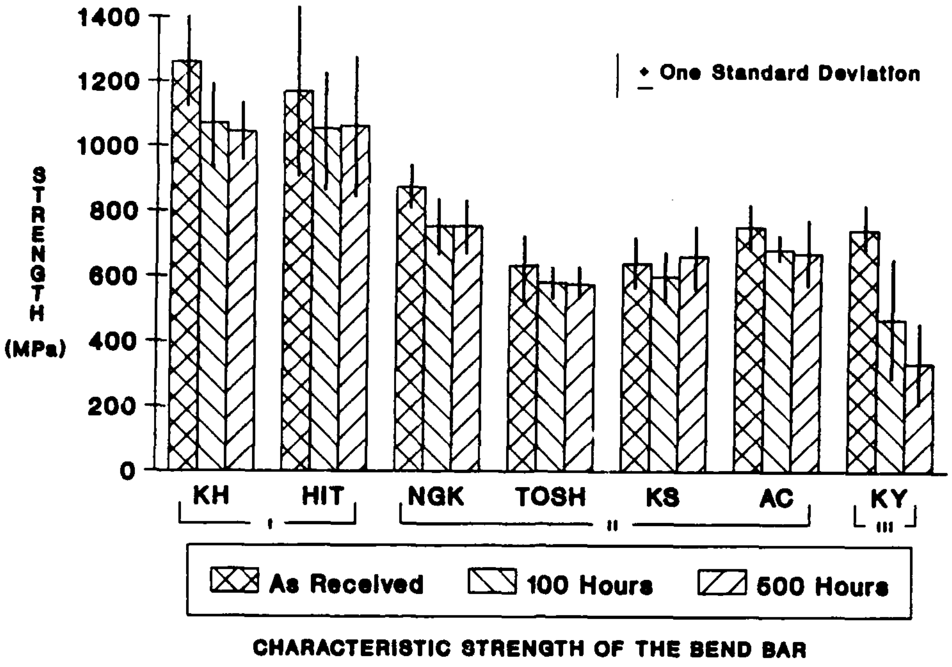

Figure 1. Strength of the seven Y-TZPs before and after heat treatment at 1000°C.

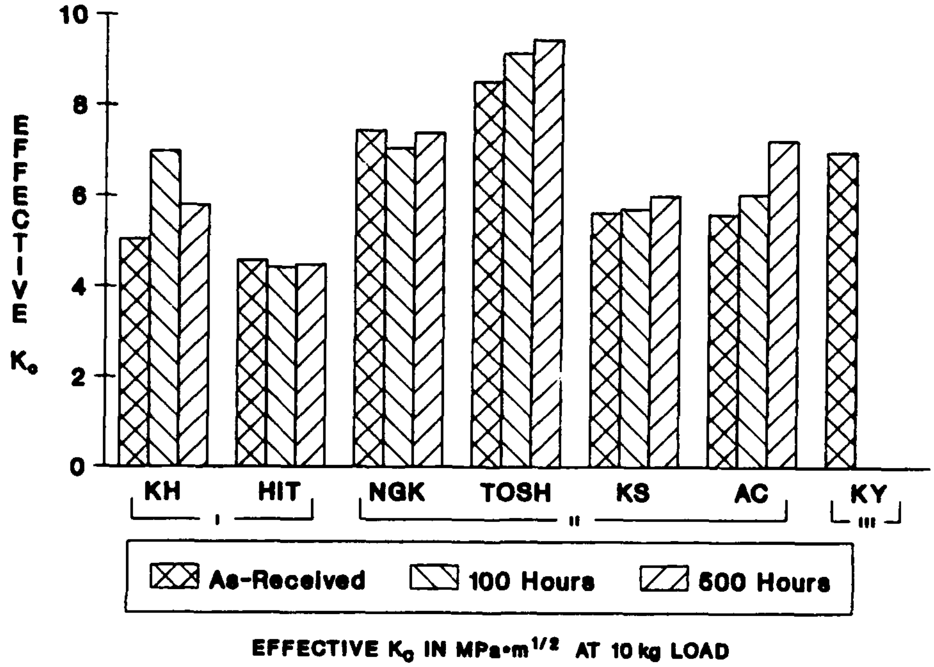

Figure 2. Fracture toughness of the seven Y-TZPs
before and after heat treatment at 1000°C.

Group I includes Koransha "HIP'ed" (KH) and Hitachi "1985" (HIT). Both exhibit excellent as-received strength, 1261 and 1169 MPa, respectively, and a slight strength loss ($\sim 15\%$) after 100 hours at 1000°C, but no further loss after 500 hours at 1000°C. However, the effective fracture toughness was very low for both between 4 to 5 MPa$*$m$^{1/2}$ before and after heat treatments. The KH TZP also showed a color change with heat treatments. The as-received material was dark gray but after both heat treatments it became off-white, similar to the other six TZPs.

Group II includes NGK-Locke Z-191 (NGK), Toshiba "TASZIC" (TOSH), Koransha "Sintered" (KS), and AC Sparkplug TZP-110 (AC). All of these TZPs have good as-received strength, NGK having the highest at 873 MPa and TOSH the lowest at 633 MPa. All were able to retain up to 85% of their strength after heat treatments.

The effective fracture toughness varied from material-to-material, and in two materials, as a function of heat treatment time. The TOSH and AC TZPs both showed an increase in K_c from their as-received values as the length of heat treatment increased. TOSH increased from 8.5 to 9.5 MPa$*$m$^{1/2}$ and AC increased from 5.6 to 7.2 MPa$*$m$^{1/2}$. NGK and KS had constant K_c of 7.3 and 5.8 MPa$*$m$^{1/2}$ before and after heat treatments.

The mechanical properties reported here for NGK agree very well with those reported by Larsen and Adams[3] before and after exposure to 1000°C for 1000 hr, and with the as-received properties reported by Hecht, et al.[19] Also, Lintula, et al.,[20] determined the as-received mechanical properties of NGK and KS. They report higher strength for both, but they use smaller load spans, 10 mm and 30 mm, and only two to six specimens. The fracture toughness of the NGK was about 40% less than reported here, but the results for KS agreed.

Group III included Kyocera Z-201 (KY). It has good as-received strength of 745 MPa, but looses 37% and 55% of this strength after 100 and 500 hours, respectively, at 1000°C. The as-received K_c was 7 MPa$*$m$^{1/2}$. Toughness (K_c) could not be obtained due to warping of the bars during the heat treatment.

Others[19,20] have also determined the as-received properties of the Group III TZP. Hecht, et al.,[19] obtained a much higher strength (957 MPa) and a lower toughness (5.4 MPa$*$m$^{1/2}$), while Lintula, et al.,[20] reported even higher strength (1050 MPa) but the toughness agreed (6.3 MPa$*$m$^{1/2}$). The discrepancy for the Hecht, et al., data cannot be accounted for, but the higher strength reported by Lintula, et al., can be attributed to the different load spans and sample population.

Fractography

Optical fractography was done on all broken bars subjected to flexure strength testing. Flaw origins along with mirror, mist, and hackle regions were easily observed in the Group I, II, and the as-received bars of Group III. However, these regions on the fracture surfaces of the Group III heat-treated bars were extremely difficult to see.

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19. HECHT, N. L., MCCULLUM, D. E., GRANT, D. W., WOLF, J. D., GRAVES, G. A., and GOODRICH, S. *The Experimental Evaluation of Environmental Effects in Toughened Ceramics for Advanced Heat Engines.* Proceedings of the 24th Automotive Technology Development Contractors' Coordination Meeting, Society of Automotive Engineers, Warrendale, PA, April 1987, p. 209-222.
20. LINTULA, P., LEPISTÖ, T., LEVÄNEN, E., MÄNTYLÄ, T., and LEPISTÖ, T. *Characterization of Commercial Zirconia Ceramics.* Ceram. Eng. Sci. Proc., v. 9, no. 9-10, 1988, p. 1279-1288.

Although optical fractography was helpful in examining the fracture surface features, in most cases, it did not lend itself to determination of the flaw type. As a result, SEM was used to examine selected fracture surfaces. Figure 3 shows that in most cases, the flaw type is porosity related (i.e., pore, porous region, etc.) for all seven TZP materials, but other types of flaws, such as large grain(s), inclusions, and machining damage were also observed. Generally, the flaws identified in Group I were much smaller than the flaws indentified in either Group II or III. In the case of the heat-treated Group III TZPs, employment of the SEM improved flaw type determination, but the process was extremely difficult, time-consuming, and in many instances, the cause of fracture still could not be determined.

Microstructure

Figure 4 shows that all seven TZPs are extremely fine grained ($<1.0\ \mu m$) and the grain size is essentially independent of heat treatment time. In general, the grain size of Group I is slightly finer than in Groups II and III except for NGK. Figures 5a through 5g are examples of each microstructure. The micrographs indicate that each TZP has an essentially uniform grain size distribution. However, large grains (3 to 5 times larger than the mean) were found randomly dispersed in all but the HIT. The AC material also had randomly dispersed platelets of alumina (Figure 5f).

TEM was used to determine the composition of any grain boundary phases. This revealed a thin, uniform boundary phase for all TZPs as shown in Figures 6a through 6f. Due to the fine grain size and the small amount of grain boundary phase, attempts to determine the chemical compositions proved inconclusive. Twinned grains, probably m-ZrO_2, were commonly found in the KY material as in Figure 6f, but not nearly as frequently in the remaining materials.

Phase Stability

The change in surface monoclinic (m) phase content with heat treatment time is shown in Figure 7. The Group III TZP showed a progressive increase in m-zirconia with heat treatment time, while, on the average, Group II had higher amounts of m-zirconia than Group I, but lower than Group III. Group I and all but AC of Group II showed a decrease in m-zirconia from the as-received condition after 100 hr at 1000°C and then exhibited a large increase after 500 hr at 1000°C.

Deconvolution of the high-angle peaks revealed that only the NGK and KY TZPs contained an appreciable amount of c-ZrO_2, (between 7 and 11 volume percent for both) regardless of the heat treatment.

Table 3 summarizes the results from the X-ray analysis of the fracture surface of specimens used in toughness determination. Group I (KH and HIT) and NGK from Group II have the lowest amount of m-ZrO_2 on the fracture surface.

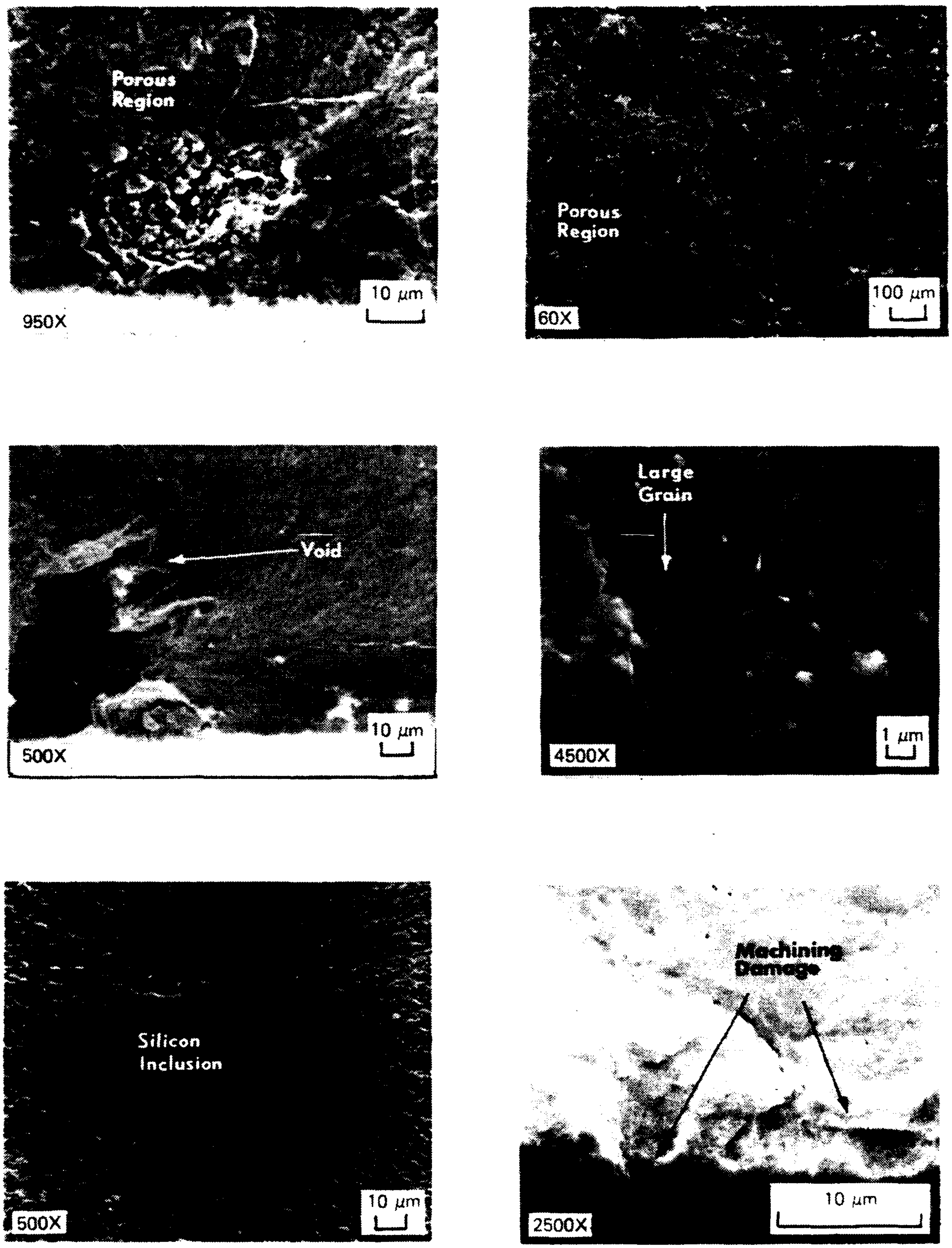


Figure 3. Common strength limiting flaws.

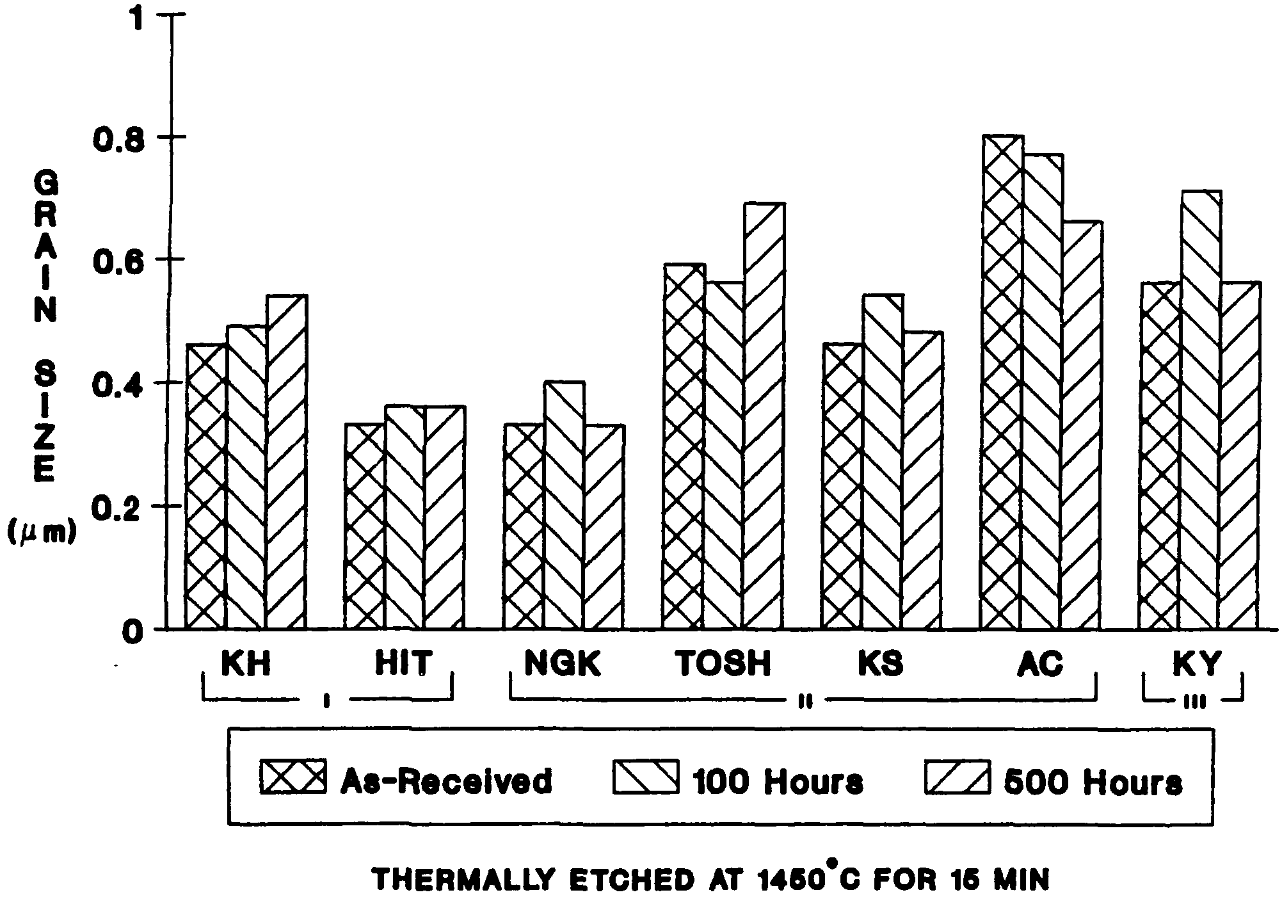
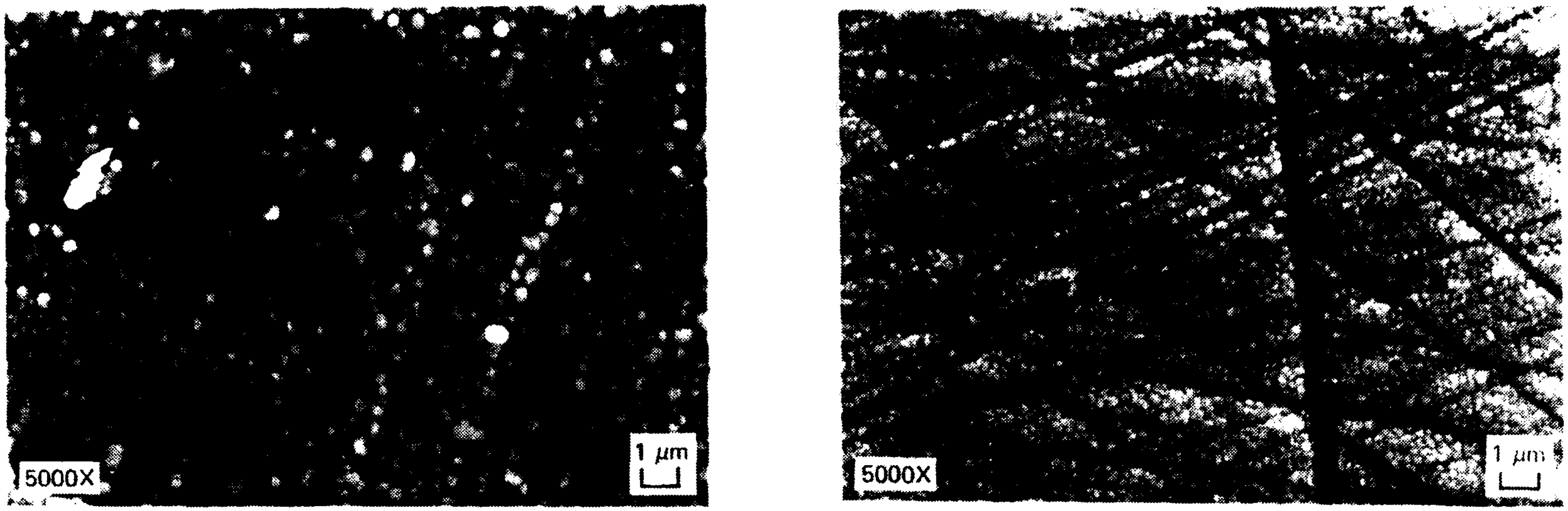
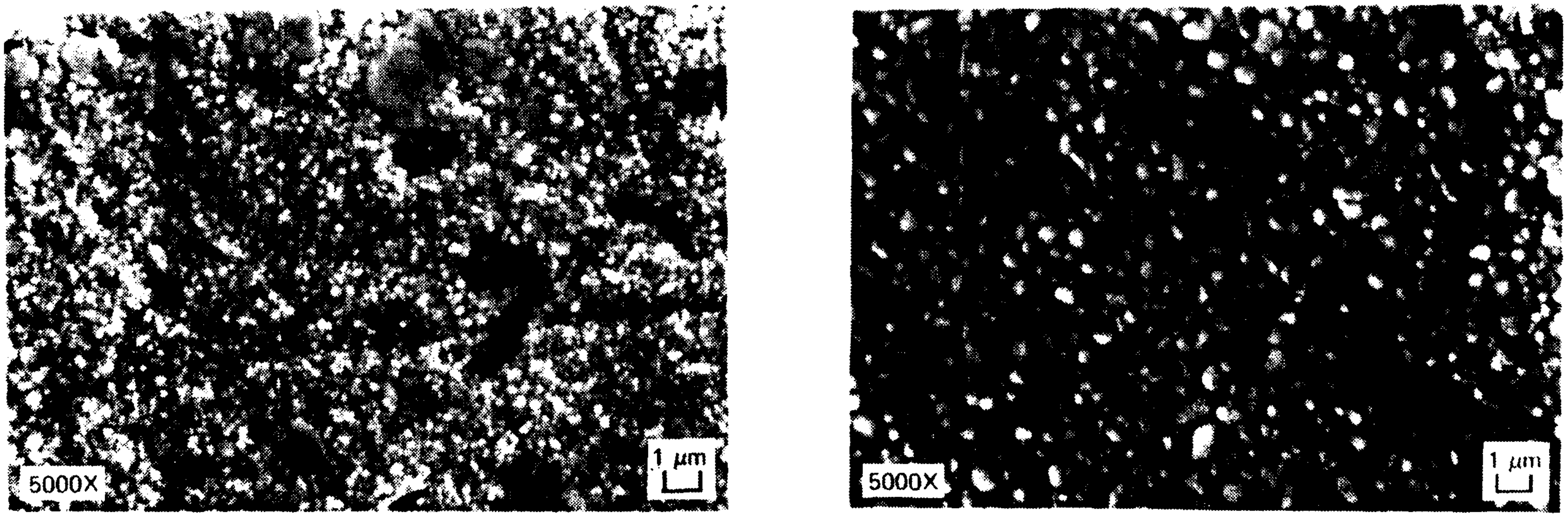


Figure 4. Grain size of the seven Y-TZPs before and after heat treatment at 1000°C.



(a) Microstructure of the Koransha "HIP'ed"

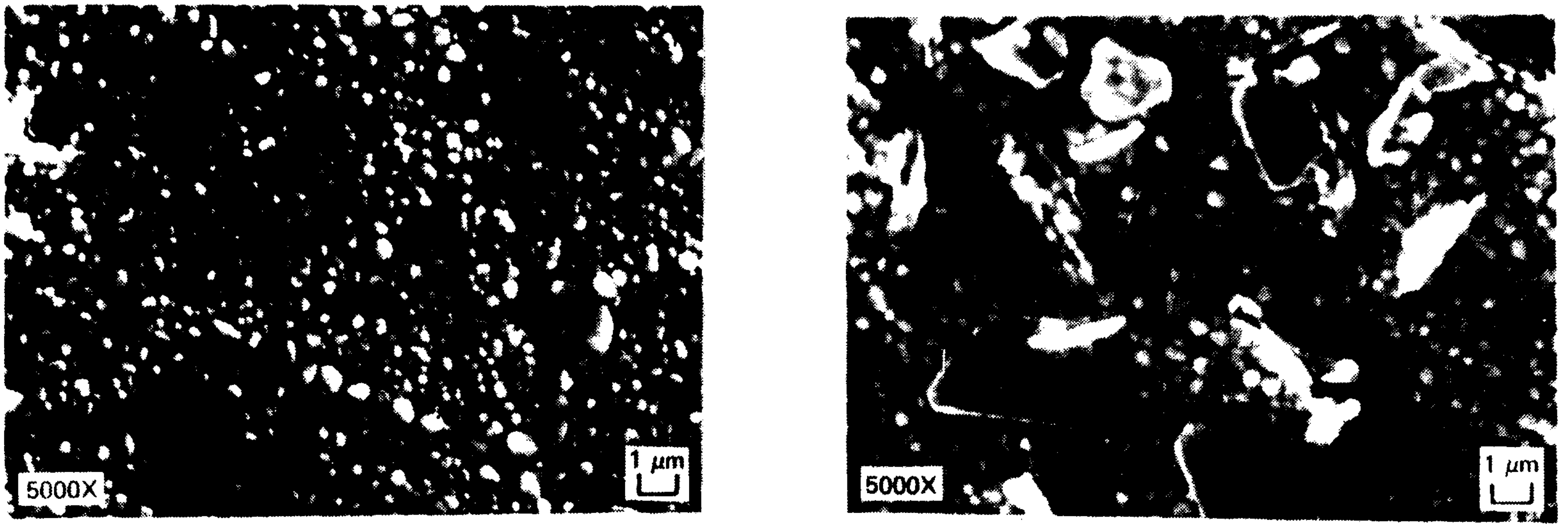
(b) Microstructure of the Hitachi "1985"



(c) Microstructure of the NGK-Locke "Z-191"

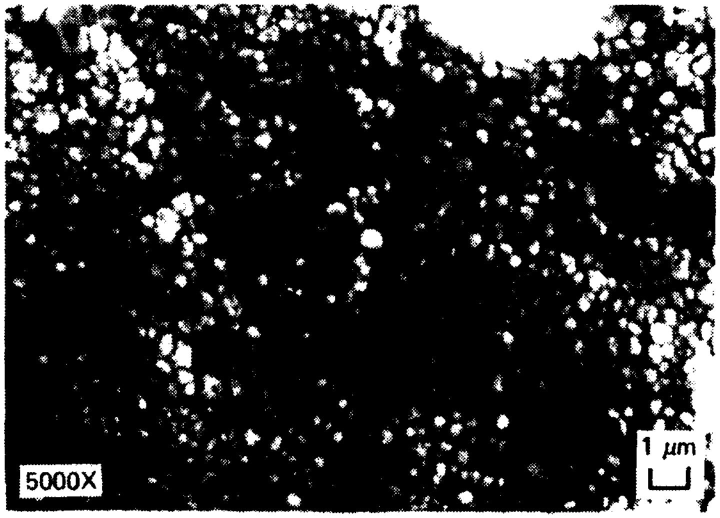
(d) Microstructure of the Toshiba "TASZIC"

Figure 5.



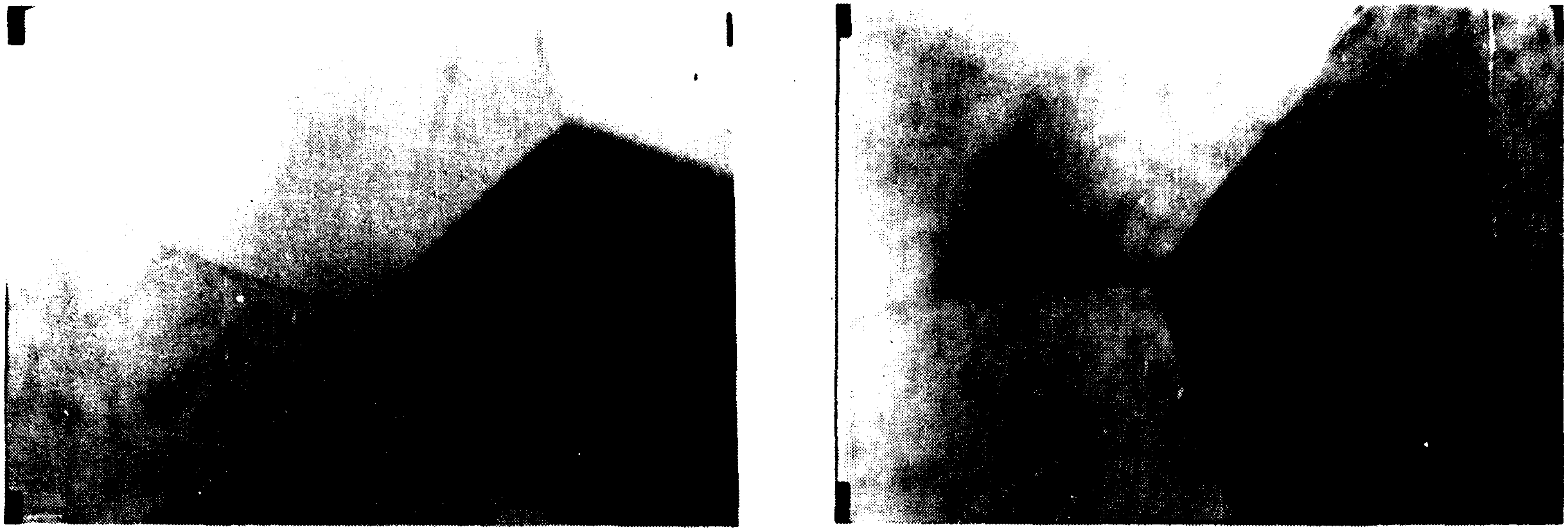
(e) Microstructure of the Koransha "Sintered"

(f) Microstructure of the AC Sparkplug "TZP-110"



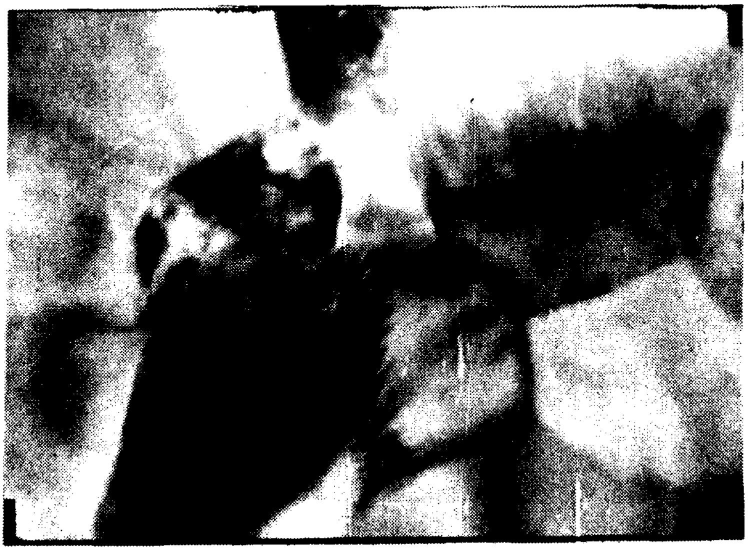
(g) Microstructure of the Kyocera "Z-201"

Figure 5. (Cont'd).



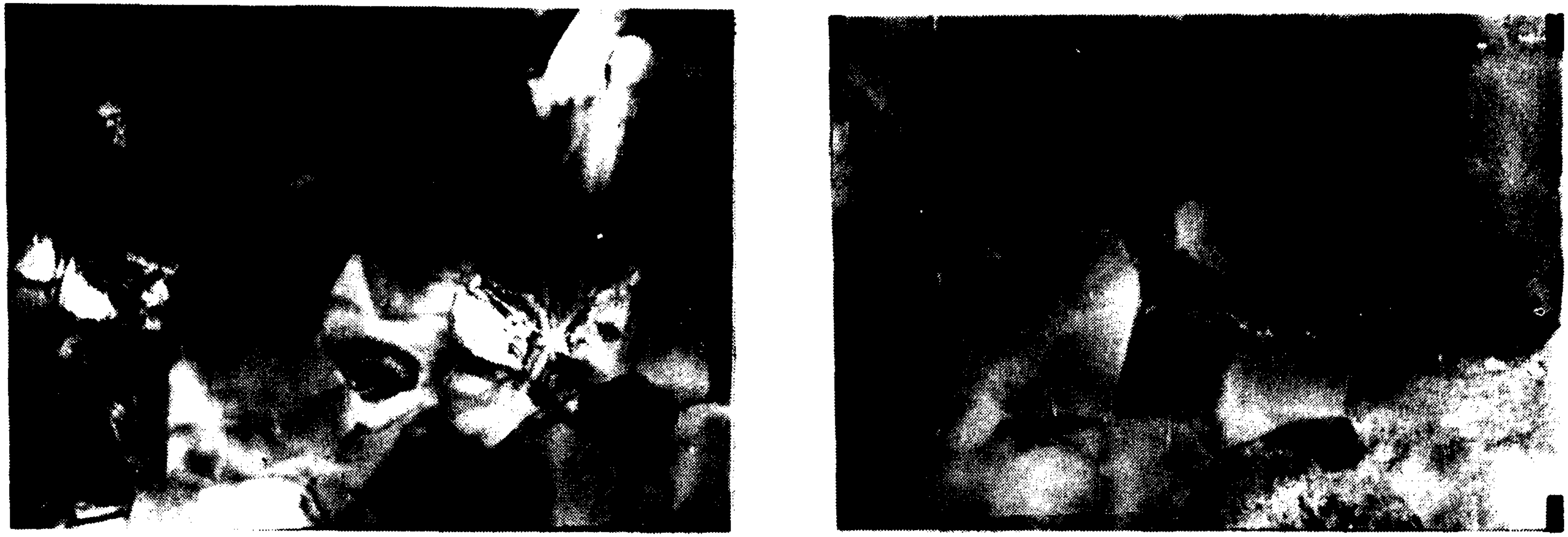
(a) Transmission electron micrograph of the
Koransha "HIP'ed" grain boundary

(b) Transmission electron micrograph of the
Hitachi "1985" grain boundary



(c) Transmission electron micrograph of the
NGK-Locke "Z-191" grain boundary

Figure 6.



(d) Transmission electron micrograph of the Toshiba "TASZIC" grain boundary

(e) Transmission electron micrograph of the Koransha "Sintered" grain boundary

(f) Transmission electron micrograph of the Kyocera "Z-201" grain boundary

Figure 6. (Cont'd).

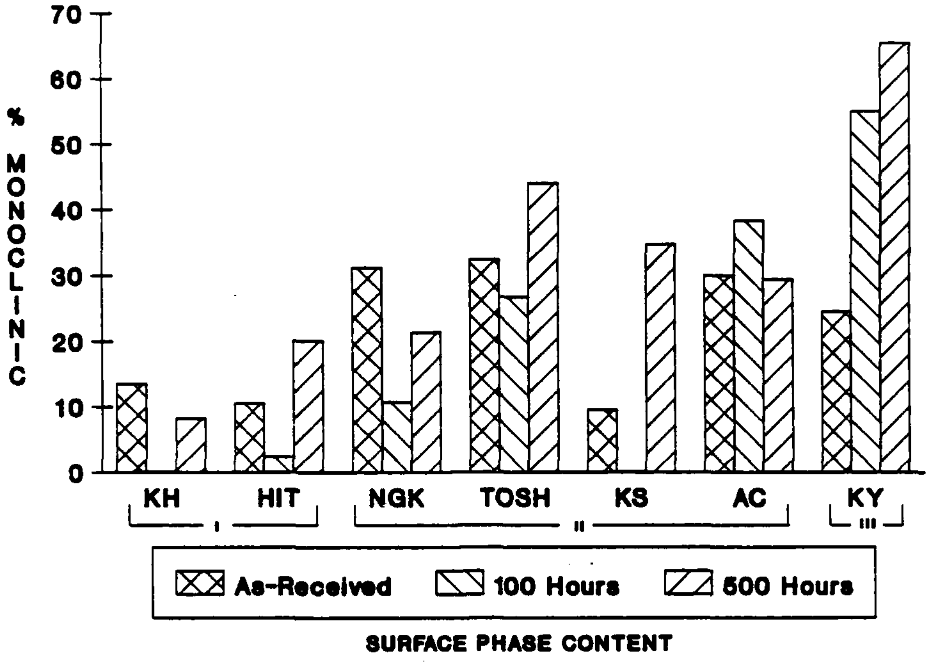


Figure 7. Surface monoclinic phase content of the seven Y-TZPs before and after heat treatments at 1000°C.

Table 3. MONOCLINIC PHASE CONTENT ON THE FRACTURE SURFACE OF AS-RECEIVED BARS

Material	% Monoclinic	% Tetragonal + Cubic
Koransha "HIP'ed"	25.4	74.6
Hitachi "1985"	14.2	85.8
NGK Locke "Z-191"	27.4	72.6
Toshiba "TASZIC"	65.0	35.0
Koransha "Sintered"	47.3	52.7
AC Sparkplug "TZP-110"	45.3	54.7
Kyocera "Z-201"	47.8	52.2

Other Property Information

Weibull numbers and other properties such as density, modulus of elasticity (MOE), and hardness were also determined for these TZPs. Weibull analysis yielded numbers which varied between materials, but also varied greatly within a given material depending on the heat treatment. Since SEM fractography was limited to only selected specimens, more involved fractography would be required to determine why the Weibull numbers varied with heat treatments the way they did.

With the exception of the Group III materials, none of the TZPs showed a change in density, MOE, or hardness with heat treatments. The Group III materials showed a slight decrease in density with heat treatment time. These results are summarized in the Appendix.

DISCUSSION

As with other materials being considered for use in advanced heat engines, an understanding of the relationship between properties and microstructure, and how these may change with time at elevated temperatures is important in determining the type and extent of application for Y-TZP materials. The results for this study will be discussed with regard to defining these relationships for the Y-TZPs examined.

The excellent as-received strength and strength retention of the Group I TZPs is due to the fine-grained microstructure which, in turn, is a result of the manufacturing technique. It is well known that the strength of a polycrystalline material increases with decreasing grain size[21] and that the use of hot isostatic pressing[22] or hot pressing[21] increases the strength by inhibiting grain growth and greatly reducing the amount and size of strength-limiting flaws such as porosity. This grain size also accounts for the phase stability of these TZPs after long times at 1000°C. As outlined previously, there is a critical grain size necessary to inhibit the spontaneous transformation of t-ZrO_2 upon cooling. It appears that the Group I TZPs are comprised of grains which are well below this critical size, since very little strength is lost and only a small amount of monoclinic ZrO_2 is present on the surface. Fractography indicated that the strength-limiting flaw in both of these TZPs is porosity related and does not change with heat treatments.

Although the fine-grained microstructure is beneficial to the strength, it has an adverse effect on the toughness of Group I. Because the t-ZrO_2 grains are so fine, very few transform even in the presence of the crack-tip stress field as seen by the results in Table 3. Since the t $\longrightarrow$ m transformation is inhibited, there is minimal transformation toughening, and thus, the effective fracture toughness is extremely low.

The color change that the KH TZP undergoes during heat treatment occurs because the TZP is slightly reduced,[23,24] during the HIPing process. Heat treating in air oxidizes the material, restoring oxygen stoichiometry. Others[25] have found that the Fe impurities, on the order of parts/million, cause a color change as the Fe ions change from Fe^{3+} to Fe^{2+} during the oxidation. Irrespective of the mechanism, this oxidation does not appear to have an effect on the room temperature properties of the TZP before or after heat treatments.

All of the Y-TZPs which comprise Group II were produced by pressureless sintering. As a result, their strengths are much lower than those of Group I because they have a higher amount of porosity and, on the average, a larger grain size. The large grain size is beneficial in that it results in a higher effective fracture toughness.

Beyond these generalizations, there are differences between the Group II Y-TZPs which, unlike Group I, requires that they be discussed individually rather than as a group.

21. KINGERY, W. D., BOWEN, H. K., and UHLMANN, D. R. *Introduction to Ceramics.* John Wiley & Sons, Inc., New York, NY, 1986.
22. TSUKMA, K., and SHIMADA, M. *Hot Isostatic Pressing of Y_2O_3-Partially Stabilized Zirconia.* Am. Ceram. Soc. Bull., v. 64, no. 2, 1985, p. 310-313.
23. SCHUBERT, H., CLAUSSEN, N., and RÜHLE, M. *Preparation of Y_2O_3-Stabilized Tetragonal Polycrystals (Y-TZP) from Different Powders.* Advances in Ceramics, v. 12, Science and Technology of Zirconia II, N. Claussen, M. Rühle, and A. H. Heuer, ed., The American Ceramic Society, Columbus, OH, 1984, p. 766-773.
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The best TZP of this group is NGK. Its average grain size is similar to that of Group I, which results in the strongest and second toughest material of Group II. However, these values are quite different from those of Group I due to the microstructure. The bimodal microstructure (Figure 5c), shows a matrix of 0.2 μm grains with larger grains (10 to 15 times) randomly dispersed. Examination of the fracture surface shows that the strength-limiting flaw tends to be an agglomerate or porous region rather than a large grain. Thus, these flaws limit the strength. However, the fine-grained microstructure ensures that a high percentage of strength is retained after heat treatments by inhibiting the transformation of t-ZrO_2.

It was shown previously that a very fine-grained tetragonal microstructure suppresses toughening via the t $\longrightarrow$ m transformation. Yet, NGK has an appreciably higher toughness than either of the Group I TZPs. It is believed that the large grains present in the microstructure are cubic, since X-ray analysis reveals the presence of the cubic phase. In order that c-ZrO_2 grains be retained at room temperature, a combination of the following must have occurred: first, the initial portion of the sintering process must have taken place in the t+c phase field to nucleate c-ZrO_2; second, the phase diagram (Figure 8 [26]) shows that to obtain c-ZrO_2 at room temperature, a minimum of ~8.0 mole percent Y_2O_3 is required. Therefore, once nucleated, the c-ZrO_2 would grow during the remainder of the sintering process, depleting the immediate surrounding grains of the Y_2O_3, enabling it to become cubic. Although the surrounding region is yttria poor, it does not transform spontaneously because the bulk material constrains it. However, these fine grains can now be easily transformed by the crack-tip stress field, resulting in transformation toughening.* This is supported by the X-ray diffraction results which show that NGK has a higher amount of m-ZrO_2 on the fracture surface than do the Group I TZPs. The presence of planar voids may also contribute to the enhanced toughness through crack blunting. The existence and extent of contribution of the latter mechanism has not been determined at this time. This appears to be a case of microstructural tailoring where the fine-grained t-ZrO_2 matrix ensures the good strength, while formation of a small amount of c-ZrO_2 provides improved toughness.

The TOSH material is one of the weakest Y-TZPs tested, but it's the toughest. The strength is limited primarily by the porosity, and to some extent, the large grain size. Fractography shows that the most common cause of failure is a large (75-100 μm), porous region, similar to that in Figure 3. The excellent toughness is a result of the large-grained microstructure. These grains are easy to transform, especially with respect to the Group I TZPs, as indicated by the large amount of m-ZrO_2 on the fracture surface.

The difference in strength between Groups I and II is evident when comparing KS (Group II) to KH (Group I). Both materials were produced from the same starting powder, but using different techniques. They have the same final grain size, but the KS material has approximately half the strength of KH. Again, this is due to the larger amount of porosity in KS due to sintering. Both have the same toughness and amount of m-ZrO_2, giving further support to the idea that grain size plays a major role in the transformability of the material.

The final Group II TZP is AC. It has the second highest strength, and fracture toughness similar to KS. However, it has the largest grain size, and the microstructure contains randomly dispersed hexagonal platelets of Al_2O_3. This does not fit the property-microstrucure

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*Private communication with G. L. Leatherman.

[26] RUH, R., MAZDIYASNI, K. S., VALENTINE, P. G., and BIELSTEIN, H. O. *Phase Relations in the System ZrO_2-Y_2O_3 at Low Y_2O_3 Contents.* J. Am. Ceram. Soc., v. 67, no. 9, 1984, p. C190-C192.

relationships previously mentioned. However, Tsukama and Takahata[27] have shown that alumina additions to Y- and Ce-TZP enhance strength while reducing toughness. For the Y-TZP materials, additions of up to ~20 volume percent alumina enhanced strength and reduced toughness.

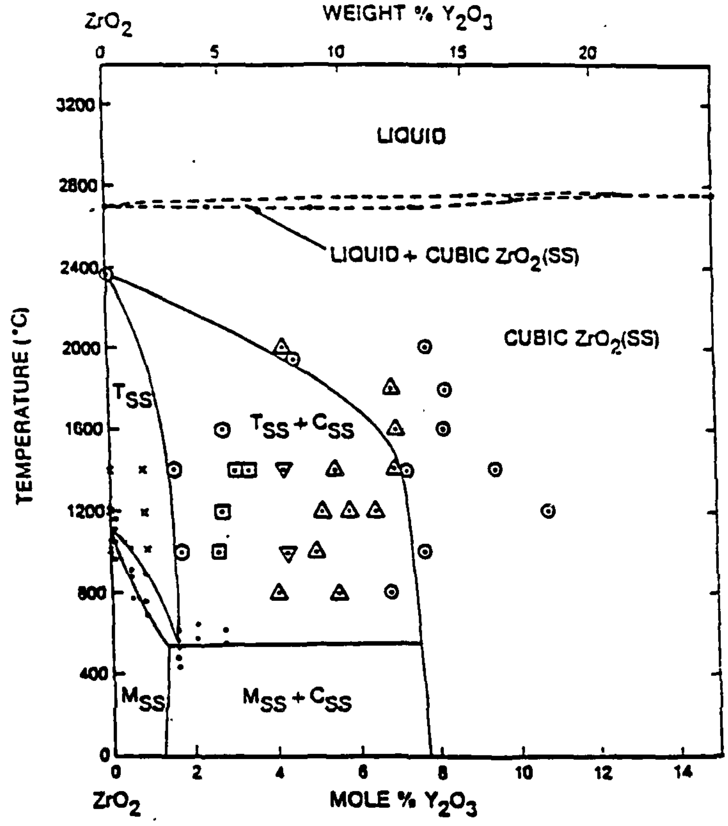

Figure 8. ZrO_2-Y_2O_3 phase diagram for low Y_2O_3 contents (Ref. 26).

Further additions caused the strength to decrease because of a decrease in the contribution from the t → m transformation. The Al_2O_3 content was obtained using a point counting technique yielding an approximate value of 8%. This amount and the platelet shape indicate that the Al_2O_3 is probably an impurity that was picked up during the ball-milling step of the processing.

The KY TZP of Group III is the only material examined which showed a significantly large density and strength decrease with heat treatment time. The large increase in the amount of m-ZrO_2 accounts for these losses. This increase is due to the ease in transforming t-ZrO_2 to m-ZrO_2. The ease of this transformation is probably due to a combination of the coarse grain size and insufficient Y_2O_3 to continue retaining t-ZrO_2. These factors are not problems in the other TZPs. As stated previously, the t → m transformation results in a 4% to 5% increase in volume, and thus, a decrease in density. As the amount of m-ZrO_2 increases, the amount of the metastable t-ZrO_2 available to transform decreases; since there is

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27. TSUKUMA, K., and TAKAHATA, T. *Mechanical Property and Microstructure of TZP and TZP/Al_2O_3 Composites.* Advanced Structural Ceramics, *P. F. Becher, M. V. Swain, and S. Sömiya, ed., Mat. Res. Soc. Symp. Proc., v. 78, 1987, p. 123-135.*

less t-ZrO_2 to transform, the strength decreases. The toughness of the as-received material was good (7 $MPa*m^{1/2}$), but any change in toughness with heat treatment time could not be determined because the specimens warped, which did not allow for proper polishing. The loss in density and strength, and the increase in m-ZrO_2 with heat treatment time, is similar to what others[3,11] have seen in MgO-PSZ materials.

The large amount of twinned grains in this material, when compared to the other TZPs, is another indication of how easy it is to transform the tetragonal grains. Twinning probably occurred due to the stresses imposed on the material during ion milling. The other TZPs have a much lower amount of twinned grains, indicating that they could handle the ion milling stresses without transforming.

CONCLUSIONS

1. When considering a Y-TZP material for a structural application, one must determine the importance of strength and toughness. If superior strength is needed, then an extremely fine-grained, HIP'ed, or hot-pressed Y-TZP would be required. On the other hand, if toughness is more important a coarser-grained, sintered Y-TZP appears sufficient.

2. In respect to the desired properties outlined in Table 1, none of the seven Y-TZPs examined would maintain all the mechanical properties after 1000 hr at 982°C. A few TZPs could maintain strength (Group I) or toughness (TOSH of Group II) but not both.

3. With the exception of Group III, the Y-TZPs examined showed very little change in room temperature mechanical properties after long-term exposure to 1000°C.

4. Results show that the KY (Kyocera Z-201) TZP would not be adequate for structural applications where temperatures of 1000°C or greater may be encountered. However, it does not exclude this TZP from tructural applications where lower temperatures may be present.

5. If a combination of excellent strength and toughness is required in a structural application, then a Y-TZP with a microstructure that could be tailored would be necessary to achieve the best combination of properties. An example is the NGK TZP, where the production of a small amount of c-ZrO_2 during processing appears to enhance the toughness of a fine-grained Y-TZP, while maintaining high strength.

6. The manufacture of a Y-TZP material using a pressure-assisted process greatly improves the room temperature strength before and after heat treatments by reducing porosity and keeping a fine grain size. However, these small grains are resistant to the $t \longrightarrow m$ transformation. As a result, fracture toughness is low because there is little transformation toughening.

7. Fracture toughness is a function of the t-ZrO_2 grain size. Small grains are difficult to transform, thus, there is minimal contribution to the toughness from the $t \longrightarrow m$ transformation. Large grains are easier to transform, and can enhance the toughness of a material.

ACKNOWLEDGMENTS

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APPENDIX. ZIRCONIA DATA AFTER ELEVATED TEMPERATURE EXPOSURE

Property		Material (Units)	KH	HIT	NGK	TOSH	KS	AC	KY
Density:	Company Listing	g/cc	*	6.08	5.91	6.05	6.05	*	5.9
	As-Received		6.05	6.04	5.87	5.88	5.97	5.84	5.85
	100 hr at 1000°C		6.06	6.03	5.86	5.88	5.97	5.84	5.80
	500 hr at 1000°C		6.06	6.04	5.86	5.88	5.97	5.86	5.77
Sonic MOE:	Company Listing	GPa	*	209	205	180	*	*	206
	As-Received		214	213	208	200	210	204	201
	100 hr at 1000°C		212	213	207	200	211	206	203
	500 hr at 1000°C		213	214	208	200	210	208	205
MOR (4-pt): (Character Strength of Bend Bar)	Company Listing	MPa	*	1000	1020	900†	1100	*	980†
	As-Received		1261	1169	873	633	640	753	745
	100 hr at 1000°C		1070	1053	754	581	600	683	470
	500 hr at 1000°C		1045	1062	754	576	663	671	334
Weibull No.:	Company Listing	None	*	*	*	*	10.2	*	*
	As-Received		8.8	3.6	15.2	6.2	9.5	12.2	8.8
	100 hr at 1000°C		5.2	5.9	10.0	14.2	8.9	18.7	2.3
	500 hr at 1000°C		12.5	5.0	10.6	13.8	4.0	5.2	3.0
MOR (4-pt): (mean)	Company Listing	MPa	*	*	*	*	*	*	*
	As-Received		1192	1045	884	587	608	722	704
	100 hr at 1000°C		974	975	718	561	567	664	413
	500 hr at 1000°C		1003	974	719	555	589	613	296
Standard Deviation:	Company Listing	MPa	*	*	*	*	*	*	*
	As-Received		140	265	65	96	75	70	75
	100 hr at 1000°C		132	181	83	47	76	42	183
	500 hr at 1000°C		89	215	80	48	98	101	122
Hardness: (Knoop 300g Load)	Company Listing	GPa	*	13.3‡	11.7	11.8**	14.7**	*	12.3‡
	As-Received		11.6	12.4	10.9	10.1	10.8	11.1	10.5
	100 hr at 1000°C		11.5	12.2	11.3	10.0	11.3	11.1	9.4
	500 hr at 1000°C		11.5	12.2	10.4	10.4	11.0	11.0	9.4
Grain Size: (mean)	Company Listing	μm	*	0.3	*	0.5	*	*	*
	As-Received		0.41	0.37	0.18	0.49	0.50	0.8	0.65
	100 hr at 1000°C		0.42	0.35	0.17	0.54	0.53	0.8	0.66
	500 hr at 1000°C		0.47	0.26	0.19	0.58	0.51	0.7	0.76
K_{Ic}: Control Flaw 10kg Indent	Company Listing	MPa•m$^{1/2}$	*	6	6.3	9	9	*	*
	As-Received		5.0	4.6	7.4	8.5	5.6	5.6	7.0
	100 hr at 1000°C		7.0	4.7	7.1	8.0	5.7	6.0	*
	500 hr at 1000°C		5.8	4.5	7.4	9.5	6.0	7.2	*

*No data available
†Believed to be 3-pt bend results
‡Vickers 500g load
**Vickers

KH - Koransha "HIP'ed"
HIT - Hitachi "1985"
NGK - NGK-Locke Z-191
TOSH - Toshiba "TASZIC"

KS - Koransha "Sintered"
AC - AC Sparkplug TZP-110
KY - Kyocera Z-201

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PROPERTIES OF YTTRIA-TETRAGONAL ZIRCONIA POLYCRYSTAL (Y-TZP) MATERIALS AFTER LONG-TERM EXPOSURE TO ELEVATED TEMPERATURES -
Jeffrey J. Swab

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Technical Report MTL TR 89-21, March 1989, 24 pp-
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Key Words
Ceramic materials
Zirconia
Zirconium compounds (Y-TZP)

Due to an unusual combination of high strength and toughness, tetragonal zirconia polycrystal (TZP) materials are candidates for use in advanced heat engines. The properties of these materials stem from the stress-assisted transformation of metastable tetragonal zirconia particles. However, after long times at elevated temperatures, this class of materials is susceptable to properties degradation due to the undesirable transformation of tetragonal zirconia to monoclinic zirconia upon cooling. Accordingly, a task was initiated to examine the extent and magnitude of this phenomenon's effect on the properties. Seven commercially available yttria-tetragonal zirconia polycrystal (Y-TZP) materials were evaluated. Room temperature properties were measured before and after heat treatments at 1000°C. Microstructure and phase stability were also examined. In all but one case, the Y-TZPs showed very little change in room temperature properties after long times at this temperature. Results show that the use of pressure-assisted processing greatly improves the strength by reducing porosity and keeping the grain size extremely fine, but this reduces the toughness because finer grains are more difficult to transform. In addition, a small amount of cubic zirconia appears to enhance the toughness of fine-grained Y-TZP while maintaining good strength. During processing, a small amount of cubic zirconia is formed and allowed to grow. This creates regions poor in yttria which can transform spontaneously in the presence of a crack-tip stress field.

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