THERMAL SHOCK RESISTANCE OF CERAMICS SUBMITTED TO SEVERE SHOCKS

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Several ceramic materials have been submitted to severe thermal shocks by water quench.

The results are discussed in the frame of the thermo-elastic analysis and a new interpretation of the water quench resistance is developped. It leads to a linear variation of the critical fall in temperature ΔT_c versus the first thermal shock resistance parameter R. Such variations are obtained experimentally and it is shown that many bibliographical data agree very well with this linear law.

INTRODUCTION

The use of ceramic materials as components for thermal engines is a project of peculiar interest because of the great advantages which should result from its achievement. A reduction of the fuel consumption, Katz (1), a reduction of atmospheric pollutions and a significant decrease in the request for critical metals used in super alloys (Cr, Ni, V, Co, W...) needed by high temperature applications are the main benefits expected.

In the challenge with refractory metals the advantages of ceramics are a better refractoriness and a better resistance to corrosion, but their inherent brittleness, even at the highest temperature of use (1400°C), is a heavy handicap. Poor resistance to shocks, mechanical shocks but also thermal shocks induced by the operation of engines, is one of the most detrimental consequences of this brittleness.

THERMAL SHOCK RESISTANCE ANALYSIS

Two types of thermal shock resistance may be considered, Nakayama and Ishizuka (2) : thermal shock fracture resistance and thermal shock damage resistance. For structural ceramics, the former is the only parameter of interest and the

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thermoelastic analysis, Kingery (3), is the most classical approach used for its calculation.

The maximum thermal stresses arising in a body submitted to a thermal shock are given by relations in the following form :

$$\sigma_{th} = E \; \alpha \; \Delta T \; f(\nu) \qquad\qquad (1)$$

where E is Young's modulus, α the coefficient of thermal expansion, ΔT the gradient in temperature and $f(\nu)$ a parameter function of Poisson's ratio and of sample geometry. This relation is a valuable one only if the heat transfer is so large that the "skin" of the sample, originally at the temperature T is changed instantly to the temperature T_0 , ($|\Delta T = T - T_0|$). Such changes, which correspond to a limiting case, are difficult to obtain and in practical experiments the finite values of the heat transfer lead to lower thermal stresses than the maximum expressed by the relation 1. In fact :

$$\sigma_{th} = \Psi E \alpha \; \Delta T f(\nu) \qquad\qquad (2)$$

Ψ is a dimensionless coefficient named coefficient of stress reduction. Its numerical value ($0 \leqslant \Psi \leqslant 1$) depends on the severity of the thermal shock which is characterized by Biot's modulus :

$$\beta = ah/k \qquad\qquad (3)$$

a is a "mean dimension" of the sample, h is the heat exchange coefficient and k is the thermal conductivity of the material.

When the magnitude of the thermal stresses reaches a critical strength of the material, fracture will occur:

$$\sigma_R = \Psi E \alpha \; \Delta T_c \; f(\nu) \qquad\qquad (4)$$

ΔT_c is the critical value of the gradient in temperature which leads to fracture. Thus, it may be written:

$$\Delta T_c = \Psi^{-1} \; \frac{\sigma_R}{E\alpha \; f(\nu)} \qquad\qquad (5)$$

with $\quad f(\nu) = 1/(1-\nu)\qquad$ for an infinite cylinder

$\qquad\qquad f(\nu) = (1-\nu)/(1-2\nu)\quad$ for a thin disc

In the case of severe thermal shock, the heat transfer is very rapid and the high value of h involves high values of β. The coefficient of stress reduction is about 1 and the corresponding value of ΔT_c is labelled "first thermal shock resistance parameter R", Hasselman (4) :

$$R = \frac{\sigma_R}{E\alpha \; f(\nu)} \qquad\qquad (6)$$

R is a characteristic property of the material : it corresponds to its ability to suffer gradients of temperature. Once R is known, this allows the calculation of ΔT_c -which relates to a sample- by use of :

$$\Delta T_c = \Psi^{-1} \; R \qquad\qquad (7)$$

EXPERIMENTS

Materials

Several materials were used, which represent the various classes of structural ceramics : oxides, nitrides and carbides. Namely, they are alumina, partly stabilized zirconia, aluminium nitride, reaction bonded silicon nitride, silicon oxynitride and silicon carbide. Some of these materials were of commercial quality (Al_2O_3, R.B.S.N., P.S.Z. ...), the others were sintered in the "Laboratoire de Céramiques Nouvelles - Univ. Limoges", Billy et al (5), Boch et al (6). The samples were in the form of bars (4x4x25 mm) or of discs (Ø 30 x 2,5mm).

Thermal shocks

The samples were submitted to thermal shocks by quenching in a bath of water maintained at room temperature (20°C). Before quenching, the samples were heated for 1 hour in an electric furnace at temperature T($\Delta T=T-20$) ; during the cooling, they were vigorously stirred in the bath for a few minutes ; then they were dried for 15 mn at 105°C.

Measurements

Three test methods were used :
i) The classical test, Hasselman (7) of measurement of strength after shocks was performed by three point bending for bars and by biaxial flexure for discs.

ii) The measurement of elastic and anelastic properties by an original method at medium frequency (10-50 kHz) was also used. We have shown previously, Glandus and Boch (8), Glandus and Boch (9) that the parameters of free vibrations of a sample (resonance frequencies and damping) are strongly sensitive to the degree of fracture induced by shock.

The main advantage of this method is its non destructivity : few samples are needed and cumulative tests may be performed.

iii) The visual control by dye penetrant which was also possible because of the full density of the materials.

RESULTS AND DISCUSSION

1) When the fall in temperature reaches the critical value ΔT_c, the mechanical energy is too large to be stored in the sample in form of strain energy and fracture occurs to dissipate this energy by creation of new surfaces. The size ℓ of inherent flaws, starting from microscopic size, is changed instantly to macroscopic size.

Figures 1 to 3 illustrate the effects of fracture on the measured mechanical properties :

- Fig. 1 : the extent of the most critical defects leads to a correlative decrease in strength ($K_{1_c} \sim \frac{\sigma R}{\sqrt{\ell}}$).

- Fig. 2 : A loss of rigidity of the sample is induced by fracture and it results in a decrease in resonance frequencies, Glandus (10).

- Fig. 3 : Solid friction arises from the displacements of the fracture surfaces and gives rise to a significant increase in the measured damping (10).

2) Table 1 lists the thermomecanical properties and the measured values of ΔT_c for all the materials tested.

Matériaux	E_{GPa}	ν	σR_{MPa}	$\alpha(10^{-6})$	R_K c=cyl. d=disc	ΔT_{c_K}
Al_2O_3	364	0,245	250	8,1	65 c	180
ZrO_2	200	0,308	510	9,8	145 d	270
AlN	276	0,242	240	5,1	115 d	225
AlN (H.P)	315	0,245	360	5,1	150 d	260
Si_2N_2O	222	0,190	210	3	235 d	390
RBSN	140	0,260	160	2,8	300 c	470
SiC	397	0,170	470	4,9	190 d	340

TABLE 1 Thermomecanical properties of some ceramic materials.

3) Starting from the R values, the calculation of ΔT_c by means of relation 7 calls for an accurate knowledge of ψ^{-1}. Unfortunately, the analytic expression of ψ^{-1} involves Biot's modulus (β = ah/k) which is very difficult to estimate :

i) The "mean dimension a" is not rigorously definded and subjective evaluations of it are possible.

ii) The heat exchange coefficient, h, is generally unknown, especially in the case of water quench, because of the disturbance of the heat field in the vicinity of the sample during the first stages of quenching. The singularities of the h(T) function have been underlined by Becher (11) who found a maximum of h for sample temperatures in the range 200-400°C. This conclusion agrees very well with Mac Adams (12) who reports that the double phase change of water in the vicinity of the sample at the begining of cooling (vaporization on the "skin" of the sample and condensation in the cold bath) leads to the fastest heat exchanges possible.

The thermal shock by water quench, involving very high values of h (and then of β) leads to Ψ values of about 1. So it is a severe thermal shock and our interpretation takes this fact into account.

4) During the first stages of quenching the water surrounding the sample is instantly heated to 100°C and it remains at this temperature as long as the sample wall temperature is itself greater than 100°C. When the equality of these two temperatures is achieved, the boiling stops and the heat transfer rate decreases as illustrated by figure 4. Fracture occurs, necessarily, during the stage of very high heat exchange (high value of β and then of Ψ^{-1}), namely at a temperature T_{fr}, greater than 100°C:

$$T_{fr} = 100 + \delta T \qquad (8)$$

So, the effective critical drop in temperature may be written :

$$\Delta Tc_{eff} = T_C - (100 + \delta T) \qquad (9)$$

Moreover, due to the finite values of heat transfer ($\beta < \infty$), $\Delta T_{c_{eff}}$ is slightly greater than R (cf equation 7) :

$$\Delta Tc_{eff} = \lambda R \qquad (10)$$
$$(\text{with } \lambda \text{ slightly} > 1)$$

and one has :

$$T_C = 100 + \delta T + \lambda R \qquad (11)$$

which shows that if λ is almost constant -which is the case of Ψ^{-1} for high β values, Manson (13)-, T_C is a linear function of R.

The ΔT_C values listed in table 1 are plotted versus R in figure 5. Indeed one obtains the linear variation expected, and a least mean squares treatment gives :

$$\Delta T_C = 100 + 1,2 R \qquad (12)$$
$$(\text{the correlation coefficient r being } 0,991)$$

The bath temperature being 20°C, relation 12 becomes :

$$T_C - 20 = 100 + 1,2 R \qquad (13)$$
$$\text{or} \quad T_C = 100 + 20 + 1,2 R \qquad (14)$$

This last relation is in perfect agreement with relation 11 and it shows that, in the conditions of this experiment, δT is about 20°C and λ is 1.2, which corresponds to Biot's modulus of about 50.

It can be observed in figure 5 that the scattering of results is about 20 K on both sides of the least mean squares straight line and that many bibliographical data are self consistent with our results.

6) For samples of given geometry (bars 4x4x25 mm, discs $\emptyset$ 30 x 2,5 mm) and for materials whose R parameter is less than 300 K, one may conclude that the critical fall in temperature is correctly bounded by :

$$\Delta T_c \ (\pm 20 \ K) = \left[100 + 1,2 \ R\right] K \ (15)$$

For greater values of R, few bibliographical data are available and further experiments must be carried out before this approach can be generalised. However, for other geometries than bars and discs used for the present work, we have shown (10) the good applicability of relation 15 in the case of massive cylinders ($\emptyset$ 16x16 mm) and of long bars ($\emptyset$ 6x80 mm) ; therefore the geometrical characteristics of samples do no seem to introduce strong restrictions.

REFERENCES

1. KATZ, N., 1980, Science, 208, 841
2. NAKAYAMA, J. and al, 1966, Am. Ceram. Soc. Bul., 45(7), 666
3. KINGERY, W., 1955, Jour. Am. Ceram. Soc., 38(1), 3
4. HASSELMAN, D.P.H., 1970, Am. Ceram. Soc. Bul, 49(12), 1033
5. BILLY, M., and al, 1981, Ceram. Internat., 7(1), 13
6. BOCH, P., and al, 1982, Ceram. Internat., 8(1), 34
7. HASSELMAN, D.P.H., 1969, Jour. Am. Ceram. Soc., 52(11), 600
8. GLANDUS, J.C., and BOCH,P., 1980, Mat. Sc. Monographs, Elsevier, 6, 661
9. GLANDUS, J.C., and BOCH, P., 1980, L'industrie Ceram, 738(4), 238
10. GLANDUS, J.C., 1981, Thesis, University of Limoges
11. BECHER, P.F., and al, Am. Ceram. Soc. Bul., 59(5), 542
12. Mac ADAMS, W.H., 1951, "Heat Transmission", Mac Graw Hill
13. MANSON, S.S., 1958, Machine Design, 12, 114
14. ZIEGLER, G., and HEINRICH, J., 1980, Ceram Internat., 6(1), 25
15. GOGOTSI, G.A., 1980, Ceram Internat., 6(1), 31
16. HASSELMAN, D.P.H., 1970, Journ. Am. Ceram. Soc., 53(9), 490
17. BECHER, P.F., 1981, Journ. Am. Ceram. Soc., 11, C17
18. DAVIDGE, R.W., and al, 1967, Trans. Brit. Ceram. Soc., 66 (8), 405
19. BOISSON, J., 1974, Thesis, University of Limoges
20. HASSELMAN, D.P.H., and al, 1973, "Sc. of Ceramics", vol 7, 107
21. AINSWORTH, S.H., 1968, Thesis, University of Rolla Missouri
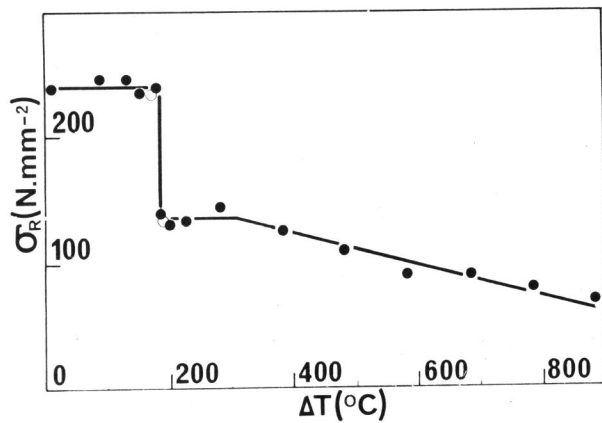
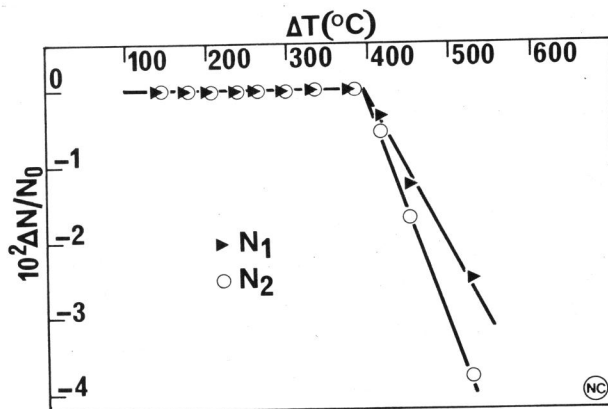Fig.1 Strength versus drop in temperature for bars of alumina.

Fig.2 Non dimensional resonance frequencies variations versus drop in temperature for discs of silicon oxynitride.
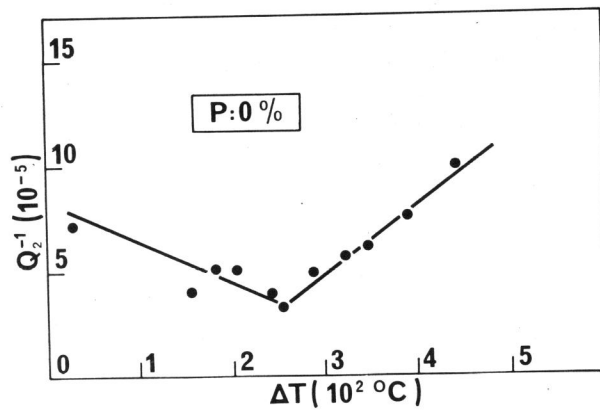

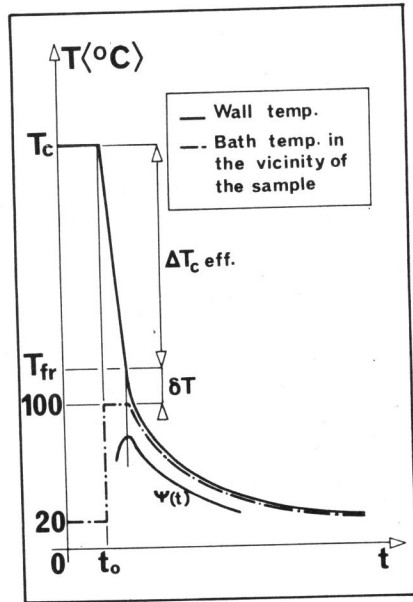Fig.3 Damping capacity versus drop in temperature for discs of aluminium nitride.

Fig.4 Wall temperature and bath temperature versus time during the first stages of quenching.
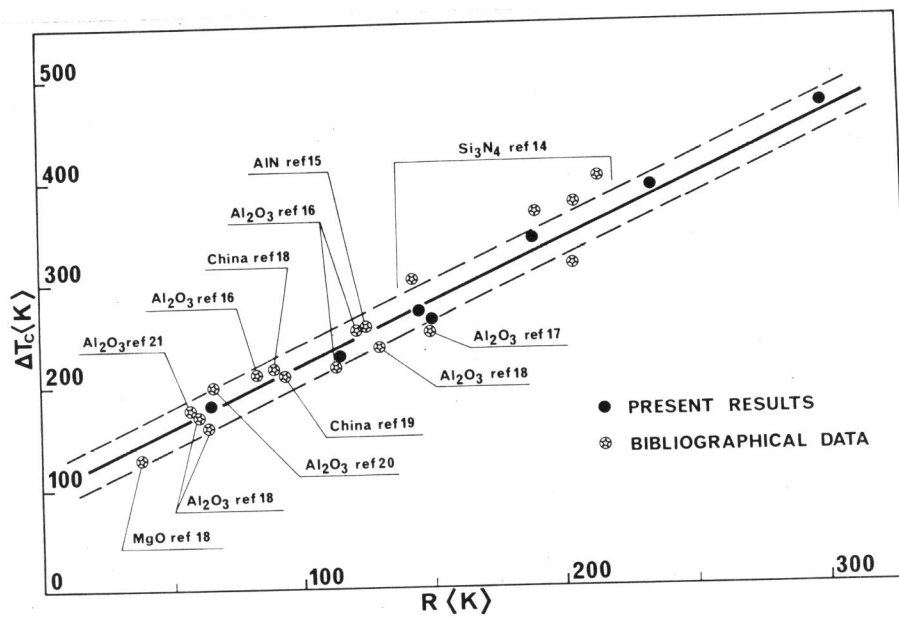

Fig.5 Critical drop in temperature versus R parameter for several ceramics.