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ABSTRACT

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The physical properties of zirconia with 15 mole percent titanium were investigated as functions of temperature in an attempt to identify those properties responsible for the improved thermal shock resistance compared with that of pure zirconia. The heat capacity was practically the same as that reported in the literature for pure zirconia. The total expansion during the transformation was substantially larger than that previously reported for zirconia with 15 mole percent titanium. The modulus of elasticity versus temperature curve shows a maxima in the transformation range. At room temperature, the moduli of elasticity in tension and compression are practically the same. The modulus of rupture of zirconia with 15 mole percent titanium is much larger than that of calcia-stabilized zirconia of equivalent porosity, and the high-temperature strength of the former is much larger. The thermal conductivity of zirconia with 15 mole percent titanium was consistently higher than that of calcia-stabilized zirconia. Comparison of calculated and experimental thermal shock resistances shows that none of the above properties can account for the improvement in thermal shock resistance for quenches through the transformation range of zirconia. It is surmised that the discrepancy may be due to plasticity in this range. For quenches from below the transformation range, the calculated and experimental thermal shock resistances are practically identical, and their high value is

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attributed mainly to the high modulus of rupture. Author

SUMMARY

The parameters entering into the thermal shock equation were investigated individually.- most of them as functions of temperature - in an attempt to identify those responsible for the improved thermal shock resistance of zirconia with titanium additions compared with that of pure zirconia. Most of these investigations required equipment that was developed specifically for this study.

The heat capacity of zirconia with 15 mole percent titanium was practically the same as that reported in the literature for pure zirconia. The coefficient of linear thermal expansion and the transformation temperatures were substantially the same as those previously reported for the same type of material, but the total expansion during the transformation was substantially larger than that previously reported. The modulus of elasticity versus temperature curve shows a hump at the transformation temperature. At room temperature, the moduli of elasticity in tension and in compression are practically the same. The modulus of rupture of zirconia with 15 mole percent titanium is much larger than that of stabilized zirconia of equivalent porosity, and this could account for the higher thermal shock resistance of zirconia-titanium compositions for quenches from below the transformation range. The zirconia with 15 mole percent titanium compositions also retain high values of modulus of rupture at high temperatures compared with those of stabilized zirconia. The thermal conductivity of zirconia with 15 mole percent titanium was consistently higher, particularly at low temperature, than that of calcia-stabilized zirconia reported in the literature.

The experimental thermal shock resistance of zirconia with 15 mole percent titanium obtained in a previous investigation was compared with the calculated thermal shock resistance obtained by substitution of the properties obtained in this investigation in the thermal shock equation. For quenches from below the transformation temperature of zirconia, the experimental and calculated thermal shock resistances were practically identical. For quenches through the transformation range, the experimental thermal shock resistance was about seven times larger than the calculated value.

For quenches from below the transformation range, the good thermal shock resistance of zirconia with 15 mole percent titanium, compared with that of calcia-stabilized zirconia, was traced mainly to the relatively higher modulus of rupture of the former. It is surmised that this higher modulus of rupture may be due in part to the smaller grain size of the zirconia with 15 mole percent titanium.

The physical properties of zirconia with 15 mole percent titanium obtained in this investigation cannot account for the discrepancy between calculated and experimental thermal shock resistances. It is surmised that this discrepancy may be due to plasticity through the transformation range of zirconia.

I. INTRODUCTION

An experimental determination of the thermal shock resistance or zirconia with 15 mole percent titanium has shown that, for quenches from below the transformation range of zirconia, the thermal shock resistance of these compositions is superior to that of calcia-stabilized zirconia.[1] On the other hand, although the thermal shock resistance of these zirconia-titanium compositions is slightly inferior to that of calcia-stabilized zirconia for quenches through the transformation range, it is nonetheless superior to that expected on consideration of the fact that the allotropic transformation of the zirconia remains unchanged (for all practical purposes) by additions of titanium.[2,3] For this reason, an investigation of the factors known to affect thermal shock resistance[4-6] was carried out.

It can be shown that the thermal shock parameter ΔT - already investigated experimentally for the zirconia with 15 mole percent titanium compositions[1] - is a function not only of shape and quench severity (defined as the product of the heat-transfer coefficient h and the maximum radius of the disk r_m) but also of the strength σ, modulus of elasticity E, coefficient of thermal expansion α, thermal conductivity k, and (for some shapes) Poisson's ratio ν.[5,6] Except for Poisson's ratio, all these properties are determined as a function of temperature from room temperature to above the transformation range. In addition, the heat capacity of zirconia with 15 mole percent titanium is also determined as a check in the determination of h. These data will be used to calculate the thermal shock resistance of zirconia with 15 mole percent titanium and compare it with the experimental thermal shock resistance in an attempt to clarify the role played by titanium in improving the thermal shock resistance of zirconia. Most of these investigations required special equipment that was developed for this study by the author.

II. MATERIALS AND SPECIMEN PREPARATION

RAW MATERIALS

The raw materials used in this investigation were pure zirconia (CP Zirox, TAM Division, National Lead Co.), titanium metal powder (-325 mesh, Metal Hydrides, Inc.), and 5.33 w/o calcia-stabilized zirconia

(Zircoa B, Zirconium Corp. of America).

SAMPLE PREPARATION

Standard powder-metallurgy techniques were used for the preparation of the specimens used for the determination of physical properties. The specimens designated as ZT-15 were prepared by mixing pure zirconia with 15 mole percent titanium metal powder in cone blenders, adding 5 weight percent water as a temporary binder, cold-pressing into prismatic bar specimens in split steel dies at 10,000 to 20,000 psi, hydrostatically pressing the bars (encased in evacuated plastic tubing) at 46,000 to 50,000 psi, drying in a vacuum desiccator, and vacuum-sintering in tungsten boats at $1870 \pm 30^{\circ}$ C for 1 hour under pressures of less than 0.5 micron of mercury.

Specimens designated as ZT-15-M were prepared by milling pure zirconia with 15 mole percent titanium in tungsten carbide mills with tungsten carbide balls and acetone as grinding media. The powders were milled for 72 hours at 80 rpm. The powders were then dried in a stream of warm air and prismatic bars and cylindrical specimens prepared as outlined above for ZT-15.

Specimens designated as BM were made from calcia-stabilized zirconia (Zircoa B) by the same methods used for ZT-15-M except that sintering was done in air at 1800° C for 3 hours, and only prismatic bars were made.

Bars and cylinders were surface ground all over to the required sizes by using diamond wheels. All ground specimens had a surface finish of 50 microinches or better. All sharp edges in the prismatic bars were given a radius of about 0.005 inch. As will be indicated in the proper places, some of the bars were polished to a mirror finish with diamond powder. All specimens were tested for cracks and pinholes by means of dye penetrant.

III. DETERMINATION OF PROPERTIES

DENSITIES

The densities of the specimens were determined by water immersion.

HEAT CAPACITY

The change in enthalpy ΔH from 25° C to about 850° C was determined in bars of ZT-15-M only by the drop method with equipment described in reference 7. The heat capacity C_p was determined from the defining equation $C_p = (\partial \Delta H/\partial T)_p$ as the slope of the ΔH against temperature T curve.

THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY

The thermal conductivity of ZT-15-M was determined by the radial method[8] in vacuum or inert atmospheres. The thermal conductivity near room temperature was determined by the same method but water was used as the cooling medium. Cylindrical specimens were 1.375 inches in outside diameter by 1.000 inch high with a center hole 23/64 inch in diameter for the location of the heater and with 0.040-inch-diameter thermocouple holes located 0.294 and 0.662 inch from the axis of the cylinder. The top and bottom guards were made of the same material and with the same dimensions.

The thermal diffusivity a was calculated from the thermal conductivity k, the heat capacity C_p, and the density ρ, with the equation

$$a = \frac{k}{C_p \rho} \qquad (1)$$

The equipment used for the determination of the thermal conductivity has been described in reference 7.

THERMAL EXPANSION

The thermal expansion curve (and from it the coefficient of linear thermal expansion) was determined from room temperature to about 1200° C with a vacuum dilatometer. This all-tungsten vacuum dilatometer has been described in detail in reference 7. The dilatometer was calibrated with a tungsten rod. The ZT-15-M specimen used was 3,000 inches long by 0.400 inch wide by 0.400 inch thick.

All thermal expansion work was carried out in vacuum at better than 0.5 micron of mercury. Dial gauge readings were taken near equilibrium temperatures with heating and cooling rates of less than 0.1° C per minute during the readings. Temperatures were determined both with a tungsten against tungsten plus 26 percent rhenium thermocouple and also with a disappearing-filament optical pyrometer.

MODULUS OF RUPTURE IN BENDING

The modulus of rupture of ZT-15-M was determined from room temperature to 1850° C in vacuum. The modulus of rupture of ZT-15 was determined in vacuum from room temperature to 1600° C. The modulus of rupture of BM was determined in vacuum from room temperature to 1400° C. In all these cases the modulus of rupture was determined under three-point loading with the apparatus described in reference 9, with prismatic bars 2.35 inches long by 0.500 inch wide by 0.250 high. These specimens were polished metallographically on the bottom and side surfaces in order to remove possible stress raisers.

The modulus of rupture of ZT-15-M was also determined at room temperature under four-point loading with prismatic bar specimens 6 inches long by 1/2 inch wide and thicknesses from 0.100 to 0.300 inch. This modulus of rupture at room temperature under four-point loading was used to convert the modulus of rupture at any temperature T under three-point loading to the value at the same temperature under four-point loading. The reasons for doing this are that, as shown by Manson and Smith,[4] the value of stress to be used in the thermal shock equation for the thin disk is the modulus of rupture under four-point loading, and in the present investigation property values at the temperature at which rupture occurs will be used. To carry out the conversion of modulus of rupture values the following equation was used

$$\sigma_{M_{T,2}} = \left(\frac{\sigma_{M_2}}{\sigma_{M_1}}\right)\sigma_{M_{T,1}} \tag{2}$$

where

$\sigma_{M_{T,2}}$	modulus of rupture at T and four-point loading
σ_{M_2}	modulus of rupture at room-temperature and four-point loading
$\sigma_{M_{T,1}}$	modulus of rupture at T and three-point loading
σ_{M_1}	modulus of rupture at room-temperature and three-point loading

MODULUS OF ELASTICITY

The modulus of elasticity of ZT-15-M in tension was determined in vacuum from room temperature to 1450° C by the bending method. The specimens used had nominal dimensions of $4\frac{7}{8}$ inches long by 3/4 inch wide by 1/8 to 1/4 inch thick. The apparatus used has been described in reference 7. The deflection of the apparatus was determined by using a tungsten standard.

The modulus of elasticity of ZT-15-M at room temperature was also determined by the sonic method as a check.

The modulus of elasticity in compression was also determined for ZT-15-M at room temperature in order to ascertain the validity of the equation used for modulus of rupture determination.[10] Cylinders 1 inch in diameter by 1 inch high provided with strain gauges were used.

IV. RESULTS AND DISCUSSION

DENSITY

The average densities were 5.7 g/cc for ZT-15-M, 5.23 g/cc for ZT-15, and 5.22 g/cc for BM types of materials.

MICROSTRUCTURES

Because of the probable importance of porosity and grain size in thermal shock resistance, photomicrographs of the three types of material used in the present investigation were obtained by standard techniques. Photomicrographs of ZT-15-M, ZT-15, and BM are shown in Figs. 1, 2, and 3, respectively. In the unetched photomicrographs of Figs. 1(a) and 2(a), the white areas are metal. In Figs. 1(a), 2(a), and 3 the black areas are pores and the gray background the ceramic matrix. The great improvement in the density and structure of zirconia with 15 mole percent titanium brought about by milling the raw materials should be noted.

HEAT CAPACITY

The change in enthalpy ΔH and the heat capacity C_p, as a function of temperature, are shown in Fig. 4. The results of this part of the investigation are in agreement with data for pure zirconia published in the literature.[11]

THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY

A plot of the thermal conductivity of ZT-15-M as a function of temperature is shown in Fig. 5 together with a plot of the thermal conductivity of stabilized zirconia from reference 12. The thermal diffusivity of ZT-15-M was calculated from the thermal conductivity, heat capacity,and density with the aid of equation (1), and is shown as a function of temperature in Fig. 6.

The thermal conductivity of zirconia with 15 mole percent titanium is seen to be consistently higher than that of stabilized zirconia. This higher thermal conductivity of the zirconia-titanium composition appears to be an intrinsic property of the zirconia matrix as an analysis given in reference 7 will show.

THERMAL EXPANSION

The thermal expansion of milled zirconia with 15 mole percent titanium (ZT-15-M) as a function of temperature is shown in Fig. 7. The transformation temperatures, both on heating and on cooling, as well as the shape of the thermal-expansion - temperature curves are essentially the same as those given in reference 13. The actual expansion through the transition temperature was 0.92 percent against approximately 0.47 percent reported in reference 13 for materials of similar compositions. In the present investigation, the coefficient of thermal expansion α, between 25° and 900° C was $7.05\times10^{-6}/^{\circ}C$ against $7.65\times10^{-6}/^{\circ}C$ from the data in reference 13. In either case, the value of α for the zirconia-titanium composition is lower than the value of $10.0\times10^{-6}/^{\circ}C$ reported in the literature for calcia-stabilized zirconia.[14] It was also noted in the present investigation that the expansion through the transformation range could be arrested by holding the temperature constant even in the regions of maximum slope. This suggests that the transformation may be of the martensitic type.

MODULUS OF RUPTURE

For four-point loading, the number of specimens was too small to determine the effects of beam height, width, and distance between the points of load application on the modulus of rupture. Taken together, however, the average of 24 values under four-point loading was 32,400 psi against an average of 42,900 psi for eight specimens broken under three-point loading, all at room temperature. This gave a ratio of room-temperature modulus-of-rupture values of 0.76. Then, from equation (2),

$$\sigma_{M_{T,2}} = 0.76\ \sigma_{M_{T,1}} \tag{3}$$

The modulus of rupture $\sigma_{M_{T,1}}$ as a function of temperature for zirconia with 15 mole percent titanium, milled, cold-pressed, and sintered (ZT-15-M) is shown in Fig. 8, that for ZT-15 is shown in Fig. 9, and that for BM is shown in Fig. 10.

The large modulus of rupture of ZT-15-M compared with that of ZT-15 is probably due to porosity effects as Figs. 1 and 2 show, since the grain sizes of the two materials are about the same. As shown in Fig. 8, there is a maximum in the modulus of rupture against temperature curve at about 950° C. The same maximum is suggested for ZT-15 in Fig. 9, but this maximum is not very definite because of the large scatter in the modulus-of-rupture values for this material. This scatter is attributed to the porosity of this composition. It is surmised that the maxima in these curves is due to the higher strength of the tetragonal phase.

Comparison of Figs. 9 and 10 shows that the modulus of rupture of the zirconia with 15 mole percent titanium composition is almost twice that of stabilized zirconia at low temperatures for equivalent porosity. At high temperatures, the modulus of rupture of the zirconia-titanium compositions is definitely superior to that of stabilized zirconia. For example, at 1200° C, the modulus of rupture of ZT-15 is 30,000 psi against about 4000 psi for calcia-stabilized zirconia. The reason for this could be the inherent strength of tegragonal zirconia or the strengthening effect of the metal (i.e., by relieving stress concentrations). Although at high temperatures the strength of the zirconia-titanium compositions is definitely superior to that of stabilized zirconia, the low-temperature superiority in strength probably reflects grain size effects in addition to inherent material differences.

MODULUS OF ELEASTICITY

The static modulus of elasticity E as a function of temperature for milled, cold-pressed, and sintered zirconia with 15 mole percent titanium (ZT-15-M) obtained by the bending method[15] is shown in Fig. 11. The dynamic modulus of elasticity at room temperature was 29.6×10^6 psi compared with 28.0×10^6 psi for the static modulus by bending. From the room-temperature - load-deflection curves obtained on compressing a cylinder of ZT-15-M, the modulus of elasticity in compression was 28.2×10^6 psi and Poisson's ratio was 0.242. The static moduli of elasticity of zirconia with 15 mole percent titanium (ZT-15-M) - both in tension and compression, are, for all practical purposes, identical, and the modulus of rupture needs no correction.

The static modulus of elasticity in tension for the zirconia-titanium composition (ZT-15-M) is larger than the reported value of 20.45×10^6 psi at room temperature for 5 weight percent calcia-stabilized zirconia with a density of 4.93 grams per cubic centimeter.[16] Although the curve for modulus of elasticity against temperature for 5 weight percent calcia-stabilized zirconia[16] tends to flatten out at about 700° C, it does not have the hump shown by the curves for the zirconia-titanium material at about 1000° C (Fig. 11). The discrepancy in the values of E of ZT-15-M and calcia-stabilized zirconia may be due, in part, to the relatively low density of the stabilized zirconia. The effects of grain size on E appear to be negligible.[17]

Some of the bars of ZT-15-M used for the determination of E as a function of temperature showed a slight curvature after a series of runs. This curvature may be associated with the low temperature creep and plasticity reported in the literature[18] for similar zirconia-titanium compositions.

V. COMPARISON OF CALCULATED AND EXPERIMENTAL THERMAL SHOCK RESISTANCE

THEORETICAL CONSIDERATIONS

In this investigation, the experimental thermal shock resistance of milled zirconia with 15 mole percent titanium (ZT-15-M) obtained in the investigation of reference 1 is compared with the thermal shock resistance calculated by substituting the values of the physical properties of the same material in the thermal shock equation for the thin disk.

In the work of reference 4, the thermal shock equation for the thin disk was obtained from the relation between the physical properties of the material, severity of quench, and time. This relation is shown in terms of dimensionless variables in Fig. 12, where these variables are defined in terms of the physical properties of the material, heat-transfer coefficient h, maximum radius of the disk r_m, initial uniform temperature of the disk T_i, final uniform temperature of the disk T_f, and time t. The disk specimen cracks when the tangential stress reaches the rupture stress $\sigma_{\theta_{max}}$ of the material. This maximum (rupture) tangential stress develops at the periphery of the disk when the conditions defined by the maxima in the curve of Fig. 12 obtain. The relation between the variables mentioned above at the moment of rupture is shown in Fig. 13 in terms of dimensionless variables. This relation can also be expressed mathematically (in the range of interest in this investigation) by the thermal shock equation[4,6]

$$\Delta T = T_i - T_f = \frac{\sigma_{\theta_{max}}}{E\alpha} \times f(\beta) = \frac{\sigma_{\theta_{max}}}{E\alpha}\left(2 + 4.3\,\frac{k}{hr_m}\right) \qquad (4)$$

The properties in equation (4) are those corresponding to the temperature at the periphery of the disk $(r = r_m)$ at the time when rupture occurs. The time at the moment of rupture can be obtained from Fig. 13 if the severity of quench hr_m, and the thermal conductivity k, of the material are known. Then, if the properties in the thermal shock equation are known as a function of temperature, ΔT as a function of assumed values of hr_m can be determined from the relations between the various variables expressed by Fig. 13 or equation (4). This ΔT is usually taken as a measure of relative thermal shock resistance, and plots of ΔT against hr_m allow the selection of materials on the basis of their thermal shock resistance under the actual heat-transfer coefficient where they are to be used.[5,6] The values of ΔT obtained by substitution of the properties in the thermal shock equation (Eq. (4)) will be termed the calculated thermal shock resistance, as distinguished from that obtained by quenching experiments from the work of reference 1, which will be termed the experimental thermal shock resistance.

In the present investigation, the preceding theory applies only to specimens quenched from below the transformation temperature range. On quenches through the transformation temperature, the surface is in compression and the center is in tension at the moment of rupture, because α is negative through the transformation range. Since the compressive strengths of ceramics are several times larger than the tensile strengths,[3,14] the disks fail in tension at the center on cooling through the transformation range. From the equations for the stresses in a thin disk during heating or cooling given in reference 15, it can be shown that if E and α are assumed constant and, as is the case in the present investigation, the temperature distribution in the disk is parabolic, the numerical value of the stress at the center is about one-half that of the stress at the rim of the disk but opposite in sign. Consequently, ΔT for quenches through the transformation range is twice that given in equation (4). A look at the thermal-expansion - temperature curve for the zirconia-titanium composition under consideration (Fig. 7) will show that, because of the very large negative values of α on cooling through the transformation range, if the disk is to crack under the given h with the testing method used in this investigation, rupture will occur when the center reaches the temperature corresponding to the start of the transformation, because it is at this point that the tensile stresses at the center are a maximum.

The validity of using the thermal shock equation for a material undergoing an allotropic transformation is subject to question; however, in this investigation, the equation will be used for comparing calculated and experimental thermal shock resistances. Because of the possible formation of stress-raining cracks during the transformation, it can be surmised that, if the material behaves elastically and the other properties entering into the thermal shock equation are substantially constant, the net effect of the cracks would be to make the experimental thermal shock resistance lower than the calculated thermal shock resistance.

The stress gradient (i.e., the partial derivative of the stress with respect to the radius) at the center of the disk is zero, and, consequently, for the calculated thermal shock resistance on quenching through the transformation range of the zirconia-titanium compositions, the tensile strength rather than the modulus of rupture of the material is to be used in the thermal shock equation. As is customarily done for brittle materials, the tensile strength will be assumed to be one-half the modulus of rupture.[19] This new factor of one-half cancels the factor two obtained in the previous argument, and the thermal shock equation (Eq. (4)) applies equally well for quenches both from below and through the transformation range, provided that the modulus of rupture $\sigma_{M_{T,2}}$ is used for $\sigma_{\theta_{max}}$. For the reasons already stated, this value of modulus of rupture - as well as all the other properties in the thermal shock equation - is that at the temperature corresponding to the start of the transformation.

PROCEDURE FOR CALCULATING THERMAL SHOCK RESISTANCE FROM MATERIAL PROPERTIES

In this procedure for calculating the curve of ΔT against hr_m, the properties to be used in the thermal shock equation (Eq. (4)) are those obtained at the time and position at which rupture occurs. Two distinct cases will be considered: quenches from below the transformation range and quenches through the transformation range.

For quenches from below the transormation range it is convenient to restate the thermal shock equation (Eq. (4)) in a different form. From the definition of relative temperature at $r = r_m$,

$$U_{1.0} = \frac{T_s - T_f}{T_i - T_f} = \frac{T_s - T_f}{\Delta T} \tag{5}$$

where T_s is the temperature at $r = r_m$ at time t from the start of cooling. Substituting ΔT from equation (5) into equation (4), replacing $\sigma_{\theta_{max}}$ by the modulus of rupture $\sigma_{M_{T,2}}$ from equation (3), and rearranging terms yield

$$U_{1.0} f(\beta) = \frac{E\alpha}{0.76\ \sigma_{M_{T,1}}} (T_s - T_f) \tag{6}$$

At the moment of rupture, E, α, and $\sigma_{M_{T,1}}$ are taken as the properties at T_s.

In order to facilitate computations, it is advantageous to plot the right side of equation (6) as a function of $T_s - T_f$. This plot is shown in Fig. 14 for two different values of T_f.

Plots of β as a function of $U_{1.0}$ and of τ are also required. These plots are shown in Fig. 15. The data for these plots were obtained from Russell's tables.[20]

Theprocedure used to obtain the points to plot the curve of ΔT against hr_m for quenches from below the transormation range is illustrated with an example as follows:

(1) A value of Biot's modulus $\beta = 8.2$ was assumed. From Fig. 13, $f(\beta) = 2.10$ and $\tau = 0.04$.

(2) From the pair of values from step (1) (β, τ) and Fig. 15, $U_{1.0} = 0.275$.

(3) From the product of the values of $f(\beta)$ and $U_{1.0}$ from steps (1) and (2) and from Fig. 14, $T_s - T_f = 104^\circ$ C and $T_s = 129^\circ$ C.

(4) From the value of $T_s - T_f$ from step (3) and equation (5), $\Delta T = 378^\circ$ C.

(5) From Fig. 5 and $T_s = 129^\circ$ C from step (3), $k = 0.0136$.

(6) From the value of assumed β, $k = 0.0136$ from step (5), and the defining equation for β (see Fig. 12), $hr_m = 0.112$.

(7) The value of ΔT from step (4) and hr_m from step (6) gave a point on the curve. Similarly, other points were plotted to obtain the whole curve.

For the reasons already stated, the calculated ΔT for quenches through the transformation range were obtained from the values of the properties at 880° C (region of maximum α).

COMPARISON OF EXPERIMENTAL AND CALCULATED THERMAL SHOCK RESISTANCE OF ZT-15-M

The values of ΔT and hr_m obtained by the procedure described in the previous section were plotted as shown in Fig. 16. Comparison with the experimental thermal shock resistance (from Ref. 1) in the same figure shows that, for quenches from below the transformation range of ZT-15-M, the thermal shock resistances obtained from theory and experiment are, for all practical purposes, identical. For quenches through the transformation range, on the other hand, the experimental thermal shock resistance is about seven times the calculated value.

The relatively good thermal shock resistance of ZT-15-M for quenches from below the transformation range of zirconia is due in large measure to the relatively high modulus of rupture of ZT-15-M. Considering that the strength of most ceramics increases with decreasing grain size[17,21] this high modulus of rupture and correspondingly high thermal shock resistance can be attributed at least in part to the small grain size of ZT-15-M, since the other properties in the thermal shock equation (Eq.(4)) are not significantly affected by grain size.

Although the small grain size of the zirconia-titanium compositions undoubtedly contributes to improved thermal shock resistance for quenches through the transformation range as well it cannot account for the large discrepancy between experimental and calculated values of thermal shock resistance. The bent modulus-of-elasticity bars already mentioned suggest that this discrepancy may be due to plastic deformation but further work would be required to elucidate this point.

VI. CONCLUSIONS

From the results of the present investigation the following conclusions can be drawn:

1. The technique of milling the raw materials greatly improves the density and strength of zirconia with 15 mole percent titanium.

2. The modulus of rupture of zirconia with 15 mole percent titanium is almost twice as large as that of calcia-stabilized zirconia of equivalent porosity at room temperature.

3. The high-temperature strength of zirconia with 15 mole percent titanium is much superior to that of calcia-stabilized zirconia.

4. The superior strength of zirconia with 15 mole percent titanium compared with that of calcia-stabilized zirconia may be due in part to the smaller grain size of the former.

5. The heat capacity of zirconia obtained in this investigation is practically the same as that reported in the literature.

6. The thermal conductivity of zirconia with 15 mole percent titanium was consistently higher than that of stabilized zirconia reported in the literature.

7. The coefficient of linear thermal expansion and the transormation temperature for zirconia with 15 mole percent titanium obtained in this investigation are practically the same as those reported in the literature for similar materials, but the total expansion through the transformation range was found to be larged in the present investigation.

8. The modulus of elasticity versus temperature curve for zirconia with 15 mole percent titanium shows a maximum in the transformation range indicating that at the transformation temperature the modulus of elasticity of tetragonal zirconia is higher than that of monoclinic zirconia.

9. At room temperature, the moduli of elasticity of zirconia with 15 mole percent titanium in tension and compression are practically identical.

10. For quenches from below the transformation range of zirconia, the experimental and calculated thermal shock resistances are practically identical.

11. For quenches through the transformation range, the experimental thermal shock resistance is about seven times the calculated value. It is surmised that the discrepancy may be due to plastic deformation in this range.

12. The superior thermal shock resistance of zirconia with 15 mole percent titanium for quenches from below the transformation range compared with that of calcia-stabilized zirconia is attributed primarily to the larger modulus of rupture of zirconia with 15 mole percent titanium.

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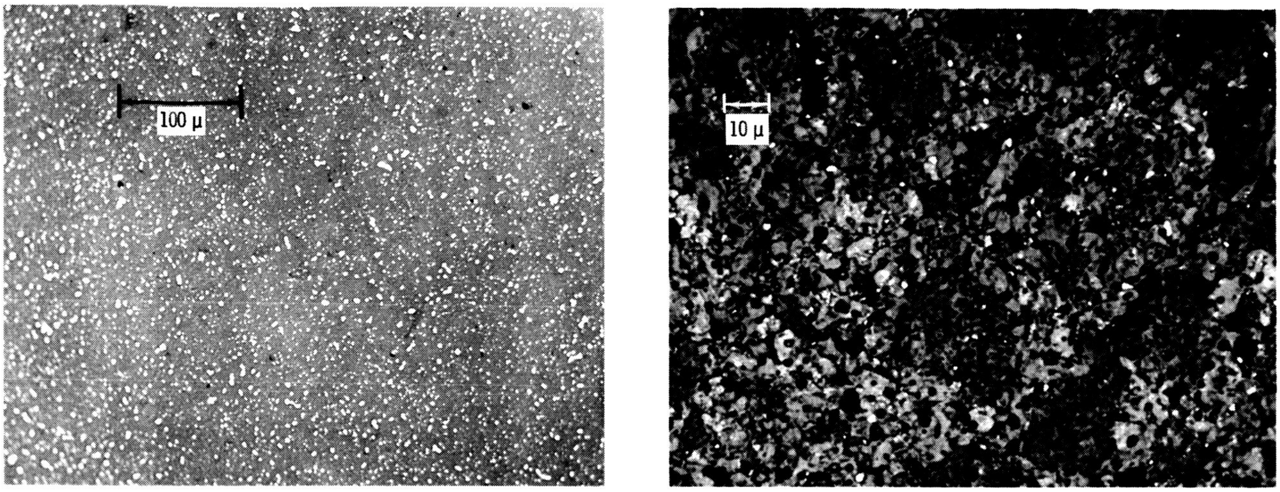
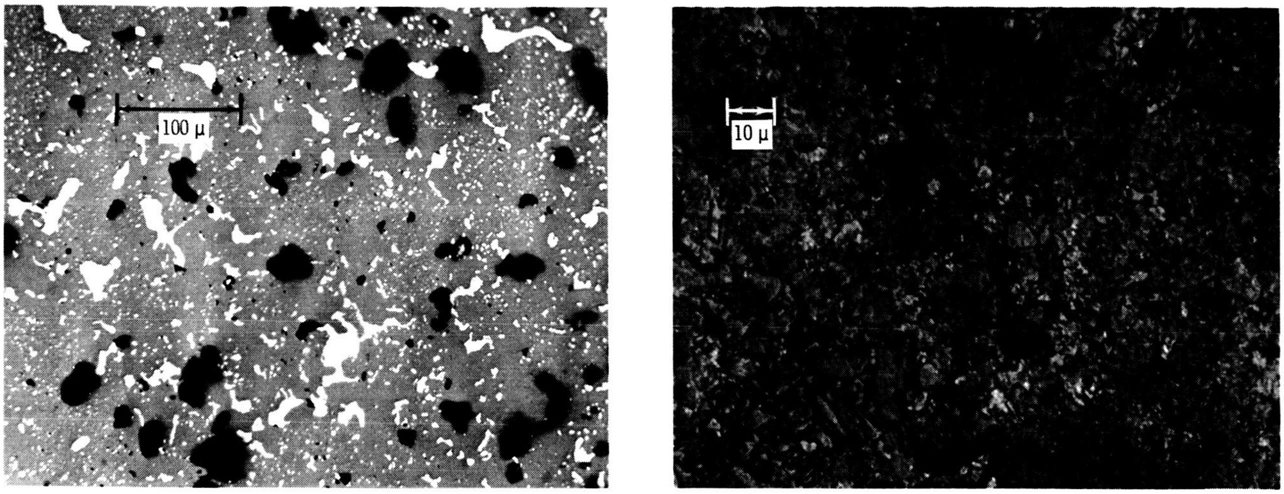


(a) Unetched.

(b) Etchant, potassium bisulfate.

Figure 1. - Microstructure of zirconia with 15 mole percent titanium, milled, cold-pressed, and sintered in vacuum at 1870° C for 1 hour.



(a) Unetched.

(b) Etchant, hydrofluoric acid.

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Figure 2. - Microstructure of zirconia with 15 mole percent titanium, cold-pressed, and sintered in vacuum at 1870° C for 1 hour.

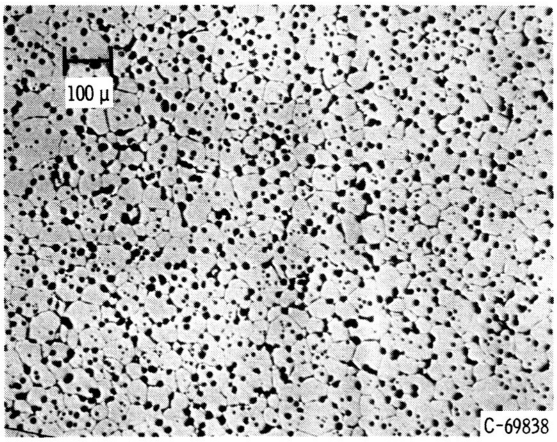

Figure 3. - Microstructure of calcia-stabilized zirconia (Zircoa B), milled, cold-pressed, and sintered in air at 1800° C for 3 hours. Etchant, fused potassium bisulfate.

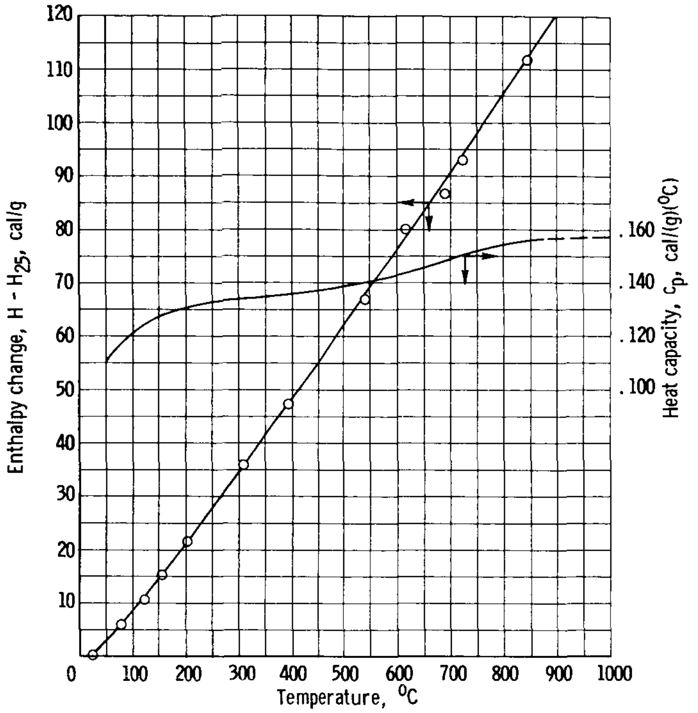

Figure 4. - Enthalpy and heat capacity of zirconium oxide with 15 mole percent titanium (ZT-15-M) as function of temperature.

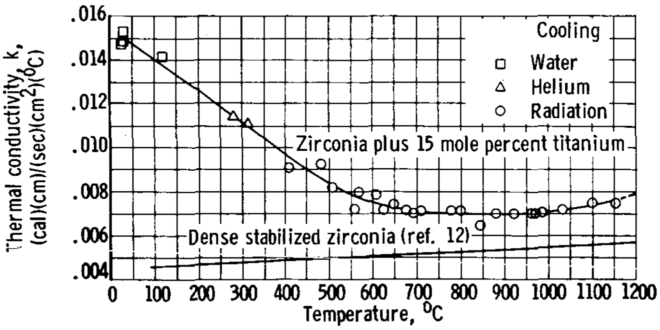

Figure 5. - Thermal conductivity of zirconium oxide with 15 mole percent titanium (ZT-15-M) as a function of temperature compared with that of stabilized zirconia (ref. 12).

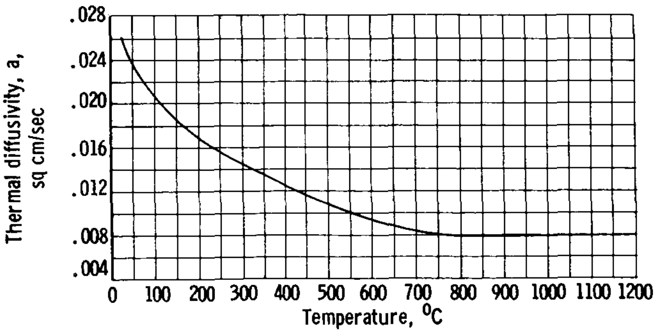

Figure 6. - Thermal diffusivity of zirconium oxide with 15 mole percent titanium (ZT-15-M).

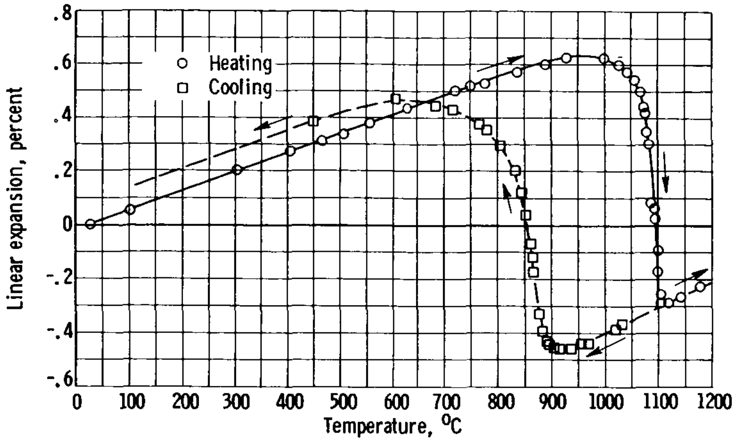

Figure 7. - Linear thermal expansion of zirconium oxide with 15 mole percent titanium (ZT-15-M).

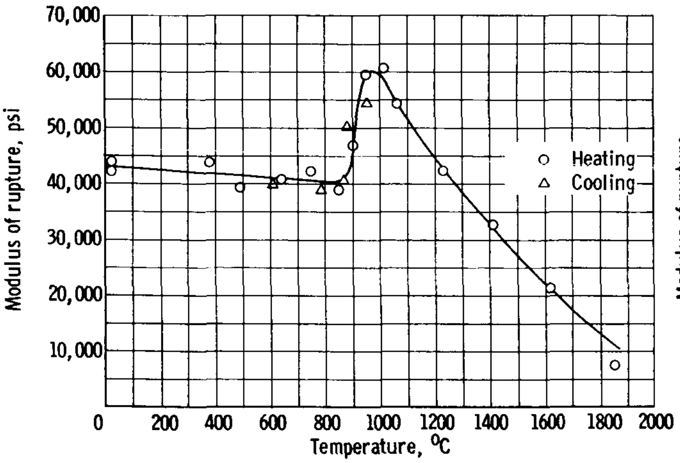

Figure 8. - Modulus of rupture under three-point loading for zirconium oxide with 15 mole percent titanium (ZT-15-M) as function of temperature.

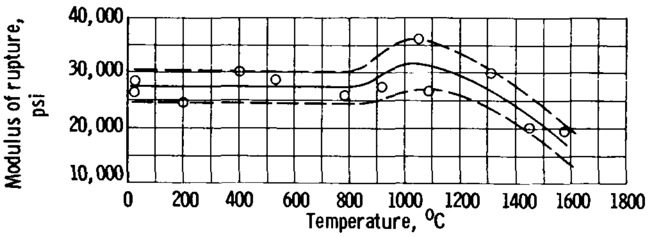

Figure 9. - Modulus of rupture under three-point loading for zirconia with 15 mole percent titanium (ZT-15) as function of temperature (heating cycle only).

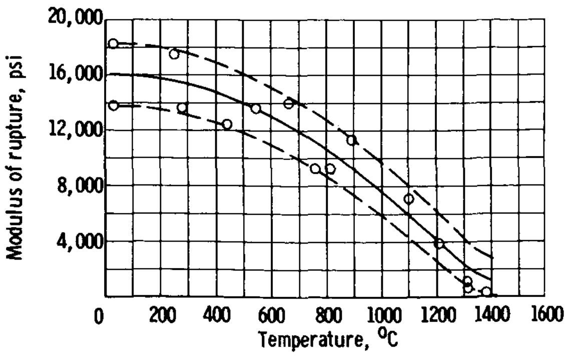

Figure 10. - Modulus of rupture under three-point loading for 5 weight percent calcia-stabilized zirconia as function of temperature (heating cycle only).

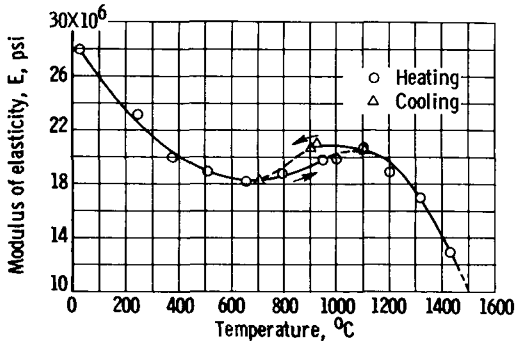

Figure 11. - Modulus of elasticity of zirconium oxide with 15 mole percent titanium (ZT-15-M) as function of temperature.

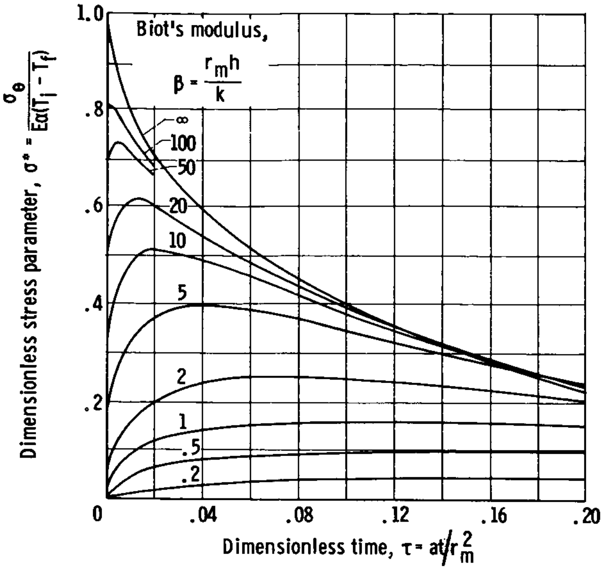

Figure 12. - Dimensionless stress against dimensionless time for several values of Biot's modulus (ref. 10).

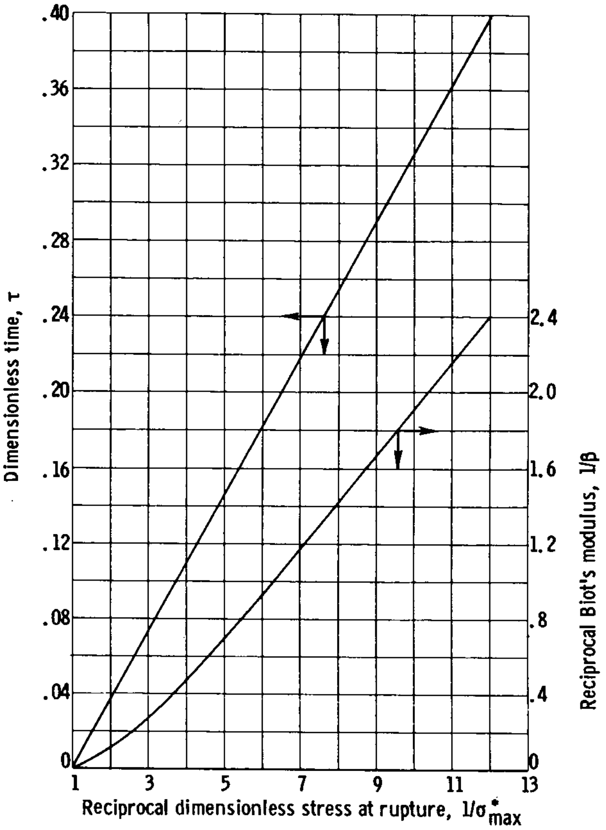

Figure 13. - Plots of dimensionless time against reciprocal dimensionless stress at rupture and reciprocal Biot's modulus against reciprocal dimensionless stress at rupture for a thin disk.

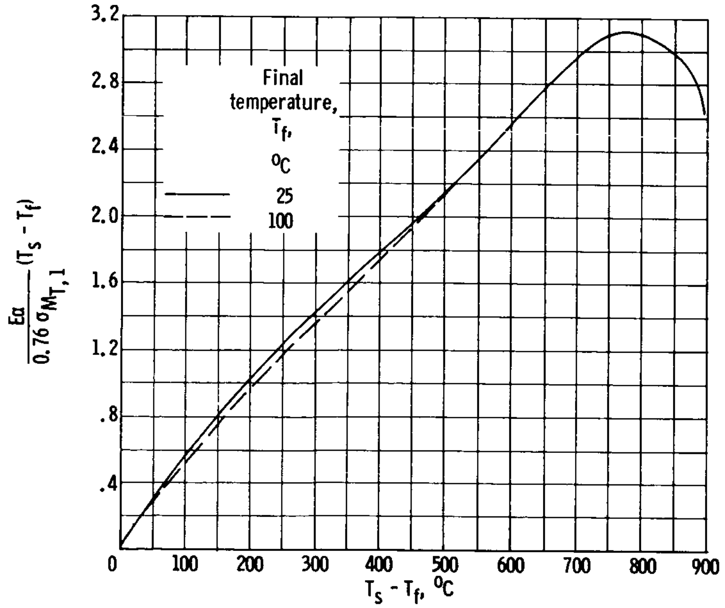

Figure 14. - Variation of $\frac{E\alpha}{0.76\,\sigma_{M_{T,1}}}(T_s - T_f)$ as function of $T_s - T_f$.

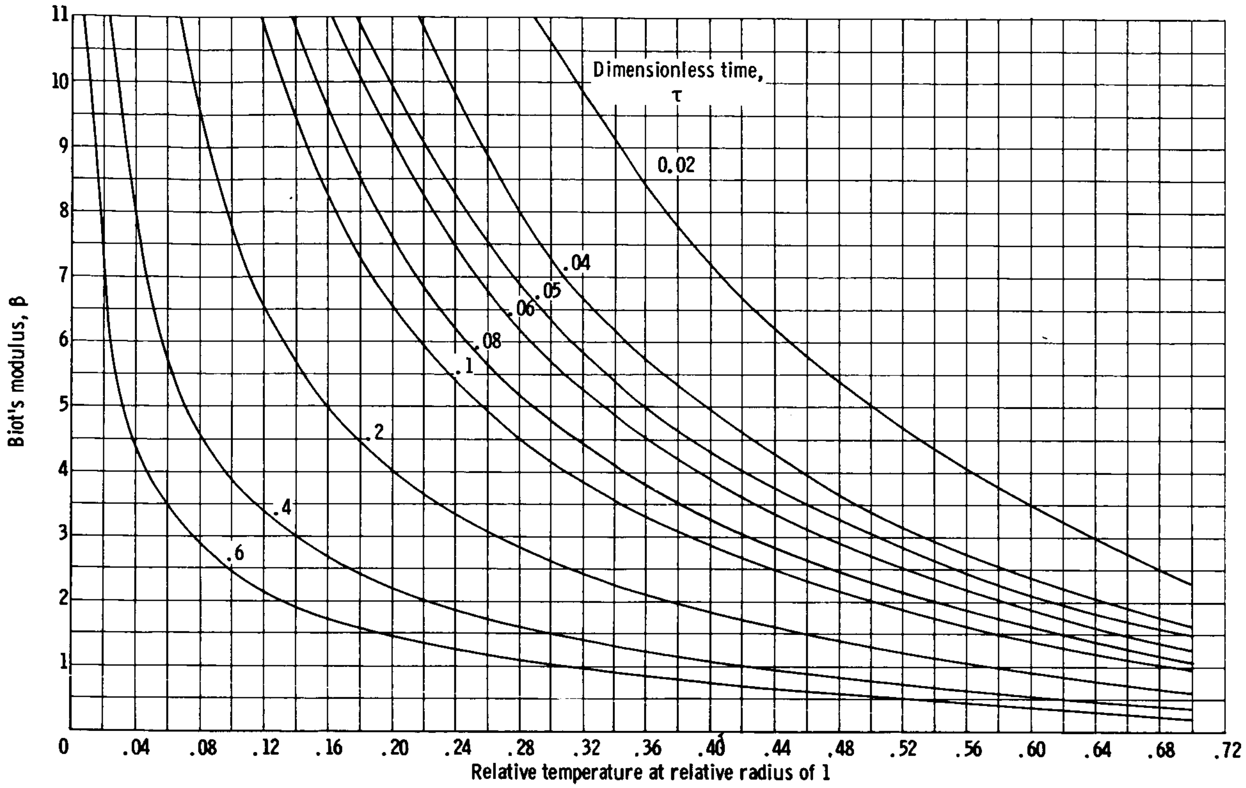

Figure 15. - Plot of Biot's modulus against relative temperature at relative radius of 1.

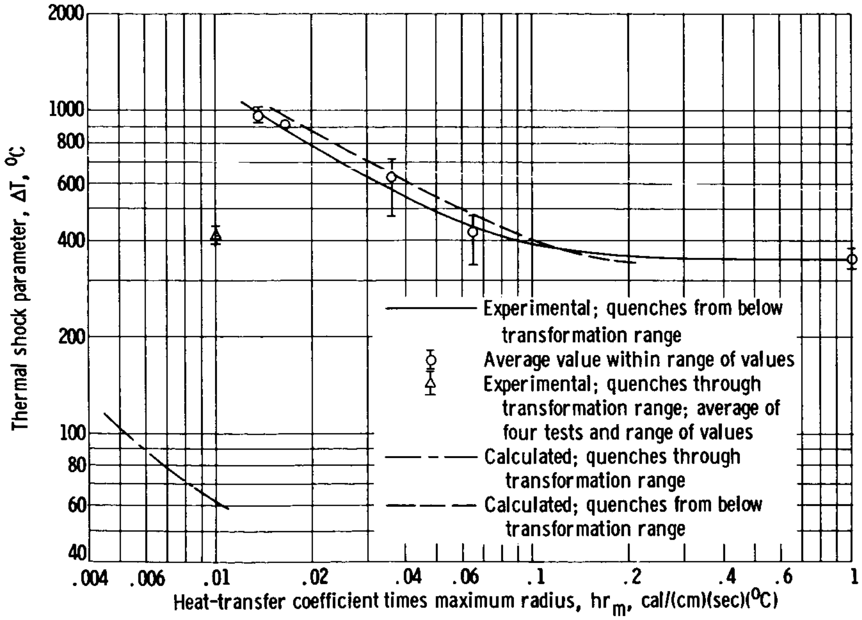

Figure 16. - Variation in maximum quenching temperature as function of heat-transfer coefficient times maximum radius for zirconium oxide with 15 mole percent titanium (ZT-15-M).