Journal of the European Ceramic Society 22 (2002) 1883–1889

www.elsevier.com/locate/jeurceramsoc

Parameters for measuring the thermal shock of ceramic materials with an indentation-quench method

P. Pettersson, M. Johnsson*, Z. Shen

Department of Inorganic Chemistry, Stockholm University, S-106 91 Stockholm, Sweden

Received 31 January 2001; received in revised form 2 November 2001; accepted 11 November 2001

Abstract

An indentation-quench method for measuring thermal shock has been evaluated. Experimental parameters such as sample thickness, initial crack length, and water bath temperature were surveyed. It was found that one single sample could be used throughout a whole test series of different quenching temperatures. The method can detect small differences in thermal shock resistance between materials, and was applicable to investigating thermal fatigue. The tested materials were two β-sialons with intergranular glass phase and with completely different thermal shock behaviour. The best resolution was obtained with a sample diameter Ø = 12 mm, height $h = 4$ mm, initial crack length = 100 μm. and a water bath temperature = 90 °C.

Keywords: Sialons; Test-methods; Thermal shock resistance

1. Introduction

One of the major factors making ceramic materials attractive is their usefulness at high temperatures. Good thermal-shock resistance is advantageous, since use at high temperatures often involves rapid heating and cooling of the material. The thermal-shock properties of a material depend on many parameters such as tensile strength, fracture toughness, Biot modulus, Young's modulus, and thermal expansion coefficients. In addition to these materials properties, which can be tabulated, the microstructural character is also of importance and influences the thermal-shock behaviour of a material. Due to the many parameters influencing thermal shock behaviour of materials, it is difficult to model this property, especially for composite materials. This scientific field is comparatively unexplored, because of the problems mentioned and also the lack of an efficient standardised method for thermal-shock measurements. There is, thus, a lack of experimental data to show in what way different materials parameters influence thermal-shock properties, and there is also a need for establishing a standardised efficient thermal-shock test. Such a test method should provide a clear ranking of different materials, and it should keep time-consuming and costly sample preparation at a minimum.

An indentation-quench method based on pre-cracked disc-shaped specimens to determine thermal-shock properties as developed by Andersson and Rowcliffe[1] has been used in the present study. Compared to e.g. the Hasselman test,[2] the evaluation procedure is simple, the sample preparation is easy and only a small number of samples are needed for a series of measurements at different temperatures.

Our aim was to test some experimental parameters in order to evaluate how useful and reliable this method is for measuring thermal-shock properties and for ranking the thermal-shock resistance of Si_3N_4 based materials. The parameters tested are initial crack length, sample thickness and water-bath temperature. We also compared re-using the same sample for a whole series of testing temperatures instead of using a fresh sample for each temperature. The quenching conditions were selected to force the indented cracks to grow in a controlled way. Two different β-sialons containing an intergranular glass phase were selected for the evaluation. β-sialon is a solid-solution phase with a structure similar to β-Si_3N_4, having the formula $Si_{6-z}Al_zO_zN_{8-z}$ ($0 \leqslant z < 4.2$). One of

* Corresponding author. Tel.: +46-8-674-7067; fax: +46-8-15-21-87.
E-mail address: matsj@inorg.su.se (M. Johnsson).

0955-2219/02/$ - see front matter
PII: S0955-2219(01)00504-0

the materials, with $z=0.6$ and containing 20 vol.% intergranular glass phase, had previously been found,[3] to have excellent thermal-shock resistance. The other material ($z=2.0$, 10 vol.% glass) was in the same study found to have much poorer thermal-shock resistance. These two materials were chosen for our study because they represent two different types of thermal-shock behaviour.

2. Experimental

2.1. Preparation of materials

Two types of β-sialon materials with different thermal-shock properties were prepared (see Table 1). The materials have different z values and amounts of intergranular glass phase. The added glass phase has the nominal composition $Y_{1.75}Si_{2.625}Al_{1.0}O_{7.5}N_{1.25}$ (28Y; 56Si; l6Al; 80O; 20N in equivalent% of the cations and anions respectively).[3,4]

Specimens were prepared from commercial powders of Si_3N_4 (UBE, SN-E10), AlN (H.C. Starck-Berlin, grade A), Y_2O_3 (99.9%, Johnson Matthey Chemicals Ltd.) Al_2O_3 (Alcoa, A16SG) and SiO_2 (99.9%, <325 mesh, Johnson Matthey Chemicals Ltd.), and corrections were made for the small amounts of oxygen present in the Si_3N_4 and AlN raw materials. The starting-material mixtures were milled in water-free propanol for 24 h in a plastic jar, using sialon milling media. The dried powder mixtures were hot pressed in order to ensure full density, at a temperature of 1750 °C and a pressure of 30 MPa for 90 min.

2.2. Characterisation techniques

The densities of the sintered specimens were measured according to Archimedes' principle. Before the mechanical and microstructural studies, the specimens were polished by standard diamond polishing techniques down to 1 μm diamond suspension. The hardness (HV_{10}) and indentation fracture toughness (K_{1C}) at room temperature were obtained with a Vickers diamond indenter, using a 98 N load, and the fracture toughness was evaluated according to the method of Anstis et al.,[5] assuming a value of 300 GPa for Young's modulus. Five indentations were made on each sample. The microstructure was investigated in a scanning electron microscope (SEM, Jeol 880) equipped with an energy-dispersive spectrometer (EDS, LINK *ISIS*) that allows detection of boron and heavier elements. To obtain the best contrast between different phases, the micrographs were recorded in back-scattered electron mode (BSE) at an acceleration voltage of 20 kV. The amount of intergranular glass phase was evaluated with an image-analysing package supplied with the LINK *ISIS* system. Images were collected at 10 kV acceleration voltage, and the contrast difference between the β-sialon grains and the yttrium-containing glass phase was used to estimate the content of these phases in vol.%. This percentage was assumed valid for the whole sample volume (see Table 2). Estimates of the minimum and maximum amount of glass phase gave an error of ±1%.

The samples were crushed and characterised by their X-ray powder diffraction (XRD) patterns collected with a Guinier–Hägg focusing camera. Cu$K_{\alpha1}$ radiation ($\lambda=1.540598$ Å) was used and powdered silicon ($a=5.43088$ Å at 25 °C) was added as internal standard. The recorded films were evaluated with the computer programs SCANPI[6] and PIRUM.[7] The latter program was also used to determine and refine the unit-cell parameters. An experimental z value of the β-sialon phase was obtained from the unit-cell dimensions, using the equations given by Ekström et al.[8] (see Table 2).

2.3. Thermal shock measurements

Cylindrical samples, with a diameter of 12 mm were used in all test series. The samples were ground to make the two surfaces parallel, and one side was then polished down to 1 μm diamond suspension. Well-defined cracks were initiated with a Vickers indenter (model 8561, Instron, High Wycombe, England) allowing variation of the load as well as the time of loading, holding and unloading. The loading and unloading times were 10 s each, and the holding time at maximum load was 20 s. Four indents were made on each sample, and each

Table 1
Overall compositions of the starting materials (in wt.%)

Sample	Nominal z value	GP[a] vol.%	Y_2O_3	Si_3N_4	AlN	Al_2O_3	SiO_2
G20B06	0.6	20	10.84	73.33	4.14	6.19	5.49
G10B20	2.0	10	5.56	62.74	7.73	23.95	–

[a] GP = Intergranular glass phase.

Table 2
The measured composition and unit cell parameters of the β-sialon phase

Sample	Unit cell dimension a-axis (Å)	Unit cell dimension c-axis (Å)	Measured z value	Measured vol.% glass	Measured density (g/cm^3)	K_{IC} (MPam$^{1/2}$)	HV_{10} (GPa)
G20B06	7.6211(4)	2.9186(3)	0.5	26	3.26	5.3±0.3	15.8±0.3
G10B20	7.6616(4)	2.9542(3)	1.9	14	3.17	3.4±0.1	16.3±0.2

indent generated four cracks (see Fig. 1), so that 16 cracks were made on each sample.

Unless otherwise stated, the following parameters were held constant: the sample thickness was 4.0 ± 0.3 mm, the initial crack length was 103 ± 9 μm (due to the hardness difference between the two different sialon materials, the indenting load had to be optimised to 70 N for G20B06 and 40 N for G10B20), and the water bath temperature was 90 °C.

The crack length was measured in an optical microscope (Olympus PMG3). The samples were heated, one by one, in air at $\leqslant$ 1100 °C in a vertical tubular furnace; they were thermally equilibrated for 20 min and subsequently quenched by free fall into a water bath. The maximum temperature was chosen in order to avoid oxidation. No obvious formation of an oxidation skin was observed during the course of the experiments.

The furnace temperature was selected to give the desired difference, ΔT, from the water bath temperature. The crack growth was measured at each temperature step, and the total percentage crack growth (Δc) was calculated. If one or two cracks deviated from the growth of the other cracks, then Student's t test at 95% confidence was used to check if they should be included or excluded in the calculation of the average crack growth.

The following test series were performed: (a) Re-use of one sample versus use of a fresh sample for each new temperature step (G20B06). (b) Thermal cycling: repeated cycling at constant ΔT. (c) Variation of sample thickness: a number of samples of both materials with a thickness in the range 2–6 mm were prepared, and the thermal-shock properties were evaluated at different ΔT-values. The influence of varying the sample diameter has not been investigated, since this parameter is easy to keep constant during compaction in a die with defined diameter. (d) The influence of the initial crack length: there will always be a deviation from the intended crack length, and when comparing different materials it is important that small deviations in the initial crack length between different samples should not cause severe differences in the measured percentage crack growth after thermal shock. Different initial crack lengths in the range 35–140 μm were tested with both sialon materials. The quenching temperature differences, $\Delta T = 800$ and 200 °C, were selected so that the crack growth should be in the stable region and thus give comparable results. (e) A series of experiments were performed where the water-bath temperature was varied in the range 0–100 °C; separate samples were used at each water temperature. Plastic bags containing ice were placed at the bottom of the bath to keep the temperature at 0 °C. A thermostat was used to control the other water-bath temperatures. The surface heat transfer, h, is usually not known precisely and is strongly dependent on the temperature difference, ΔT, and the water temperature, T_w, see discussion below.

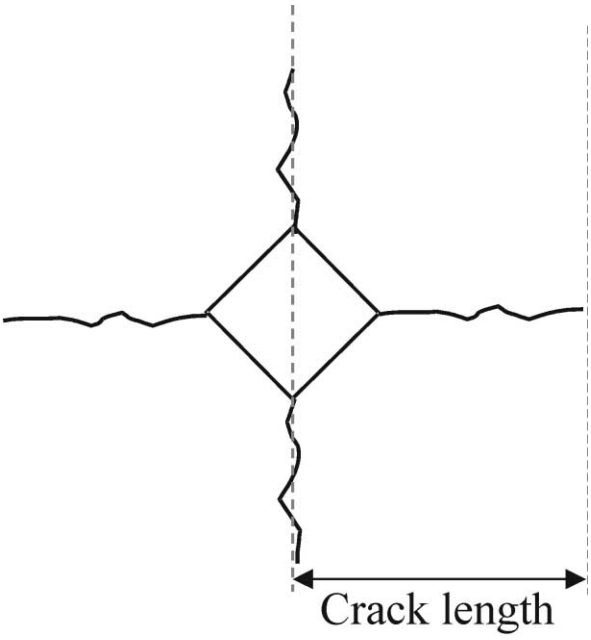

Fig. 1. Definition of the initial crack length. Each Vickers indent generates four cracks.

3. Results and discussion

3.1. The materials

Both ceramic samples were fully densified, and the measured densities are listed in Table 2. The density was confirmed by SEM investigation of polished surfaces, i.e. no pores or voids were observed. Micrographs of polished surfaces of both samples are shown in Fig. 2. The grain size of the β-sialon phase increases with increasing z value, and the β grains, which otherwise show an equiaxed morphology,[3] become elongated when an intergranular glass phase is present. G20B06 has higher fracture toughness than G10B20, but the hardness of the two samples is more or less the same (see Table 2). As has

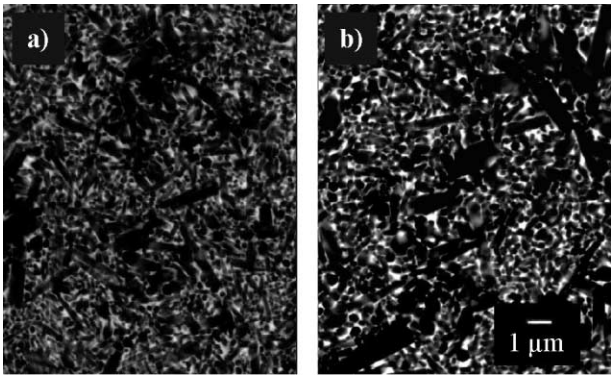

Fig. 2. SEM micrographs of polished surfaces of (a) G10B20 and (b) G20B06 recorded in BSE mode. The glass phase appears white and the β-sialon phase appears dark.

already been discussed in our previous work,[3] increasing aluminium content in the crystals (i.e. increasing z value) makes the material easier to fracture.

3.2. Thermal-shock properties

3.2.1. Re-use of samples

A study was made, comparing repetitive use of one sample with using a new sample at each quenching temperature. The material with the best thermal-shock properties (G20B06) was selected for this comparison. No significant difference between the two series was found, see Fig. 3. From those results it can thus be concluded that the same sample can be used repetitively for a series of temperatures, at least for a material with good thermal-shock resistance. This result is important because it confirms that the thermal shock properties of a group of similar materials can be ranked by use of very few samples.

3.2.2. Thermal cycling

Both materials were cycled at a ΔT causing the cracks to grow by about 8% in the first quenching cycle, i.e. $\Delta T = 800$ and 200 °C for G20B06 and G10B20, respectively. In the G20B06 sample the average crack growth was only 2% in addition after 29 repeated quenching cycles, compared to the first cycle, whereas the cracks in the other sample, G10B20, grew by about 14% in addition after 15 cycles, compared to the first cycle, see Fig. 4. A low resistance to momentary thermal shock thus also implies that the material is more sensitive to thermal fatigue, even at low ΔT values. On the other hand, the crack extension in the material with good resistance to momentary thermal shock is not sensitive to thermal cycling. This result confirms that the thermal shock behaviour, as determined by the indentation-quench method, is sensitive to inherent materials properties. The method is, therefore, suitable for ranking materials. Preferably the temperature steps should be equal, e.g. steps of 50 or 100 °C, for samples to be compared so that they have the same thermal history.

In high-temperature applications the materials are often cycled between room temperature and the high temperatures used. Therefore, not only the resistance to momentary thermal shock but also the thermal fatigue resistance of the materials is critical. The present method is particularly attractive because it provides an efficient way to investigate the thermal fatigue property.

3.2.3. Sample thickness

Thin samples (~2 mm) show better thermal shock resistance than thick ones (~6 mm), as expected. There was a very small influence of the thickness on the crack growth in the range 3.5–5.5 mm for the G20B06 composition for all ΔT values tested. Above this thickness range the crack growth seems to be more sensitive to thickness (see Fig. 5a). For the less shock-resistant sample G10B20, there was a more pronounced thickness effect, especially at higher ΔT values. In the thickness range 3.5–4.2 mm, however, the crack growth was almost constant (see Fig. 5b). In order to apply the method to a series of materials with different thermal-shock properties, some deviations in sample thickness must be tolerated. The average sample thickness for such a series of experiments should be in the range 3.5–4.2 mm.

3.2.4. Initial crack length

For cracks shorter than 110 μm the two materials behaved similarly, but initial cracks lengths above 110 μm yielded differences in crack growth due to thermal shock. The material with better thermal-shock resistance can absorb the residual stress at the higher loads

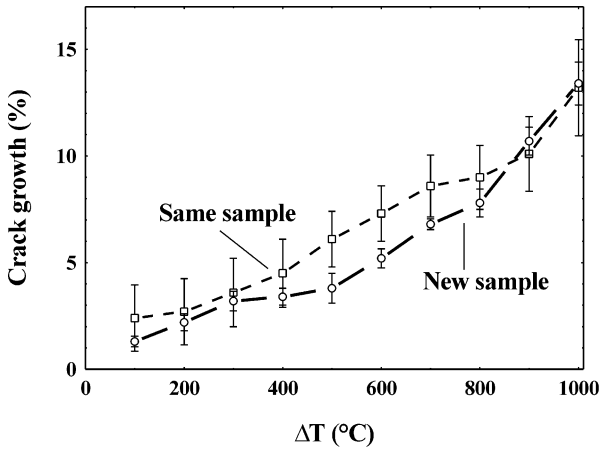

Fig. 3. Comparison between the results of thermal-shock measurements where the same sample has been re-used, and where a fresh sample is used at each new quenching temperature. The two series show no obvious difference. The G20B06 material was used in this test.

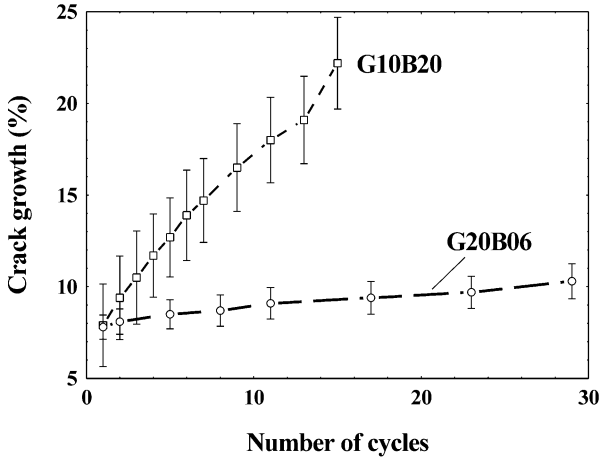

Fig. 4. Measurements of the thermal-fatigue properties by repetitive cycling of the samples at ΔT values yielding a crack growth after the first quenching cycle of about 8% for both materials. $\Delta T = 200$ °C for G10B20 and $\Delta T = 800$ °C for G20B06 were selected.

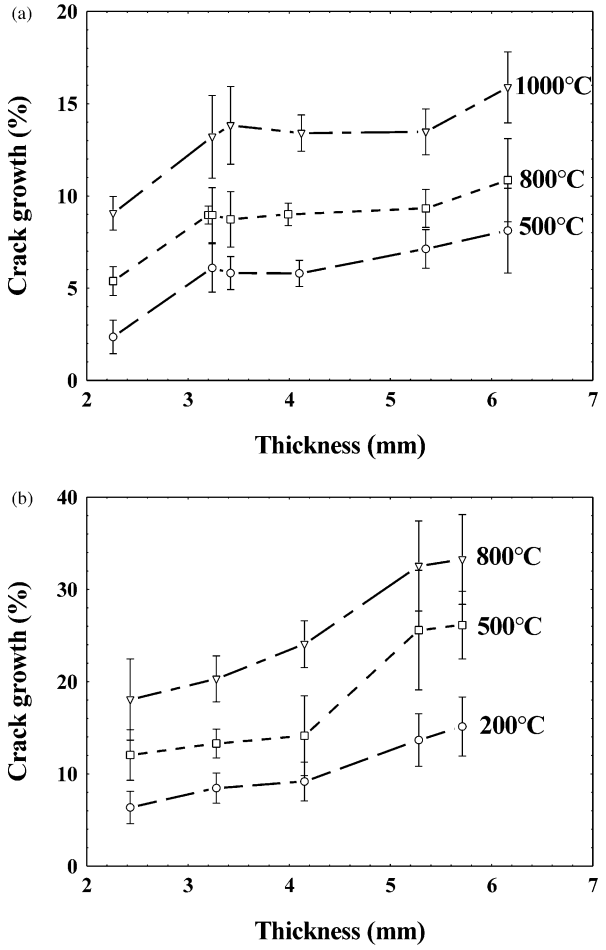

Fig. 5. Influence of sample thickness on the crack growth after quenching with different ΔT values for (a) G20B06 and (b) G10B20. Both materials show the highest tolerance to thickness deviations in the range 3.5–4.2 mm.

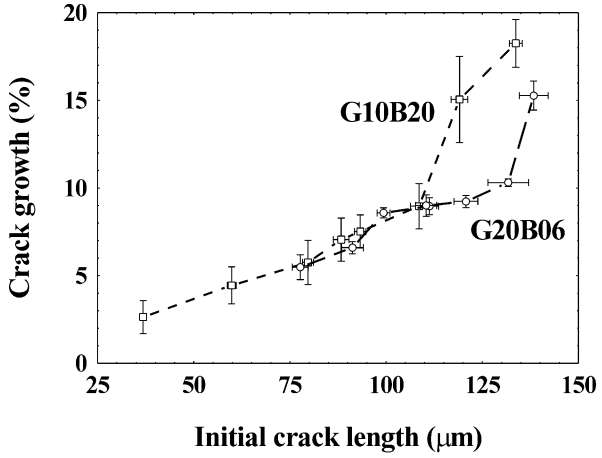

Fig. 6. Influence of the initial crack length on the crack growth after quenching with $\Delta T = 800\ ^{\circ}C$ for the G20B06 material and $\Delta T = 200\ ^{\circ}C$ for the G10B20 material. The crack growth was found to be stable for initial crack lengths shorter than 110 μm. For longer cracks, relaxation of tensions in the materials due to the indentation will also influence the crack growth, in addition to the growth induced by thermal shock.

better than the poorer material. When a too high load has been used (i.e. the initial cracks are too long) the crack growth depends both on the relaxation of residual stress in the material and on the thermal shock. A good choice seem to be an initial crack length of 100 ± 10 μm, then the deviation in the average crack growth of each material is only $\pm 1.5\%$ at a total growth of 8%, see Fig. 6. A shortest crack length of about 100 μm is also preferable, in order to minimise the relative importance of observational error.

3.2.5. Water bath temperature

The water bath temperature was found to be critical for the crack growth induced by quenching. Using a 100 °C bath entails the mildest quenching conditions while an ice bath gives the toughest (see Fig. 7a and b). According to Davidge and Tappin,[9] the heat transfer between the hot body and the water bath can occur by at least three mechanisms. (i) At low temperatures the body does not cause the water to boil, and the heat is

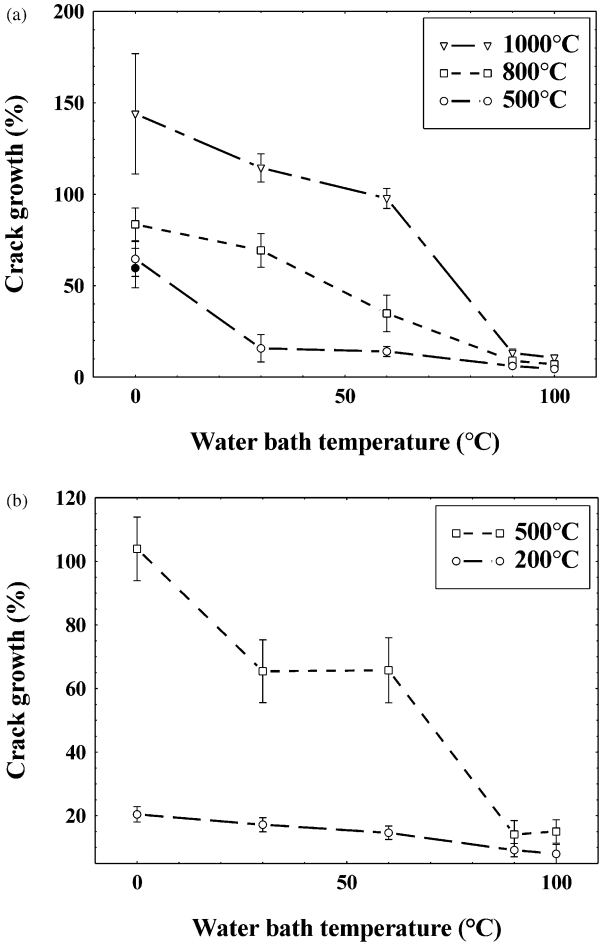

Fig. 7. The influence of the water-bath temperature on the crack growth for different quenching temperature differences, ΔT. (a) G20B06, (b) G10B20.

Table 3
Influence of quenching temperature difference, ΔT, and water bath temperature, T_w, on the heat transfer mechanism and the Biot modulus[a]

	Low ΔT + low T_w	High ΔT + low T_w	Low ΔT + high T_w	High ΔT + high T_w
Type of heat transfer mechanism	i	ii	i, ii	iii
Biot modulus, β	Low	High	Low	Low

[a] See text for explanation of heat transfer mechanisms.

slowly transferred by convection solely. (ii) At higher temperatures nucleated boiling occurs at preferred sites on the surface of the body, and the resulting steam bubbles produce vigorous agitation of the liquid, to give very rapid heat transfer. (iii) At still higher temperatures the body may become enveloped in a layer of steam, and the heat transfer rate will fall. A film of gaseous water around the sample easily develops at water temperatures close to the boiling point, and to a lesser extent at lower bath temperatures. After quenching with a certain ΔT, the standard deviation in measured crack growth increases with decreasing bath temperature, due to the tougher conditions. The combined effect of the quenching ΔT and the water bath temperature will influence the Biot modulus, β ($\beta = ah/k$, a = shortest heat-transfer length, h = surface heat-transfer coefficient, k = thermal conductivity of the body), which is an important thermal-shock parameter (see Table 3). A high Biot modulus gives a tougher test and an increase in the risk for uncontrolled crack growth.

3.3. On the selection of water bath temperature

The water bath temperature affects the resolving power of the technique. A water bath temperature of 0 °C will result in severe crack growth also for small ΔT values while a water bath temperature close to the boiling point will need a substantially larger ΔT in order to get similar crack growth. The water bath temperature should, therefore be selected with respect to the resolution of the results. The test samples are equilibrated at each temperature step, but if the difference in temperature between the steps is too small, the uncertainty in the measurements will increase. The water bath temperature should therefore be selected so that ΔT steps of about 50 °C can be used. Our experience is that the water-bath temperature should generally be close to the boiling point for testing ceramic materials, and Becher[10] also concludes that boiling water has several attractive features. However, in order to avoid negative influence on the sample caused by the water steam we have settled for a water bath temperature of 90 °C, which is easy to keep constant by use of a thermostat.

The temperature of the sample before quenching must be lower than the upper limit of its stability or the temperature at which the material may start to be oxidised. For comparison of materials with very good thermal-shock properties, a 90 °C water bath is not suitable for resolving differences in shock behaviour; thus cold water should be selected instead to give a tough test.

4. Conclusions

In order to apply the indentation-quench technique to comparing the thermal shock resistance for a group of materials, the samples should be prepared so that the resolution of the technique is optimised. Critical preparation parameters are sample thickness and initial crack length. Those parameters should be selected so that the tolerances for deviations from intended values are as high as possible.

In a study comparing repetitive use of one sample of a thermal shock resistant material with using a new sample for each quenching temperature, no significant difference between the two series was found. This observation reveals that, at optimum, a material with good thermal-shock resistance can be quickly distinguished from one with poorer properties by use of only one sample for each material. The use of the same sample for a whole series of temperatures is the most pronounced advantage of the indentation-quench method, compared to many other thermal-shock methods where new samples have to be prepared for each temperature. The thermal-fatigue properties of a material can also be predicted from the indentation-quenching tests.

It is our opinion that there should be an agreement on standardisation of the experimental parameters for the indentation-quench method in order to improve its reliability, and to make it easy to compare results from different studies. We would like to suggest a sample diameter $Ø = 12$ mm, height $h = 4$ mm, initial crack length = 100 μm, water bath temperature = 90 °C.

Acknowledgements

This work has been performed within the Inorganic Interfacial Engineering Centre, supported by the Swedish National Board for Industrial and Technical Development (NUTEK) and the following industrial partners: Erasteel Kloster AB, Ericsson Cables AB, Höganäs AB, Kanthal AB, OFCON Optical Fiber Consultants AB, Sandvik AB, Seco Tools AB and Uniroc AB.

References

1. Andersson, T. and Rowcliffe, D. J., Indentation thermal shock test for ceramics. *J. Am. Ceram. Soc.*, 1996, **79**, 1509–1514.
2. Hasselman, D. P. H., Strength behaviour of polycrystalline alumina subjected to thermal shock. *J. Am. Ceram. Soc.*, 1970, **53**, 490–494.
3. Pettersson, P., Shen, Z., Johnsson, M. and Nygren, M., Thermal shock properties of β-sialon ceramics. *J. Eur. Ceram. Soc.*, 2002, **22**(8), 1357–1365.
4. Ekström, T. and Nygren, M., Sialon ceramics. *J. Am. Ceram. Soc.*, 1992, **75**, 259–276.
5. Anstis, G. R., Chantikul, P., Lawn, B. R. and Marshall, D. B., A critical evaluation of indentaion techniques for measuring fracture toughness: I, direct crack measurements. *J. Am. Ceram. Soc.*, 1981, **64**, 533–538.
6. Johansson, K. E., Palm, T. and Werner, P. E., An automatic microdensiometer for X-ray diffraction photographs. *J. Phys. E. Sci. Instrum.*, 1980, **13**, 1289–1291.
7. Werner, P. E., A Fortran program for least-squares refinement of crystal structure cell dimensions. *Arkiv för Kemi*, 1969, **31**, 513–516.
8. Ekström, T., Käll, P. O., Nygren, M. and Olsson, P. O., Dense single phase β-sialon ceramics by glass encapsulated hot isostatic pressing. *J. Mater. Sci.*, 1989, **24**, 1853–1861.
9. Davidge, R. W. and Tappin, G., Thermal shock and fracture in ceramics. *Trans. Bri. Ceram. Soc.*, 1967, **66**, 405–422.
10. Becher, P. F., Effect of water bath temperature on the thermal shock of Al_2O_3. *J. Am. Ceram. Soc.*, 1981, **64**, C17–C18.