

Factors Affecting Thermal Stress Resistance of Ceramic Materials

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The sources and calculation of thermal stresses are considered, together with the factors involved in thermal stress resistance factors. Properties affecting thermal stress resistance of ceramics are reviewed, and testing methods are considered.

I. Introduction

THE susceptibility of ceramic materials to thermal stresses has been recognized for a long time. More than one hundred years ago equations for the thermal stresses arising from temperature gradients in a cylinder were derived by Duhamel (1838).¹ Since that time, about thirty papers have appeared which mainly consider the calculation of thermal stresses in an infinite cylinder subjected to temperature gradients. It is apparent that thermal stresses are not a new or uninvestigated phenomenon.

The first quantitative treatment of thermal stress fracture in ceramic materials was prepared by Winkelmann and Schott (1894).² Hovestadt and Everhart (1902)³ gave a correct solution for the case of infinitely rapid cooling. A number of investigators considered testing methods for glasses and for refractories and their correlation with service results. Norton (1926)⁴ studied the problem and first suggested that shear stresses must be considered as well as tensile stresses. More recently, several investigators, particularly those interested in special refractory applications, have considered the problem of thermal stresses from both theoretical and experimental points of view. New attempts have been made to define and to measure a material property which can be called "resistance to thermal stresses." Although these attempts have not been completely successful in a quantitative way, they have led to a much improved understanding of the factors that contribute to thermal stress resistance. It is the purpose of the present paper to consider these factors and their effect on thermal stress resistance.

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¹ J. M. C. Duhamel, "Memoire sur le calcul des actions moleculaires developpees par les changements de temperature dans les corps solides," *Memoirs . . . de l'institute de France*, V, 440 (1838).

² A. Winkelmann and O. Schott, "Ueber thermische Widerstandskoeffizienten verschiedener Gläser in ihrer Abhängigkeit von der chemischen Zusammensetzung," *Ann. Physik. Chem.*, 51, 730 (1894).

³ H. Hovestadt and J. D. Everhart, Jena Glass, Macmillan Co., New York, 1902, p. 228.

⁴ F. H. Norton, "Mechanism of Spalling," *J. Am. Ceram. Soc.*, 9 [7] 446-61 (1926); "A General Theory of Spalling," *ibid.*, 8 [1] 29-39 (1925).

II. Nomenclature

The nomenclature and letter symbols employed in the consideration of thermal stresses have varied considerably. In this paper the following definitions will be employed:

Thermal stress: A stress arising from a temperature gradient.

Thermal stress resistance: Resistance to weakening or to fracture from thermal stresses.

Spalling: The breaking away of pieces of a shape or structure.

Thermal spalling: Spalling caused by thermal stresses.

Thermal fracture: Fracture caused by thermal stresses.

Thermal endurance: Resistance to weakening or fracture when subjected to conditions causing thermal stresses.

Thermal shock: A sudden transient temperature change.

Thermal shock resistance: Resistance to weakening or fracture when subjected to thermal shock.

III. Origin and Calculation of Thermal Stresses

The origin of thermal stresses is the difference in thermal expansion of various parts of a body under conditions such that free expansion of each small unit of volume cannot take place.⁵ This condition can arise in a number of ways.

(1) Stresses Arising at Uniform Temperature

If a ceramic body is changed from an initial temperature, t_0 , to a new uniform temperature, t' , no stresses arise providing that the body is homogeneous, isotropic, and unrestrained (free to expand). Under these conditions, the linear expansion of each volume element is $\alpha(t' - t_0)$ and the shape of the body is unchanged.

If the body is not homogeneous and isotropic, as in a polycrystalline material with anisotropic crystals or in a mixture of two materials (such as a glass-mullite porcelain), stresses will arise due to the difference in expansion between crystals or phases. The magnitude of the stresses will depend on the elastic properties and expansion coefficients of the components. These "microstresses" or "tessellated stresses" have been thoroughly investigated in connection with magnetic and fatigue properties.⁶ In extreme cases they may lead to serious weakening or fracture.⁷ A similar effect on a larger scale is the stresses caused by differences of expansion between a

⁵ S. Timoshenko, *Theory of Elasticity*, McGraw-Hill Book Co., Inc., New York, 1934. 415 pp.

⁶ (a) F. László, "Tessellated Stresses," *J. Iron Steel Inst.* (London), 148 [1] 173-99 (1943).

(b) F. P. Bowden, "Experiments of Boas and Honeycombe on Internal Stresses Due to Anisotropic Thermal Expansion of Pure Metals and Alloys," *J. Inst. Metals, Symposium on Internal Stresses in Metals and Alloys*, Preprint No. 1100, 6 pp. (1947).

(c) J. P. Nielsen and W. R. Hibbard, Jr., "X-ray Study of Thermally Induced Stresses in Microconstituents of Aluminum-Silicon Alloys," *J. Appl. Phys.*, 21, 853-54 (1950).

⁷ (a) N. N. Ault and H. F. G. Ueltz, "Sonic Analysis for Solid Bodies," *J. Am. Ceram. Soc.*, 36, [6] 199-203 (1953).

(b) W. R. Buessens, N. R. Thielke, and R. V. Sarakauskas, "Thermal Expansion Hysteresis of Aluminum Titanate," *Ceram. Age*, 60 [5] 38-40 (1952).

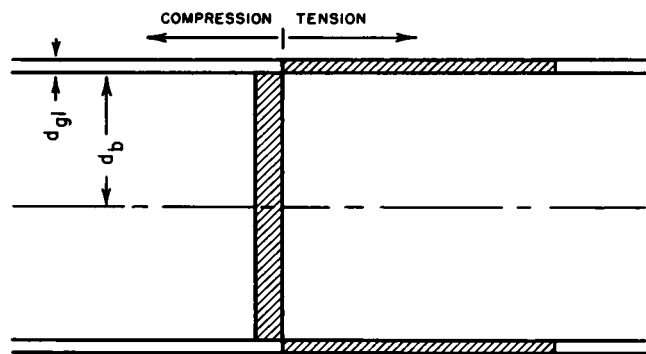


Fig. 1. Stresses in glaze on infinite slab.

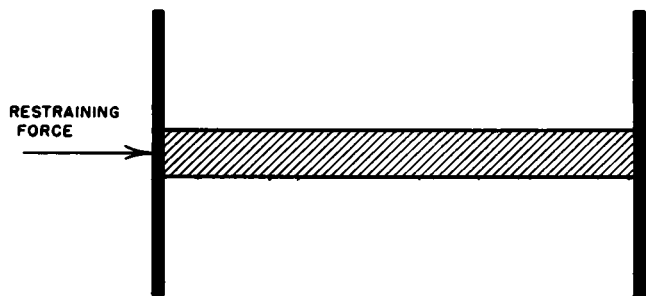


Fig. 2. Restraint of expansion by fixed supports.

glaze or enamel and the underlying ceramic or metal. If stress-free at t_0 , the stresses will depend on the new temperature, t' , on the elastic properties, and on the coefficients of expansion. For a thin glaze on an infinite slab, the stresses will be as shown in Fig. 1. The stresses⁸ are given in equations (1) and (2) for the simplest case where the elastic properties of glaze and body are the same.

⁸ (a) J. N. Goodier, "On the Integration of Thermo-elastic Equations," *Phil. Mag.*, **23**, 1017 (1937).

(b) W. M. Hampton, "Study of Stresses in Flashed Glasses," *J. Soc. Glass Technol.*, **20**, 273 (1936).

Table I. Surface and Center Stresses in Various Shapes

Shape	Surface	Center
Infinite slab	$\sigma_x = 0$ $\alpha_y = \sigma_z = \frac{E\alpha}{(1-\mu)}(t_a - t_c)$	$\sigma_r = 0$ $\sigma_y = \sigma_z = \frac{E\alpha}{(1-\mu)}(t_a - t_c)$
Thin plate	$\sigma_y = \sigma_z = 0$ $\sigma_x = \alpha E(t_a - t_c)$	$\sigma_y = \sigma_z = 0$ $\sigma_r = \alpha E(t_a - t_c)$
Thin disk	$\sigma_r = 0$ $\sigma_\theta = \frac{(1-\mu)E\alpha}{(1-2\mu)}(t_a - t_c)$	$\sigma_r = \frac{(1-\mu)E\alpha}{2(1-2\mu)}(t_a - t_c)$ $\sigma_\theta = \frac{(1-\mu)E\alpha}{2(1-2\mu)}(t_a - t_c)$
Long solid cylinder	$\sigma_r = 0$ $\sigma_\theta = \sigma_z = \frac{E\alpha}{(1-\mu)}(t_a - t_c)$	$\sigma_r = \frac{E\alpha}{2(1-\mu)}(t_a - t_c)$ $\sigma_\theta = \sigma_z = \frac{E\alpha}{2(1-\mu)}(t_a - t_c)$
Long hollow cylinder	$\sigma_r = 0$ $\sigma_\theta = \sigma_z = \frac{E\alpha}{(1-\mu)}(t_a - t_c)$	$\sigma_r = 0$ $\sigma_\theta = \sigma_z = \frac{E\alpha}{(1-\mu)}(t_a - t_c)$
Solid sphere	$\sigma_r = 0$ $\sigma_t = \frac{E\alpha}{(1-\mu)}(t_a - t_c)$	$\sigma_t = \sigma_r = \frac{2E\alpha}{3(1-\mu)}(t_a - t_c)$
Hollow sphere	$\sigma_r = 0$ $\sigma_t = \frac{\alpha E}{(1-\mu)}(t_a - t_c)$	$\sigma_r = 0$ $\sigma_t = \frac{\alpha E}{(1-\mu)}(t_a - t_c)$

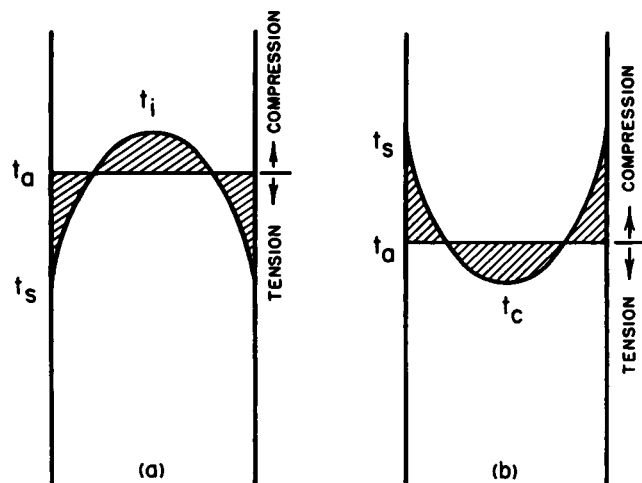


Fig. 3. Temperature and stress distribution for (a) cooling and (b) heating a slab.

$$\sigma_{r1} = E(t_0 - t')(\alpha_{g1} - \alpha_b)(1 - j)(1 - 3j + 6j^2) \quad (1)$$

$$\sigma_b = E(t_0 - t')(\alpha_b - \alpha_{g1})(j)(1 - 3j + 6j^2) \quad (2)$$

where $j = d_{g1}/d_b$.

Similarly, if a bar of material is completely restrained from expanding by application of restraining forces due to the design of a part, stresses arise as for Fig. 2, where

$$\sigma = \frac{E\alpha(t_0 - t')}{(1 - \mu)} \quad (3)$$

Stresses such as these, although not due to a temperature gradient and therefore not classified as thermal stresses as the term has been defined here, will be additive with any thermal stresses developed and must be considered in any practical applications of thermal stress resistance.

(2) Stresses Arising from Temperature Gradients⁹

A temperature gradient does not necessarily give rise to thermal stresses. For instance, in an infinite slab with a linear temperature gradient, the body can expand without incompatible strains and no stresses arise. In general, however, the temperature is not a linear function of dimension and free expansion of each volume element would lead to separation of the elements so that they could not be fitted together. Since they are constrained in the same body, stresses arise which can be exactly calculated for a number of purely elastic bodies from the theory of elasticity. Without going into these calculations in detail, it can be shown that for symmetrical temperature distributions, the stresses resulting for simple shapes are those given in Table I. The stress at any point is determined by the temperature distribution, by the shape of the body, and by the physical constants E , α , and μ , which are taken as independent of temperature. If these factors are known, the stress can be calculated at any point for sufficiently simple shapes.

The temperature and stress distribution for heating and cooling the surface of an infinite slab at a constant rate is shown in Fig. 3. On cooling, the maximum stress is the tensile stress on the surface and the center is in compression. On heating, the maximum stress is the compressive stress on the surface, and the center is in tension. There also are shear stresses equal to

half the difference between the principal stresses. These shear stresses are equal during heating and cooling, and are maximum at the surface. For nonsymmetrical temperature distributions, there are also bending stresses (which can be calculated from elastic theory).⁶

IV. Temperature Distribution

It is clear that in order to calculate thermal stresses a knowledge of the temperature distribution is necessary. Two cases can be considered.

(1) Steady State⁹

In the steady state the temperature distribution is determined by the rate of heat flow, by the specimen shape, and by the thermal conductivity. In a hollow cylinder, for example, the temperature distribution is logarithmic. For simple shapes the distribution can be obtained by integration of the heat flow equation containing the thermal conductivity as a material property relating heat flow and temperature gradient,

$$q = -kA \frac{dt}{dx} \quad (4)$$

This may be integrated for k as a function of temperature, but k is generally taken as a constant mean value. For complex shapes not susceptible to analytical treatment, numerical methods are available which allow the calculation of temperature distribution to any desired accuracy.^{9(b), 10}

(2) Unsteady or Transient State^{9, 10}

In this case the temperature at any point changes with time, in a manner depending on the thermal conductivity, k , and on the heat capacity per unit volume (ρc_p), as follows:

$$\frac{dt}{d\theta} = \frac{k}{\rho c_p} \left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2} \right) \quad (5)$$

This equation applies strictly only when k , ρ , and c_p are independent of temperature, position, and direction. If k or c_p is not constant, an analytical solution is usually not possible, but numerical or analogue methods can be employed in these cases.¹⁰

In determining temperature at various times by analytical methods, somewhat arbitrary boundary conditions must be assumed. Well-known solutions are available for the cases where (a) the surface is immediately changed to its new temperature, t' ; (b) the surface temperature changes at a constant rate; and (c) the surface heat transfer coefficient, h , is independent of temperature. Each of these assumptions is a good approximation to certain practical cases, but cannot be arbitrarily applied to any case. No analytical solution is available for the case where cooling is by radiation alone, which is also an important case. Analytical solutions are also available for the case of a composite slab (glaze or enamel).¹¹ In Fig. 4, temperature distributions for different conditions of surface heat transfer are indicated.

If any arbitrary boundary condition is known or assumed, numerical or graphical methods can be employed to determine the temperature distribution at various time intervals.^{9(b), 10} Tables and graphical solutions for a number of common cases

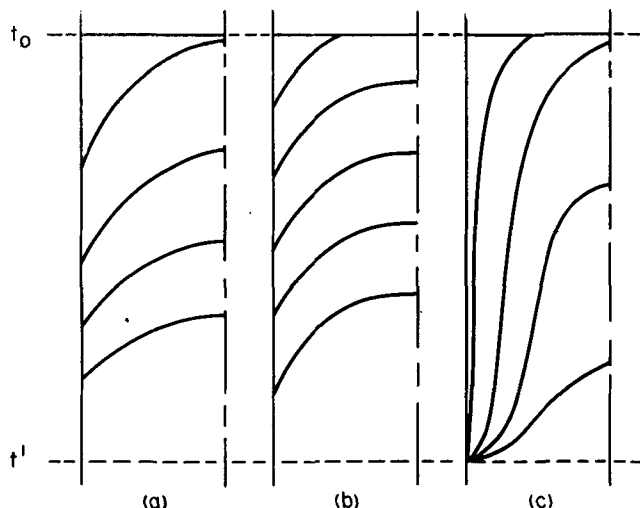


Fig. 4. Temperature decrease through a slab with (a) constant surface heat transfer coefficient, (b) linear rate surface temperature decrease, and (c) immediate cooling of surface from t_0 to t' .

also are available in the literature in terms of the nondimensional parameters involved.¹²

V. Calculation of Resistance to Thermal Stresses^{2-5, 13}

The essential method of calculating the resistance to thermal stresses which has been used by all investigators is to determine a temperature distribution under certain conditions and from this to determine the thermal stresses. This method has been applied analytically to various simple shapes and conditions to calculate material property factors. It can also be applied to more complex conditions and shapes by numerical or graphical methods.

A factor of considerable practical interest, and one which

¹² (a) A. J. Ede, "New Form of Chart for Determining Temperatures in Bodies of Regular Shape During Heating or Cooling," *Phil. Mag.*, **36**, 845 (1945).

(b) E. D. Williamson and L. H. Adams, "Temperature Distribution in Solids During Heating or Cooling," *Phys. Rev.*, **14**, 99 (1919).

(c) H. P. Gurney and J. Lurie, "Charts for Estimating Temperature Distributions in Heating and Cooling Solid Shapes," *J. Ind. Eng. Chem.*, **15** [11] 1170 (1923); *Ceram. Abstr.*, **3** [3] 87 (1924).

(d) A. Schack (translated by H. Goldschmidt and E. P. Partidge), *Industrial Heat Transfer*, John Wiley & Sons, New York, 1933. 371 pp.; *Ceram. Abstr.*, **13** [3] 64 (1934).

(e) A. B. Newman, "Heating and Cooling Rectangular and Cylindrical Solids," *Ind. Eng. Chem.*, **28**, 545-48 (1936).

(f) A. B. Newman, "Drying of Porous Solids," *Trans. Am. Inst. Chem. Engr.*, **27**, 203, 310 (1931).

(g) T. F. Russell, "Some Mathematical Considerations on Heating and Cooling of Steel," First Report of Alloy Steels Research Committee, *Iron & Steel Inst. (London)*, *Special Report No. 14*, pp. 149-87 (1936).

(h) F. C. W. Olson and O. T. Schultz, "Temperatures in Solids During Heating or Cooling; Tables for Numerical Solution of Heating Equation," *Ind. Eng. Chem.*, **34** [7] 874-77 (1942); *Ceram. Abstr.*, **21** [9] 196 (1942).

¹³ (a) Bernard Schwartz, "Thermal Stress Failure of Pure Refractory Oxides," *J. Am. Ceram. Soc.*, **35** [12] 325-33 (1952).

(b) O. G. C. Dahl, "Temperature and Stress Distributions in Hollow Cylinders," *Trans. Am. Soc. Mech. Eng.*, **46**, 161 (1924).

(c) C. H. Kent, "Thermal Stresses in Spheres and Cylinders Produced by Temperature Varying with Time," *Trans. Am. Soc. Mech. Eng.*, **54**, 188 (1932); "Thermal Stresses in Thin-Walled Cylinders," *ibid.*, **53**, 167 (1931).

(d) E. M. Baroody, W. H. Duckworth, E. M. Simons, and H. Z. Schofield, "Effect of Shape and Material on Thermal Rupture of Ceramics," AECD-3486, U. S. Atomic Energy Commission, *Natl. Sci. Foundation, Washington, D. C.*, 5-75, May 22, 1951.

(e) S. S. Manson, "Behavior of Materials under Conditions of Thermal Stress," N.A.C.A. Tech. Note 2933, July 1953.

⁹ (a) R. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, 1947. 386 pp.

(b) L. R. Ingersoll, O. J. Zobel, and A. C. Ingersoll, *Heat Conduction*, McGraw-Hill Book Co., Inc., New York, 1948.

(c) W. H. McAdams, *Heat Transmission*, 2d edition, McGraw-Hill Book Co., Inc., New York, 1942. 459 pp.

¹⁰ G. M. Dusenberre, *Numerical Analysis of Heat Flow*, McGraw-Hill Book Co., Inc., New York, 1949. 227 pp.; *Ceram. Abstr.*, **1952**, February, p. 30d.

¹¹ M. L. Anthony, "Temperature Distributions in Composite Slabs Due to Suddenly Activated Plane Heat Source," p. 236; "Temperature Distributions in Slabs With Linear Temperature Rise at One Surface," p. 250, *Proceedings of the General Discussion on Heat Transfer, Inst. Mech. Engrs.*, London (1951).

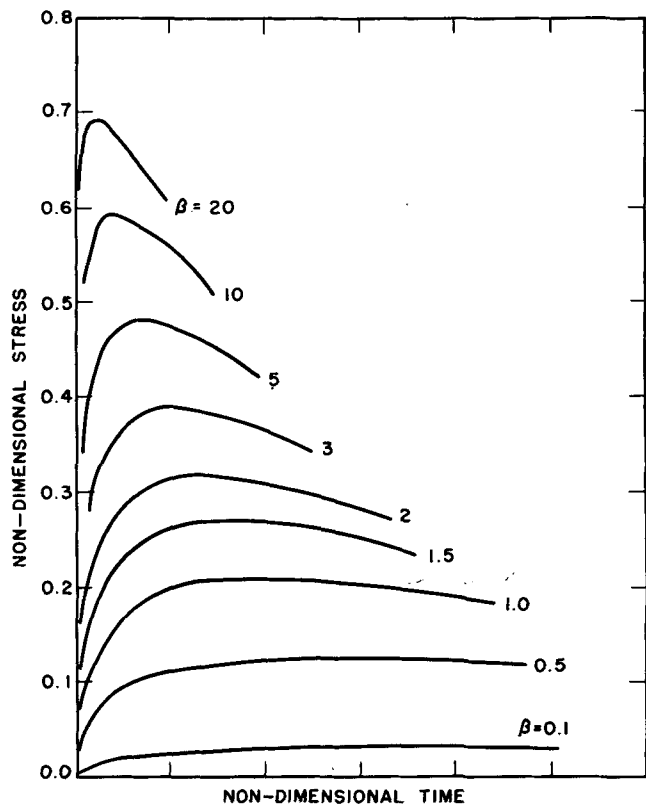


Fig. 5. Variation of dimensionless surface stress with dimensionless time for an infinite flat plate.

serves as a quantitative measure of thermal stress resistance, is the maximum temperature difference required to cause a specified fracture or weakening of a certain shape under specified thermal conditions. For purposes of calculation, the temperature difference causing stresses equal to the breaking strength of the ceramic is employed. Let us consider some typical cases.

(1) Unsteady State (h Infinite)

When the coefficient of heat transfer is so large that the surface originally at t_0 is changed instantly to t' , the average temperature of the sample as a whole is at first unchanged from t_0 . Consequently, the stress at the surface is (see Table I) for a sphere

$$\sigma = \frac{E\alpha(t_0 - t')}{1 - \mu} \quad (6)$$

$$\sigma_{\max} = 1 \quad (7)$$

(Footnote 13 continued from page 5)

(f) F. J. Bradshaw, "Thermal Stresses in Non-Ductile High-Temperature Materials," Tech. Note MET 100, British RAE, February 1949; "Improvement of Ceramics for Use in Heat Engines," Tech. Note MET 111, British RAE, October 1949.

(g) C. M. Cheng, "Resistance to Thermal Shock," *J. Am. Rocket Soc.*, 21 [6] 147-53 (1951).

(h) W. Buessem, "Ring Test and Its Application to Thermal Shock Problems," O.A.R. Report, Wright-Patterson Air Force Base, Dayton, Ohio (1950).

(i) C. H. Lees, "Thermal Stresses in Solid and in Hollow Circular Cylinders Concentrically Heated," *Proc. Roy. Soc.*, A101, 411 (1922); "Thermal Stresses in Spherical Shells Concentrically Heated," *ibid.*, A100, 379 (1921).

(j) B. E. Gatewood, "Thermal Stresses in Long Cylindrical Bodies," *Phil. Mag.*, 32, 282 (1941).

(k) J. C. Jaeger, "Thermal Stresses in Circular Cylinders," *Phil. Mag.*, 36 [257] 418 (1945).

(l) M. J. Lighthill and F. J. Bradshaw, "Thermal Stresses in Turbine Blades," *Phil. Mag.*, 40, 770 (1949).

(m) V. H. Stott, "Thermal Endurance of Glass, I," *J. Soc. Glass Technol.*, 8 [30] 139 (1924); *Ceram. Abstr.*, 3 [10] 281 (1924).

The dimensionless stress, σ_{\max}^* , is the maximum possible, and the temperature difference giving a stress equal to the breaking strength is

$$t_0 - t' = \frac{s_t(1 - \mu)}{E\alpha} \quad (8)$$

On cooling, the surface is in tension and fracture should occur at $\theta = 0$. On heating, the surface stress is compressive, and failure may occur due to shearing stresses which are half the principal stresses:

$$\tau = \frac{E\alpha(t_0 - t')}{2(1 - \mu)} \quad (9)$$

$$t_0 - t' = \frac{2s_s(1 - \mu)}{E\alpha} \quad (10)$$

If this shear stress is insufficient to cause fracture, failure may still occur owing to center tensile stresses. From a well-known solution for the temperature distribution, it can be shown that for a sphere⁶

$$\sigma_{m,x}^* = 0.386 \quad (11)$$

$$t_0 - t' = \frac{2s_t(1 - \mu)}{0.771E\alpha} \quad (12)$$

The time to fracture is

$$\theta = \frac{0.0574r_m^2}{a} \quad (13)$$

Whether the surface shear or the center tension causes fracture depends on the severity of thermal shock and on the relative shear and center tensile strength.

If a resistance factor in shear or in tension is defined as

$$R = \frac{s_t(1 - \mu)}{E\alpha}; \quad R_s = \frac{s_s(1 - \mu)}{E\alpha} \quad (14)$$

and a shape factor, S , giving the stress dependence on the shape of the specimen, the temperature change which just causes thermal stress fracture can be written as

$$\Delta t_f = R \cdot S \quad (15)$$

The material properties of importance are the breaking stress, Poisson's ratio, modulus of elasticity, and coefficient of expansion.

(2) Unsteady State (h Constant)

This case has received the most attention in the literature and is the simplest condition which approximates many practical cases. By combining known analytical solutions for temperature and stress distribution, thermal stresses can be

(n) K. Tabata and T. Moriya, "Thermal Endurance of Glass," *J. Am. Ceram. Soc.*, 17 [2] 34-37 (1934).

(o) F. W. Preston, "Theory of Spalling," *J. Am. Ceram. Soc.*, 16 [3] 131-33 (1933); "Spalling of Bricks," *ibid.*, 9 [10] 654-58 (1926).

(p) C. E. Gould and W. M. Hampton, "Thermal Endurance of Glass," *J. Soc. Glass Technol.*, 14 [54] 188-204 (1930); *Ceram. Abstr.*, 9 [10] 830 (1930).

(q) W. G. Lidman and A. R. Bobrowsky, "Correlation of Physical Properties of Ceramic Materials with Resistance to Fracture by Thermal Shock," *Natl. Advisory Comm. Aeronaut. Tech. Note No. 1918* (1949), 15 pp.; *Ceram. Abstr.*, 1952, January, p. 6j.

(r) T. W. Howie, "Spalling of Silica Bricks," *Trans. Brit. Ceram. Soc.*, 45 [2] 45-69 (1946); *Ceram. Abstr.*, 1946, November, p. 195.

(s) R. A. Heindl, "Study of Sagger Clays and Sagger Bodies," *J. Research Natl. Bur. Stand.*, 15 [3] 225-70 (1935); *Ceram. Abstr.*, 15 [1] 23 (1936).

(t) J. F. Hyslop, "Refractories and Thermal Shock," *Trans. Brit. Ceram. Soc.*, 38 [5] 304-12 (1939); *Ceram. Abstr.*, 18 [11] 302 (1939).

(u) A. T. Green and A. J. Dale, "Spalling of Refractory Materials," *Trans. Brit. Ceram. Soc.*, 25 [4] 428-68 (1925); *Ceram. Abstr.*, 6 [10] 445 (1927).

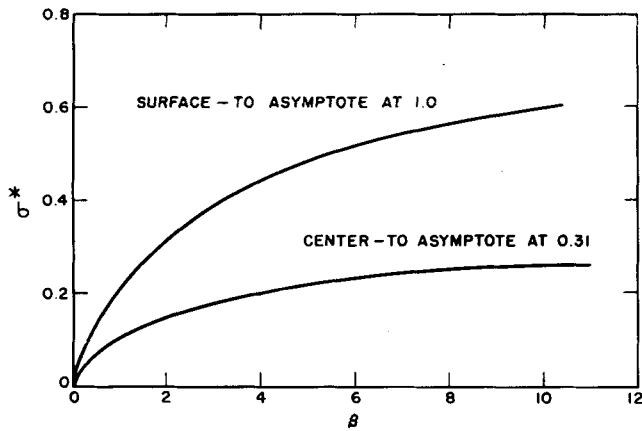


Fig. 6. Variation of dimensionless stress with relative heat transfer rate for an infinite flat plate (footnote 13(f)).

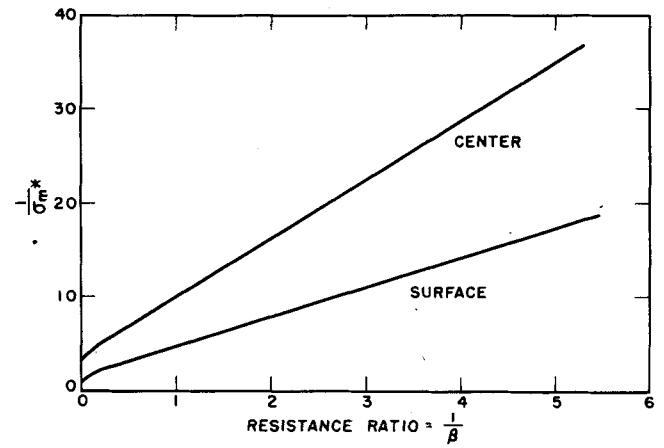


Fig. 8. Variation of $1/\sigma_{\max}^*$ with $1/\beta$ for an infinite flat plate (footnote 13(g)).

evaluated as a function of time, coordinates and heat transfer conditions in terms of dimensionless parameters. If stress is plotted as a function of time for different heat transfer conditions, a plot such as Fig. 5 is obtained. Similar curves can be obtained for the center stresses. From the analytical relations or curves such as those shown in Fig. 5, the maximum stress and time to maximum stress can be determined (Figs. 6 through 8).

In view of the complexity of the analytical relations, a number of authors have proposed approximation formulas for the relationship of maximum stress and rate of heat transfer. For relatively low values of β (which are of major importance for gas convection and radiation cooling) the following relationships have been suggested for the surface stress:

Bradshaw:^{13(f)}

$$\frac{1}{\sigma_{\max}^*} \cong \frac{4}{\beta} \quad (16)$$

Buessem:^{13(h)}

$$\frac{1}{\sigma_{\max}^*} \cong 1 + \frac{4}{\beta} \quad (17)$$

Cheng:^{13(p)}

$$\frac{1}{\sigma_{\max}^*} \cong \frac{3}{\beta} \quad (18)$$

Manson:^{13(e)}

$$\frac{1}{\sigma_{\max}^*} \cong \frac{3.25}{\beta} \quad (19)$$

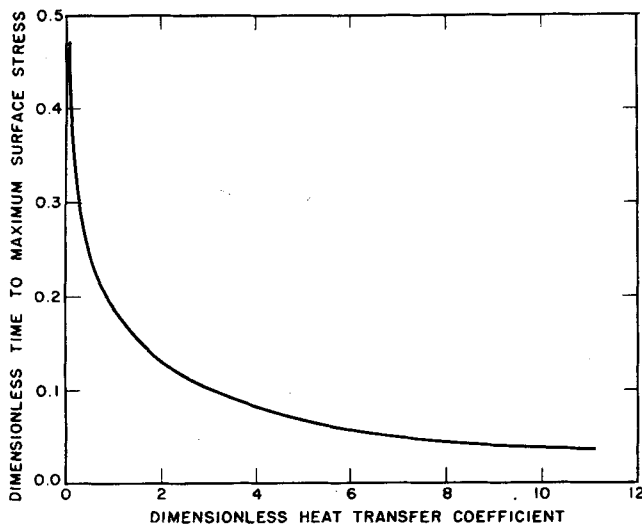


Fig. 7. Variation of dimensionless time to maximum surface stress with relative heat transfer rate.

In this condition, taking the simplest relationship, that $\sigma_{\max}^* = (\text{constant}) \beta$, the thermal stress resistance can be evaluated as

$$\frac{s_t(1-\mu)}{E\alpha(t_0-t')} = (\text{constant}) \frac{r_m h}{k} \quad (20)$$

$$(t_0 - t') = \frac{k s_t(1-\mu)}{E\alpha} \left[\frac{1}{(\text{constant}) (r_m h)} \right] \quad (21)$$

Defining a second thermal stress resistance factor

$$R' = \frac{k s_t(1-\mu)}{E\alpha} \quad (22)$$

and including the constant from equation (21) in the shape factor

$$\Delta t_f = R' \cdot S \cdot \frac{1}{h} \quad (23)$$

The thermal stress resistance factor for this case includes the thermal conductivity, k , in addition to μ , E , α , and s_t .

Over a wider range of heat transfer rates, analytical solutions have been obtained by Cheng and various approximations have been suggested. Approximation formulas have been suggested by Buessem and Manson. As the rate of heat transfer increases, the problem degrades into the case of infinite h , which was treated previously.

Another problem is the temperature at which to evaluate

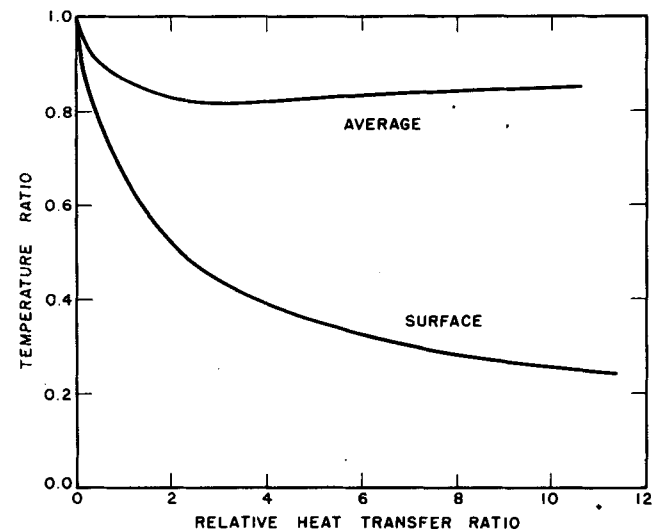


Fig. 9. Relative average and surface temperatures at time of maximum stress under various heat transfer ratios (footnote 13(e)).

the material properties involved. In Fig. 9, the average and surface temperatures at time of maximum stress are quite high, particularly for the low values of β . Consequently, values of temperature-dependent properties should usually be selected at a relative temperature of 0.8 to 0.9 rather than at a completely arbitrary mean temperature.

This analysis of thermal resistance indicates that at least two thermal resistance factors must be considered (as has been emphasized by Buessem, Bradshaw, and others). For high rates of heat transfer, the thermal resistance is proportional to $s_i(1 - \mu)/E\alpha$. At low rates of heat transfer, the thermal resistance is proportional to $ks_i(1 - \mu)/E\alpha$. No single thermal resistance factor can adequately characterize a material for various conditions.

(3) Steady State

Steady nonlinear temperature gradients give rise to thermal stresses which may be sufficient to cause thermal stress failure. The steady state temperature distribution depends on the thermal conductivity and on the rate of heat flow per unit area,

$$\frac{dt}{dx} = -\frac{q}{kA} \quad (24)$$

For any given sample, if S is a shape factor and Δt is the overall temperature difference,

$$q = -kS \Delta t \quad (25)$$

and the conditions can be uniquely defined by specifying either the heat flow or the temperature difference. For an infinite hollow cylinder with an interior heat source, the temperature distribution is logarithmic and the tensile stress at the outer surface is given by

$$\sigma = \frac{E\alpha \Delta t}{(1 - \mu)} \cdot \frac{\left(1 - \frac{2r_1^2}{r_2 - r_1} \ln \frac{r_2}{r_1}\right)}{2 \ln \frac{r_2}{r_1}} \quad (26)$$

and the maximum temperature difference is

$$\Delta t_f = \frac{s_i(1 - \mu)}{E\alpha} \cdot \frac{2 \ln \frac{r_2}{r_1}}{1 - \frac{2r_1^2}{r_2^2 - r_1^2} \ln \frac{r_2}{r_1}} = R \cdot S \quad (27)$$

for radial heat flow,

$$q = \frac{2\pi k \Delta t}{\ln \frac{r_2}{r_1}}$$

and at fracture,

$$q_{\max} = \frac{ks_i(1 - \mu)}{E\alpha} \cdot \frac{4\pi}{1 - \frac{2r_1^2}{r_2^2 - r_1^2} \ln \frac{r_2}{r_1}} = R' \cdot S \quad (28)$$

Since the possible heat flow at steady state is usually the factor of interest, the resistance factor, R' (including the thermal conductivity), is the one of interest. For some applications, the temperature difference may be of more interest, and in this case the factor R (excluding thermal conductivity) is of importance.

(4) Constant Rate of Heating or Cooling

When a furnace is heated or cooled at a constant rate, the effective value of h changes with temperature. In this case, the temperature gradients and stress depend on the rate of cooling, and if the constant rate of surface temperature change is $\phi^\circ\text{C. per second}$, the stress for a plane slab is

$$\sigma = \frac{E\alpha}{(1 - \mu)} \cdot \frac{\phi r_m^2}{3a} \quad (\text{surface}) \quad (29)$$

$$\sigma = \frac{E\alpha}{(1 - \mu)} \cdot \frac{\phi r_m^2}{6a} \quad (\text{center}) \quad (30)$$

The maximum rate of temperature change without fracture, if S is a shape and size factor, is

$$\phi_{\max} = \frac{s_i(1 - \mu)a}{E\alpha} \cdot S = R'' \cdot S \quad (31)$$

Consequently, under these conditions a third resistance factor involving material properties must be considered, which includes the thermal diffusivity.

(5) Properties Determining Thermal Stress Resistance

Consideration of three specific cases of heat-transfer conditions leads to three "resistance" factors which apply to different conditions. Other specific cases might require additional material factors. For example, under conditions of cooling by radiation, the emissivity of the surface would affect the rate of cooling, and consequently the thermal stresses. In addition, the equivalent equations for shear may apply to some cases of heating and a shape or size factor must be employed for applications to specific bodies. Consequently, it is not possible to list a single factor called "resistance to thermal stresses" as a material property such as density or coefficient of expansion. Instead, the conditions and specimen shape employed may markedly change the results found. The properties which affect thermal stress resistance are elasticity, strength, coefficient of expansion, Poisson's ratio, and, in some cases, thermal conductivity, diffusivity, or emissivity.

It should be emphasized that the results here apply exactly only to a homogeneous isotropic body whose physical properties are substantially independent of temperature. Deviations should be expected for materials with sharply temperature-dependent properties, or nonhomogeneous materials such as refractory brick containing significant amounts of grog or metal-ceramic composites.

(6) Thermal Spalling

Thus far only the stress required to initiate a fracture has been considered. An additional problem is whether propagation of the fracture with consequent spalling will follow. Once a crack begins, the stress distribution is drastically altered and mathematical analysis is not feasible.

Griffith's criterion for crack propagation¹⁴ is that the strain energy released must be equal to, or greater than, the surface energy of the new surfaces formed. Consequently, it can be expected that the spall formed will release the maximum strain energy.^{13(a)} For an infinite slab with temperature distributions such as shown in Fig. 4, the strain energy in a unit volume is given by

$$u = \frac{\sigma^2(1 - \mu)}{E} \quad (32)$$

and it would be expected that the depth of the spall should be proportional to $E/(1 - \mu)\sigma^2$. Since the residual temperature gradient in the spalled piece will be nearly linear, essentially all its strain energy will be removed on spalling. Consideration of strain energy as a criterion of spalling leads to the same stress resistance factors as does consideration of the stresses required to initiate fracture. If the necessary depth of spall is large enough, the initial crack may not propagate to this depth and surface checking without spalling can result.

Calculation of strain energy release as a function of time and depth is not difficult. The effect of cracks altering the stress distribution and the essentially similar results from calculation of maximum stress make the general usefulness of quantitative strain energy calculations questionable.

¹⁴ A. A. Griffith, "Phenomena of Rupture and Flow in Solids," *Phil. Trans. Roy. Soc.*, **A221**, 163 (1920).

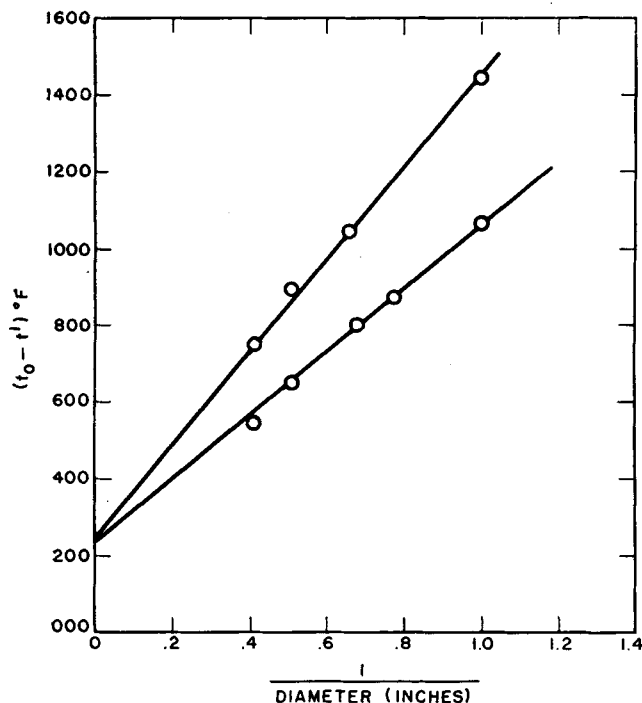


Fig. 10. Effect of specimen size on thermal stress resistance of steatite quenched by air or water blast (footnote 13(e)).

All the previous calculations of resistance to thermal stress have assumed a homogeneous body and have determined when the maximum thermal stress will be equal to the breaking strength. In practice, however, particularly under conditions of thermal shock tests, the minimum thermal stress required to cause surface checking will not fracture a normal ceramic body. In a quenching test, the maximum stress at the surface decreases rapidly and is much higher than the stress at the interior points so that the crack does not continue to fracture. In subsequent tests, these surface cracks act as stress-concentrators and the actual stress is probably too complex to calculate. We would expect that additional thermal cycles of the same magnitude as required to initiate surface cracks would lead to eventual fracture and spalling, but this may not always be true.

As far as we are aware, the only measurements reported for the depth of thermal stress fractures are those of Howie for silica brick.^{13(c)} His data are in good agreement with results predicted from considerations of maximum strain energy.

VI. Factors Affecting Thermal Stress Resistance

Although the general theory of thermal stress resistance which we have outlined seems quite satisfactory, it depends on various material properties and on simplifying assumptions. Differences in material properties and deviations from the

Table II. Temperature Differences Between Surface and Center of Various Shapes Cooled at a Constant Rate
 $\phi = dt/d\theta$

Shape	$t_c - t_s$
Infinite plate, half thickness = r_m	$0.50 \frac{\phi r_m^2}{a}$
Infinite cylinder, radius = r_m	$0.25 \frac{\phi r_m^2}{a}$
Cylinder, half length = radius = r_m	$0.201 \frac{\phi r_m^2}{a}$
Cube, half thickness = r_m	$0.221 \frac{\phi r_m^2}{a}$

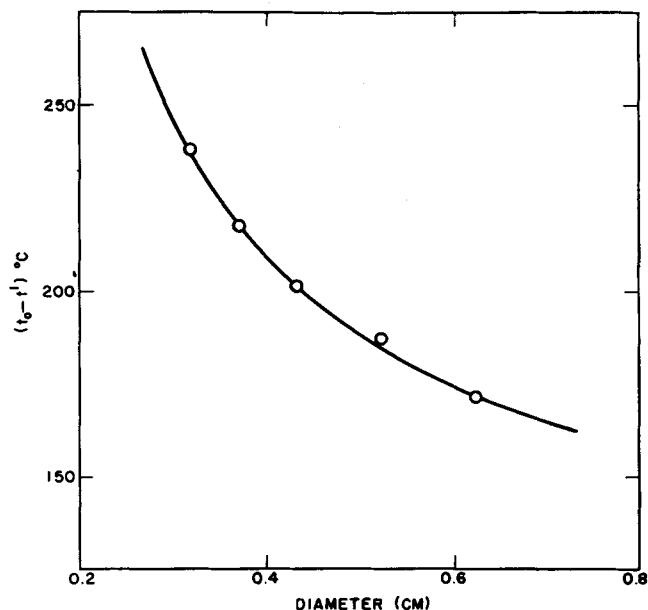


Fig. 11. Effect of rod diameter on thermal stress resistance of glass rods quenched in water bath (footnote 13(n)).

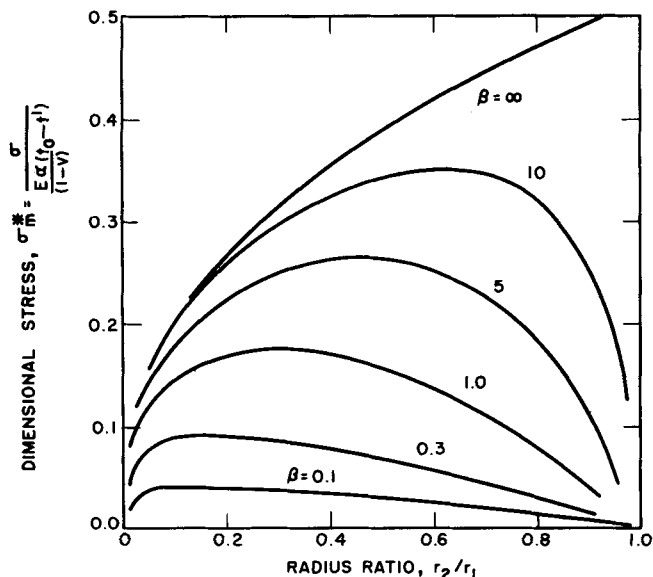


Fig. 12. Variation of surface stress (r_2) for hollow cylinder where outer radius is maintained at constant temperature, t' (footnote 13(f)).

simplifying assumptions must be considered in any practical applications.

(1) Specimen Size and Shape^{13(c)-(h)(n),15}

Neglecting end effects for a moment, the major effect of increased size is to increase the nondimensional heat-transfer parameter, $\beta = r_m h/k$. When the specimen size is sufficiently large, conditions approach the case where the surface temperature is altered without changing the mean body temperature, the thermal stress resistance is substantially inde-

¹⁵ (a) O. H. Clark, "Resistance of Glass to Thermal Stresses," *J. Am. Ceram. Soc.*, **29** [5] 133-38 (1946).

(b) J. B. Murgatroyd, "Effect of Shape on Thermal Endurance of Glass Rods," *J. Soc. Glass Technol.*, **27** [119] 5-17T (1943); *Ceram. Abstr.*, **22** [10] 170 (1943); "Effect of Shape on Thermal Endurance of Cylindrical Glass Containers," *J. Soc. Glass Technol.*, **27** [121] 77-93T (1943); *Ceram. Abstr.*, **23** [1] 8 (1944).

(c) M. D. Karkhanavala and S. R. Scholes, "Relation Between Diameter and Thermal Endurance of Glass Rods," *J. Soc. Glass Technol.*, **35** [167] 289-303T (1951); *Ceram. Abstr.*, 1952, September, p. 158i.

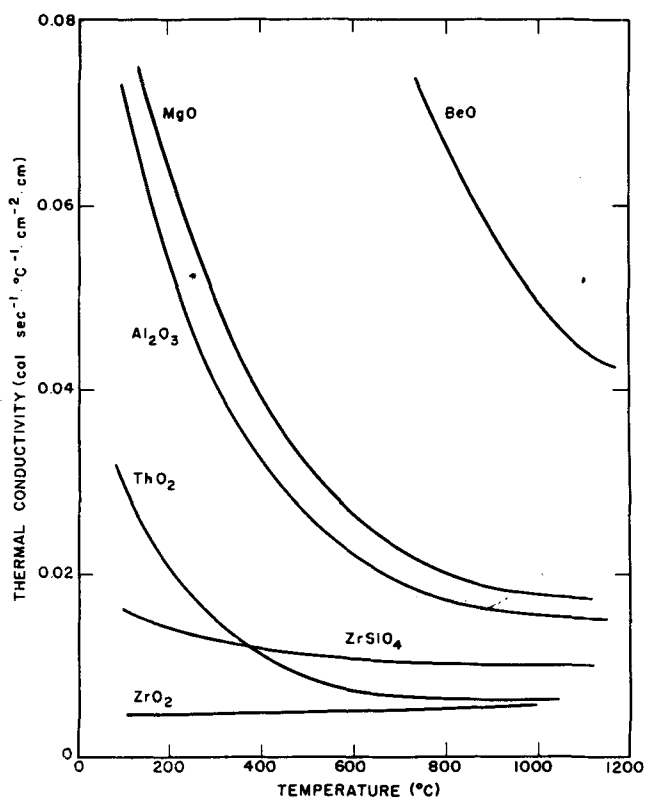


Fig. 13. Thermal conductivity of some ceramic materials.

pendent of h and k , and $\sigma_{\max}^* = 1$. Conversely, for very small specimens, even very high rates of cooling will not approach the case where $\sigma_{\max}^* = 1$. For moderate rates of temperature change, the thermal stress is approximately proportional to $r_m h/k$, and consequently thermal stress resistance is inversely proportional to specimen dimensions. Data of Manson^{13(e)} for steatite (Fig. 10) follow this relationship. For very high rates of cooling, the relationship is more complex. Data for glass rods quenched in water¹³⁽ⁿ⁾ indicate that the size effect becomes important for rod diameters below 6 to 8 mm. (Fig. 11). For the steady state, the temperature drop for a given heat flow is directly proportional to wall thickness and increased thermal stresses occur. If, however, the temperature drop (rather than heat flow) is maintained constant, no stress increase results.

In addition to the size factor, the shape is also of importance, as has been indicated by the inclusion of a general shape factor, S , in the equations for thermal stress resistance. The effect of shape for stress calculation is shown in Table I. A pronounced case is unsteady-state heat flow in hollow cylinders, as occurs in rocket nozzles. The nondimensional stress for heating the interior of a hollow cylinder with different radius ratios is shown in Fig. 12, for various rates of heat transfer in the limiting case after an infinite time.^{13(f)} The maxima are roughly on a line where $\sigma^* = 1/2 r_1/r_2$ (where $r_1 < r_2$). Similarly, the maximum temperature differences for a few shapes cooled at a constant rate of temperature change are shown in Table II. These variations give rise to considerable changes in thermal stresses.

Another important effect which is more difficult to assess is the presence of edges and corners in finite slabs, cylinders, wedges, and other shapes. For simple shapes, these can be estimated from elastic theory. Kent^{13(c)} has estimated the stresses for long thin-walled cylinders and finds an increase of about 30% in tangential stress at the ends as compared to an infinite cylinder. Baroody *et al.*^{13(d)} have made some experimental measurements for this case. Lighthill and Bradshaw¹³⁽ⁱ⁾ considered the stresses in a wedge, and found that, on

Table III. Values of Surface Heat-Transfer Coefficient, h

Conditions	h (B.t.u. hr. ⁻¹ °F. ⁻¹ ft. ⁻²)	h (cal. sec. ⁻¹ °C. ⁻¹ cm. ⁻²)
Air flow past cylinder:		
Flow rate 60 lb. sec. ⁻¹ ft. ⁻²	190	0.026
Flow rate 25 lb. sec. ⁻¹ ft. ⁻²	90	.012
Flow rate 2.5 lb. sec. ⁻¹ ft. ⁻²	20	.0027
Flow rate 0.025 lb. sec. ⁻¹ ft. ⁻²	2	.00027
Radiation to 0°C. from 1000°C.	26.0	.0035
Radiation to 0°C. from 500°C.	7.0	.00095
Water quenching	1000–10,000	.1–1.0
Jet turbine blades	35–150	.005–0.02 (Cheng, Bradshaw)

heating, the largest initial stresses were at the edge, but the maximum stress occurred at the thickest portion on both heating and cooling. Norton⁴ studied the stresses developed in brick shapes with the use of polarized light. In general, experimental measurements of this type are probably the best method for studying complex shapes. Many cases, such as built-up walls, or cylinders and slabs where the ends are not maintained at the same temperature difference as the central portion, can be satisfactorily treated as infinite bodies.

(2) Heat-Flow Properties^{9,10,11,13(e)–(h),16}

The rate of heating or cooling is an important factor in the development of thermal stresses and is affected both by the conditions imposed and by the physical properties of the material concerned.

Measurements of the heat transfer coefficient, h , which are available are largely for steady-state heat exchange. Few measurements under transient conditions are available. Some values which seem representative are given in Table III. As far as the author is aware, no measurements are available for conditions such as occur in jet engines and other current applications. Measurements at steady state are not directly applicable since surface heat transfer coefficients vary considerably with the film temperature when heat transfer is mainly by convection. Measurements of β can be obtained by determining the rate of change of temperature of any point, or the simultaneous temperature of several points. By analytical equations, or more simply by comparison with plotted or tabulated solutions, relative values of α and β can be determined for the specific conditions employed. If k and c_p are known, the surface heat transfer coefficient, h , can be determined. Materials of known and constant (with temperature) k and c_p should be employed.

The assumption that h remains constant, which is taken for most thermal stress calculations, is only an approximation for most practical cases, and can be expected to hold closely only

¹⁶ (a) W. D. Kingery, J. Franci, R. L. Coble, and T. Vasilos, "Thermal Conductivity: X, Data for Several Pure Oxide Materials Corrected to Zero Porosity," *J. Am. Ceram. Soc.*, **37** [2, Part II], 107–10 (1954).

(b) M. C. Booz and S. M. Phelps, "Study of Factors Involved in Spalling of Fire-Clay Refractories with Some Notes on Load and Reheating Tests and Effect of Grind on Shrinkage," *J. Am. Ceram. Soc.*, **8** [6] 361–82 (1925).

(c) A. R. Bobrowsky, "Applicability of Ceramics and Ceramals as Turbine-Blade Materials for the Newer Aircraft Power Plants," *Trans. Am. Soc. Mech. Engrs.*, **71** [6] 621–29 (1949); *Ceram. Abstr.*, **1951**, February, p. 28f.

(d) F. G. Code Holland, "Ceramics and Glass: I, Use of Ceramic Coatings in Gas Turbine Combination Chambers," *Selected Govt. Research Repts.*, **10**, 1–7 (1952); *Ceram. Abstr.*, **1953**, April, 56j.

(e) D. G. Moore, S. G. Benner, and W. N. Harrison, "Studies of High-Temperature Protection of a Titanium-Carbide Ceram by Chromium-Type Ceramic-Metal Coatings," *Natl. Advisory Comm. Aeronautics Tech. Note No. 2386* (1951), 26 pp.

(f) F. H. Norton, *Refractories*, 3d edition, McGraw-Hill Book Co., Inc., New York, 1951. 782 pp.

Table IV. Thermal Conductivity of Ceramic Materials*

Material	k (cal. sec. ⁻¹ °C. ⁻¹ cm. ⁻² cm.)		
	100°C.	400°C.	1000°C.
Al ₂ O ₃	0.072	0.031	0.015
BeO	.525	.222	.049
Graphite	.426	.268	.149
MgO	.086	.039	.017
Mullite	.015	.011	.010
Spinel	.036	.024	.014
ThO ₂	.025	.014	.008
Zircon	(.016)	.012	.010
ZrO ₂ (stabilized)	.0047	.0049	.0055
Fused quartz	.0038	.0045	
Soda-lime-silica glass	.0040	.0046	
TiC	.060	.032	.014
Porcelain	.0041	.0042	.0045
Fire-clay refractory	.0027	.0029	.0037
TiC cermet	.083	(.04)	(.02)

* Data for crystalline materials are for theoretical density. Values in parentheses are estimated.

Table V. Mean Coefficient of Linear Expansion for Some Ceramic Materials (30° to 1000°C.)

Material	$\alpha \times 10^{-6}$ (°C. ⁻¹)
Al ₂ O ₃	8.8
BeO	9.0
MgO	13.5
Mullite	5.3
Spinel	7.6
ThO ₂	9.2
Zircon	4.2
ZrO ₂ (stabilized)	10.0
Fused quartz	0.5
Soda-lime-silica glass	9.0
TiC	7.4
Porcelain	6.0
Fire-clay refractory	5.5
TiC cermet	9.0

when $(t_0 - t')$ is small. This is a reasonable approximation for glasses and ceramic bodies having relatively poor thermal stress resistance; it is probably poor for the better materials and for more rigorous applications such as jet engines and refractory furnaces. Other important cases are where the surface temperature changes linearly (as in the controlled heating or cooling of a furnace, or as an approximation to more complex conditions), and where the heat transfer is proportional to $(t_0^4 - t'^4)$ as in radiant heat transfer.

Another factor which complicates the picture and has been essentially neglected in analytical calculations is changes in c_p and k with temperature. A sharp change in heat capacity changes the temperature distribution and, consequently, the stresses considerably in the transient state. Although such changes are not usual in ceramic materials, a sharp decrease in the thermal conductivity of dense crystalline ceramics does normally occur as shown in Fig. 13. BeO changes by a factor of ten between 100° and 1000°C., whereas MgO and Al₂O₃ change by a factor of six. Data for the thermal conductivity of a number of ceramic materials are given in Table IV. It might be noted that many measurements of conductivity given in the literature are not satisfactory. In addition, the changes in conductivity with temperature make results calculated from room-temperature values most doubtful. At room temperature, the variation between materials amounts to a factor of 100; at 1000°C. the variation is decreased to a factor of 10. For glasses and fire-clay refractories, the variation between roughly similar compositions is not large, and conductivity is not such an important factor. For pure crystalline materials the porosity and purity become quite important. A few per cent silica in an alumina body may decrease the conductivity to half the value for pure alumina. Similar results are found for a few per cent solid solution.

For stresses arising on cooling, a high thermal conductivity is always desirable. On heating for short time periods, a high conductivity leads to decreased surface compressive and shear stresses, but gives a somewhat increased center tensile stress at short times. If failure occurs due to a center tensile failure and times are short, a low conductivity may be advantageous depending on the time and rate of heating, on relative shear and tensile strengths, and on the relative thermal conductivities. No specific general relations or experimental data are available.

The presence of a glaze or ceramic coating on a surface acts essentially as an additional thermal resistance which decreases the effective cooling or heating rate at the interface. Consequently, even if the coating fractures, it may decrease body stresses by decreasing the intensity of thermal shock. This effect will be additive with any stresses due to the differential expansion of coating and body.

(3) Coefficient of Thermal Expansion^{2,3,4,8(b),13(r)-(u),16(f),17}

For any given temperature distribution, the thermal stresses are directly related to the thermal expansion. Compared with other properties, the expansion coefficient remains relatively constant over the temperature range of interest for homogeneous bodies unless a magnetic or polymorphic transformation occurs (as in silica, zirconia, and some other materials). Consequently, an average expansion coefficient is usually satisfactory. Values for a number of materials are given in Table V. Measurements by well-known methods are not difficult. The expansion coefficient varies considerably for different materials and will be the major factor affecting thermal stresses in most glasses and many refractory and whiteware compositions. Some materials, such as Stupalith, aluminum titanate, and fused silica, have extremely low coefficients of expansion (but may be unsatisfactory for other reasons, such as low strength or poor creep resistance).

For cases where the expansion coefficient changes with temperature (transformation, as for α - β cristobalite) or through the specimen (as for a glazed body), thermal stresses can be determined by taking the product, αt , as the temperature variable. Then, for example, for the surface stress

¹⁷ (a) J. H. McKee and A. M. Adams, "Physical Properties of Extruded and Slip-Cast Zircon with Particular Reference to Thermal Shock Resistance," *Trans. Brit. Ceram. Soc.*, **49**, 386-407 (1950).

(b) R. E. Stark and B. H. Dilks, Jr., "New Lithium Ceramics," *Materials and Methods*, **35** [1] 98-9 (1952).

(c) K. Endell, "Gegen Temperaturänderungen unempfindliche Magnesitsteine" (Magnesite Brick Not Affected by Temperature Changes), *Stahl u. Eisen*, **52** [31] 759-63 (1932); *Ceram. Abstr.*, **11** [12] 616 (1932).

(d) R. A. Heindl, "Thermal Spalling of Fire-Clay Brick in Relation to Young's Modulus of Elasticity, Thermal Expansion, and Strength," *Am. Refractories Inst. Tech. Bull.*, **58** (May 1935); *Ceram. Abstr.*, **15** [7] 210 (1936).

(e) J. J. Gangler, "Some Physical Properties of Eight Refractory Oxides and Carbides," *J. Am. Ceram. Soc.*, **33** [12] 367-74 (1950).

(f) H. R. Goodrich, "Spalling and Loss of Compressive Strength of Fire Brick," *J. Am. Ceram. Soc.*, **10** [10] 784-94 (1927).

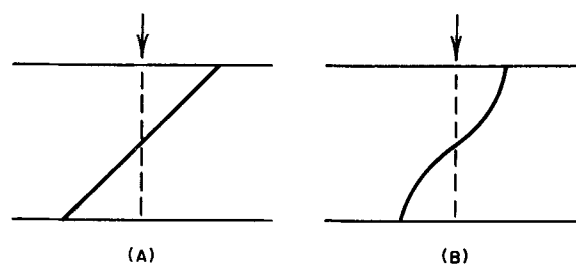


Fig. 14. Deviation from Hooke's law causes actual stress distribution (b) to differ from assumed distribution (a).

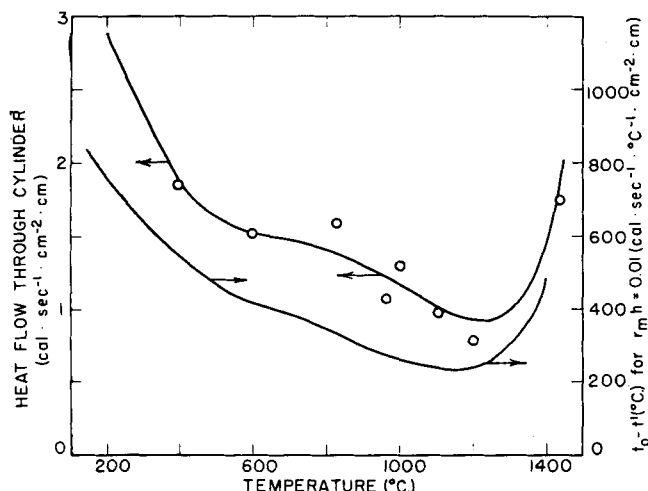


Fig. 15. Variation in thermal stress resistance with the temperature level of testing (data from Schwartz, footnote 13(a)).

$$\sigma = \frac{E}{1\mu} (t_0^\alpha t_a^\beta - t_0^\alpha t_a^\beta) \quad (33)$$

In the case of a glaze or enamel, residual stresses due to unequal cooling contraction of glaze and body will be additive with thermal stresses. These have been considered in equations (1) and (2). These stresses, together with thermal stresses calculated from the temperature distribution and from equation (33), provide a reasonable basis for studying the thermal stress resistance of glazed bodies.

(4) Elastic Properties^{13(a)(g)(u),16(f),17,18}

In the analysis of resistance to thermal stresses, we assumed that the material was perfectly elastic (no plastic or viscous flow) and obeyed Hooke's law up to the breaking stress. For brittle ceramic materials, these assumptions are quite good at low temperatures, and E is almost independent of t at low temperatures. As the temperature increases, there is a decrease in E due to grain-boundary relaxation, and at still higher temperatures, plastic or viscous flow takes place. Measurement of E is possible either in tension or in a bend test. At higher temperatures, where some plastic flow can occur, the stress distribution is different than that assumed as shown in Fig. 14, and a low value of E results. However, in thermal stress calculations, we also assume that Hooke's law applies for stresses similar to those shown in Fig. 15. Consequently, the best approximation for elevated temperatures is probably to employ E measured in bend tests, even though this may not be a true elastic constant.

In tests of commercial refractories, Heindl, Endell, and Norton have all found that the elastic deformation is an important factor which varies considerably between various materials. Experimental data for thermal spalling show a direct relation between thermal endurance and $1/\text{extensibility}$

Table VI. Values of E and μ for Ceramic Materials

Material	E , lb./sq. in. $\times 10^6$			μ
	20°C.	400°C.	1000°C.	20°C.
Al ₂ O ₃	51.0	49.2	45.0	0.20
BcO	44.	40.	30.	0.38
MgO	30.5	30.0	21.0	0.36
Mullite	21.0	19.5	11.0	0.30*
Spinel	34.5	34.3	30.4	0.31
ThO ₂	21. (39.5)	19.	17.	0.17
Zircon	13.6 (30)	13.5	12.7	0.35
ZrO ₂ (stabilized)	21.5 (26)	20.1	19.9	0.29
Fused quartz	10.5	10.9		0.15
Soda-lime-silica glass	9.5	9.5		0.20
TiC	45.	45.	40*	0.30*
Porcelain	10.	9.	6.	0.30*
Fire-clay refractory	2.5	2.3	0.5	0.30*
TiC cermet	60.	60.	55.	0.30*

* Estimated

(= E/s , where the extensibility = s/E or the strain to fracture).

Poisson's ratio, μ , which enters into the equation for thermal stress resistance, is relatively constant between materials (varying between 0.18 and 0.35) and with temperature. At higher temperatures, the measured value of μ decreases. The only case for which a very marked variation of μ is found is for anisometric materials, such as impregnated glass fiber compositions. This may become important if oriented ceramic compositions become available. Some typical values of E and μ for ceramic materials are given in Table VI.

The effect of ductility or plastic flow at elevated temperatures is known to be considerable. Numerous experiments have shown that at temperatures where ceramic materials show plastic or viscous flow, thermal stress failure is negligible. The stress resistance of some cermet bodies may be due in part to the development of some ductility at use temperatures.

(5) Strength^{13(a)(g)(u),14,15(a),16(f),17,18,19}

On cooling, the most dangerous thermal stresses are tensile; on heating, either shear or tensile stresses may be most dangerous. Since the compressive strength of ceramics is four to eight times the tensile strength, failure from compressive stresses is unimportant. Tensile strength may be measured in tensile tests, in bending tests, or in torsional tests. In tensile tests, unless extreme precautions are taken, failure may occur due to stress concentration in the grips or with additive stresses due to poor specimen alignment, which is most difficult to avoid for brittle ceramics. In bending and torsion tests (in which ceramic materials always fail in tension), the actual and theoretical stress distributions differ from materials which do not follow Hooke's law, as in Fig. 14. Consequently, the measured strengths are higher than actual strengths. In addition, the different volumes of specimen under stress may affect strength due to the probability of a flaw being present in a greater volume. These factors combine to give higher values to tensile strength measured in torsion and bend tests than that measured in tensile tests (variations from 1:1 to 3:1 are found). For thermal stress applications, the greater similarity of stress distribution in bending and torsion tests to that occurring due to temperature gradients, and the relatively greater freedom from stress concentration and alignment effects make these methods of measurement preferable.

Other complicating effects are the possibility of delayed

¹³ (a) E. Endell and F. Angeleri, "Torsion Properties of Stakolumite (Flexible Brazilian Sandstone), Crummendorf Quarzschist, and Some Sandstones," *Ber. deut. Keram. Ges.*, **19**, 359 (1938).

(b) R. A. Heindl and L. E. Mong, "Young's Modulus of Elasticity, Strength, and Extensibility of Refractories in Tension," *J. Research Natl. Bur. Stand.*, **17** [3] 463-82 (1936); RP 923; *Ceram. Abstr.*, **16** [1] 24 (1937).

(c) R. A. Heindl and W. L. Pendergast, "Deformation and Young's Modulus of Fire-Clay Brick in Flexure at 1220°C.," *J. Research Natl. Bur. Stand.*, **19**, 353-66 (1937); *Ceram. Abstr.*, **17** [1] 19 (1938).

(d) R. A. Heindl and W. L. Pendergast, "Progress Report on Investigation of Fire-Clay Brick and Clays Used in Their Preparation," *J. Am. Ceram. Soc.*, **12** [10] 640-75 (1929).

¹⁹ (a) H. S. Roberts, "Cooling of Optical Glass Melts," *J. Am. Ceram. Soc.*, **2** [7] 543-63 (1919).

(b) F. W. Preston, "Study of Rupture of Glass," *J. Soc. Glass Technol.*, **10** [39] 234-69 (1926); *Ceram. Abstr.*, **13** [3] 57 (1934).

(c) J. B. Murgatroyd, "Strength of Glass," *J. Soc. Glass Technol.*, **17** [67] 260 (1933); *Ceram. Abstr.*, **13** [3] 57 (1934).

fracture, which has been thoroughly investigated for glasses, but not for other ceramics, and the effects of surfaces. Breaking strength of glasses depends on the time of loading due to atmospheric contamination of the fracture surfaces. There has been some suggestion that time of loading may also affect dense Al_2O_3 , but the effect has not been unequivocally demonstrated. For ceramic bodies containing a considerable amount of glassy phase, the effect may be considerable. The strength for stresses at the interior of a specimen may be considerably higher than for the stresses at a surface. Consequently, the quantitative application of measured tensile strengths to center stresses is questionable.

Measurements of true shear strengths are difficult and, in general, not available. Failure in compressive tests always occurs in shear, so that the shear strength may be, in general, taken as two to four times the tensile strength. As far as the author is aware, it is always equal to or greater than the tensile strength for ceramic materials.

In general, the highest strength values are found for dense crystalline ceramics and some of the cermet materials. Strength of fire-clay refractories varies considerably, being increased by harder firing and lower porosity, whereas the tensile strength of usual glass compositions does not vary widely with composition, but may be increased considerably by suitable surface treatment. In general, materials of high strength also have high values of elastic moduli, so that firing to increase strength may not improve the ratio s_t/E which is of importance for thermal stress resistance. Values of ultimate strength for some ceramic materials are given in Table VII. As seen there, the variation between materials is considerable.

In some cases, improvements in strengths for thermal stress applications have been obtained by prestressing. The normal thermal shock resistance of tempered glass is considerably greater than annealed glass due to compressive stresses developed on the surface. The maximum quenching temperature of one glass was decreased from 145° to 120°C . by annealing. On heating, however, where compressive stresses arise, the maximum Δt_f was increased from 426° to 477°C . by annealing.²⁰ Development of prestressing by glazes has been considered previously. A study of prestressing by flame spraying a metal coating on ceramics gave encouraging results in certain cases.²¹ For any of these prestressing techniques, the possibility of stress relaxation in use must be considered.

In actual designs, the stress distribution may differ considerably from that calculated, giving lower effective strengths due to stress concentration or restraints in the design or to the effects of erosion or corrosion in use.

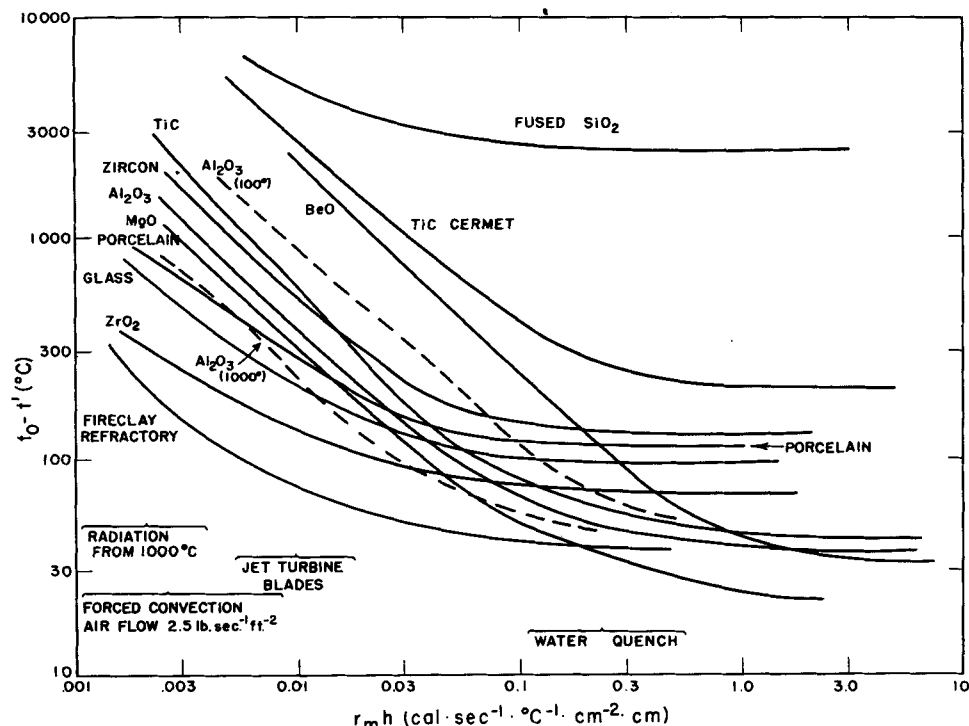


Fig. 16. Variation in maximum quenching temperature with different rates of heat transfer. (Calculated from material properties at 400°C . Dashed curves for Al_2O_3 calculated from material properties at 100° and 1000°C .)

(6) Combined Effect of Material Properties

The resistance of materials to thermal stresses generally depends on the factors $[s_t(1 - \mu)/E\alpha]$ and $[ks_t(1 - \mu)/E\alpha]$ and no one material property or condition can be taken as a uniform criterion. In general, composition changes which give rise to high strengths also increase E , so that the ratio s_t/E should be considered instead of either factor alone. The "extensibility" or maximum strain to fracture may vary considerably, and individual factors affecting it have not been analyzed separately. In general, it is low for underfired and overfired brick, but factors such as crystal development, glass formation, and porosity have not been separately investigated. Thermal conductivity and the coefficient of expansion vary considerably for different materials and have a considerable effect on thermal stress resistance. In particular, the almost direct relationship between silica content and spalling resistance of firebrick is due to increased expansion.

The temperature level of thermal stress tests may have a considerable effect even though individual material properties do not change markedly. The increase in α and decrease in s_t and k with temperature generally gives a lowering of R and R' at higher temperatures. At still higher temperatures,

Table VII. Strength of Ceramic Materials

Material	20°C .	400°C .	1000°C .
Al_2O_3	21,000	20,000	20,000
BeO	21,000	10,000	6,000
MgO	14,000	15,000	11,500
Mullite	12,000	10,000	7,000
Spinel	12,300	12,200	10,900
ThO_2	12,000	10,000	7,000
Zircon	12,000	10,000	6,000
ZrO_2 (stabilized)	20,000	17,500	14,800
Fused quartz	15,500	15,500	
Soda-lime-silica glass	10,000	10,000	
TiC	20,000	19,000	17,000
Porcelain	10,000	8,000	6,000
Fire-clay refractory	750	750	700
TiC cermet	160,000	155,000	140,000

²⁰ R. W. Douglas, "Thermal Endurance of Glass Articles," *J. Soc. Glass Technol.*, 20 [81] 517-23T (1936); *Ceram. Abstr.*, 17 [4] 139 (1938).

²¹ J. H. Westbrook, "Thermal Shock Resistance of Metallized Ceramics," Sc.D. Thesis, Department of Metallurgy, M. I. T. (1949).

Table VIII. Thermal Stress Resistance Factors for Some Ceramic Materials*

Material	100°C.		400°C.		1000°C.	
	R	R'	R	R'	R	R'
	(°C.)	(cal. sec. ⁻¹ cm. ⁻¹)				
Al ₂ O ₃	37	2.7	36	1.1	40	0.60
BeO	33	17.3	31	6.9	14	0.69
MgO	22	1.9	24	0.94	26	0.45
Mullite	75	1.1	68	0.75	84	0.84
Spinel	32	1.15	32	0.77	32	0.45
ThO ₂	51	1.3	47	0.66	37	0.30
Zircon	137	(2.2)	115	1.4	73	0.73
ZrO ₂ (stabilized)	66	0.31	62	0.30	53	0.29
Fused silica	2500	9.5	2400	10.1		
Soda-lime-silica glass	94	0.38	94	0.43		
TiC	42	2.5	40	1.3	(40)	0.56
Porcelain	116	0.48	103	0.43	116	0.52
Fire-clay refractory	38	0.14	41	0.14	178	0.48
TiC cermet	208	(17.3)	200	(8)	198	(4)

* Values in parenthesis are estimated.

the decrease in E and development of plasticity cause a sharp increase in thermal stress resistance. In Table VIII, thermal stress resistance factors are calculated for a number of ceramic materials, and in Fig. 15 the measured and calculated change of thermal stress resistance with temperature is shown.

The necessity for two thermal stress-resistance factors depending on the rate of heat transfer is shown in Fig. 16, where the fracture temperature of several materials is plotted as a function of the surface heat transfer parameter. At low rates of heat transfer, the thermal conductivity is of considerable importance, whereas at high rates of heat transfer it becomes unimportant. Consequently, the order of thermal shock resistance of ceramic materials varies depending on the heat-transfer conditions. It is apparent that no one factor or listing of ceramics can be satisfactory as a "thermal endurance" index.

VII. Test Methods for Thermal Stress Resistance

A large variety of thermal stress tests have been employed in the past. They can be classified according to the method of establishing temperature gradients and by the method of assessing thermal stress resistance. Temperature gradients have been established by cyclic heating and cooling,^{13(a), 22} by a single rapid heating or cooling,^{2, 13(c)(n), 15(c), 23} and by the establishment of steady-state thermal stresses.^{13(a)(d)(h)(r)}

²² (a) R. A. Heindl and W. L. Pendergast, "Panel Tests for Thermal Spalling of Fire-Clay Brick Used at High Temperatures," *J. Research Natl. Bur. Stand.*, **34** [1] 73-96 (1945); RP 1630; *Ceram. Abstr.*, **24** [5] 91 (1945).

(b) G. R. Eusner and W. S. Debenham, "Spalling of Fire-Clay Brick," *Bull. Am. Ceram. Soc.*, **31** [12] 489 (1952).

(c) C. W. Parmelee and A. E. R. Westman, "Effect of Thermal Shock on Transverse Strength of Fire-Clay Brick," *J. Am. Ceram. Soc.*, **11** [12] 884-95 (1928).

(d) A.S.T.M. Designation C-38-49, "Basic Procedure in Panel Spalling Test for Refractory Brick," A.S.T.M. Comm. C-8, 1952.

²³ (a) W. Steger, "Die Widerstandsfähigkeit feuerfester Baustoffe gegen Temperaturwechsel," *Stahl u. Eisen*, **45**, 249 (1925).

(b) A. C. Elliot and R. J. Montgomery, "New Type of Thermal Shock," *J. Can. Ceram. Soc.*, **6**, 44-48 (1937); *Ceram. Abstr.*, **17** [1] 20 (1938).

(c) R. A. Heindl, "Comparative Tests for Determining Resistance of Fire-Clay Brick to Thermal Spalling," *Proc. A.S.T.M.*, **31** [Part II] 703-14 (1931); *Ceram. Abstr.*, **11** [3] 184 (1932).

(d) Private communication from H. F. G. Ueltz and N. N. Ault, 1953.

(e) E. Seddon, "Proposed Standard Thermal Endurance Test Based on Use of Glass Rods. A Report of The Society of Glass Technology," *J. Soc. Glass Technol.*, **20**, 498-510T (1936).

(f) W. M. Hampton, "Thermal Endurance of Glass," *J. Soc. Glass Technol.*, **20** [81] 461-74T (1936); *Ceram. Abstr.*, **17** [4] 139 (1938).

Thermal stress resistance has been measured by loss of weight,^{22(a) (b) (d), 23(a) (b) (c)} decrease in strength,^{17(a), 22(c)} or decrease in elastic properties^{17(a), 23(d)} after a specified treatment, or the severity of treatment necessary to cause a fracture,^{2, 13(a) (d) (e) (n) (q) (r), 15(c), 23(e) (f)} or a specified loss in weight, strength, or elasticity.^{17(a)} The applicability of various tests depends mainly on the testing objective. Tests are generally designed either to give results which correlate well with specific service conditions, to determine the effect of variable properties, or to provide a general index of thermal shock resistance.

The most direct tests are simulated service tests such as the A.S.T.M. panel spalling tests^{22(a) (b) (d)} and water quenching of glassware.^{2, 15(c), 23(e) (f)} The advantage of this type of test is that results can be safely applied to a particular application (except that particular and fairly common service conditions, such as slag penetration in refractories and corrosion or impact failure of turbine blades, may void the practical results of the controlled tests). The major disadvantage is that a new test is necessary for any change in application conditions, and consequently it is an expensive procedure which can usually be justified only when the range of use conditions is well known. In this kind of test, cyclical testing is desirable because it accentuates test results. Ceramic materials may show static fatigue but, in general, show no ill effects from repeated loading below the elastic limit. With measurement of resistance by fracture, weakening, or weight loss, a number of cycles will increase initially small effects.

By employing short-term cyclic tests well above the thermal stress limit, the amount of weight loss can be considerably increased. However, there is no general relation between these results and the results at a lower thermal stress level which might actually be used in service. Variation in material properties and thermal stress conditions may vary the order of merit of different materials under different conditions, and these changes cannot be predicted without a knowledge of the individual factors involved.

Another widely employed test is the use of single thermal shock cycles of increasing severity until fracture occurs, measuring the temperature difference required to cause fracture or a specified decrease in strength or elasticity. In this kind of test, fractures may occur as small surface fissures so that it is essential to examine each specimen carefully for failure after each test. In this regard, decrease in strength and elasticity are helpful, particularly for porous materials or commercial refractories with some surface discontinuities, since surface fissures are difficult to observe. The variation of material properties with the temperature level, and the general lack of heat-transfer data, make general applicability of results to other conditions questionable. For a given temperature range, the order of merit of different materials should be valid.

Tests finding increasing application are steady-state tests of thermal stress failure. In general, the most convenient shape to employ is a hollow cylinder with interior heating. Results from these tests give an easily observable and definite fracture, since a steady stress is employed. The temperature level can be varied, and the effect of various factors affecting stress resistance can be investigated. Together with thermal conductivity data, general results for an order of merit over a range of conditions can be obtained. Due to the generally unknown variation in the factors affecting thermal stress failure under various conditions, results cannot usually be quantitatively applied to a specific application. In the author's opinion, this type of test to determine a general order of merit for a given application, together with a simulated test or trial to determine a quantitative basis for the order of merit, is probably the most fruitful approach to thermal stress testing. Tests with an essentially infinite value for the relative rate of heat transfer may give essentially the same results.

Another approach to thermal stress testing is the separate evaluation of α , E , s , k , and μ at various temperature levels.^{13(a) (e) -(h)} Although these measurements are not

simple, the general agreement between the order of calculated thermal stress resistance and measured values has been reasonably good.

VIII. Methods of Improving Thermal Shock Resistance

One important consideration in many applications is proper design to avoid large thermal stresses. Very often, techniques which avoid stress concentration factors, and designs which avoid restraints and allow for expansion of various parts of the structure, can improve thermal stress resistance. In some designs, the size of component parts can be reduced without loss of utility with a consequent reduction in thermal stresses.

Physical factors can, of course, be controlled to a certain extent. Strength increases are usually accompanied by an increase in the elastic modulus, with a variable resultant change in thermal stress resistance. For some materials, such as certain cermet compositions, the increase in strength may be considerably higher than the increase in E . Very often, a range in firing temperature or density will lead to a maximum value

of s_1/E . The coefficient of expansion can also be controlled to a certain extent. Materials such as fused silica, zircon, SnO_2 , Pyrex-brand glass, and Stupalith with low coefficients of expansion may contribute considerably toward better thermal stress resistance. The thermal conductivity can be improved by increasing density and purity. A few per cent silica in aluminum oxide may decrease the thermal conductivity by half.

The possibility of prestressing ceramic materials also offers an opportunity for increasing thermal stress resistance. Ceramic or metallic coatings,²¹ thermal tempering, and other methods of prestressing are all worthy of further investigation. We were unable to find any reports in the literature of tempered dense ceramic oxides in the plastic range. We have heated some spherical samples of zirconia to 1600°C. and rapidly cooled them in air to develop compressive stresses in the surface. These samples withstood a water quenching Δt_f of 150° to 160°C., compared with 125° to 130°C. for samples which had not been heat-treated.

Thermal Shock Testing

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Practical experience has shown that thermal shock tests do not lead to generally useful test data. This is probably due to the fact that thermal shock failure is a complicated function of the external thermal shock conditions and of the temperature functions of five different material properties. These five material functions appear in a different combination in almost every thermal shock case and cannot be extracted from thermal shock test data. It is recommended that these five properties and their temperature dependence be determined by separate standard tests, not employing thermal shock. If the five property functions are known, thermal shock tests proper can be used to determine the maximum thermal shock stresses in any device.

I. General Remarks

A GREAT amount of time and effort has been spent in the past on thermal shock testing, but few useful test data are available as a result.¹ It seems worth while to discuss the significance of this fact and to determine whether it is of a principal nature or whether it can be attributed to the use of inadequate test methods.

The sole purpose of technical tests is to provide a basis for the prediction of the performance of technical devices. Thermal shock tests are intended to provide the basis for the prediction of the probability (or rather improbability) of mechanical failure in operations involving sudden temperature changes. The prediction of the performance of a device requires (1) recognition and definition of all the important factors which influence the performance, (2) measurement of these factors, (3) knowledge of the possible variations of these factors, and (4) determination of the dependence of the performance on these factors. It is obvious that in a mathematical sense the "performance" is the dependent variable and the "factors" are the independent variables; the relation between the two is the "function" which must be determined, and the possible variations comprise the range of the function. It is indispensable that the variables can be measured in

physical units. It is desirable, but not necessary, that the function can be expressed in an analytical formula. Any functional representation, e.g., in tables or in graphs, can serve the same purpose.

A successful performance is one in which no mechanical failure occurs. The performance can be measured by a performance index which is defined as the ratio of the maximum stress (σ_{\max}) during the shock to the strength (s) of the material of the solid body.² If f_1, f_2, f_3, \dots are the factors influencing the performance, the performance index can be expressed by the performance function

$$P = \frac{\sigma_{\max}}{s} = F(f_1, f_2, f_3, \dots) \quad (1)$$

The prediction of the performance consists then in the evaluation of equation (1) for the whole range of the function. If P reaches the value 1, or surpasses this value, the device is bound to fail. If all P values are lower than 1, the difference

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² C. M. Cheng, "Resistance to Thermal Shock," *J. Am. Rocket Soc.*, 21, 147-53 (1951).