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Comparison of two β-SiAlON ceramics prepared from synthetic and natural raw materials

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Abstract

Two types of β-SiALON ceramics (denoted SiALON-S and SiAlON -N) were synthesized by carbothermal reduction and nitridation. The starting raw materials used were commercial synthetic powders (AlN, Al_2O_3 and Si_3N_4) for SiAlON-S and natural aluminosilicate raw materials (pyrophilite) for SiAlON-N. Sintering of materials has been achieved by hot- isostatical pressing procedure at 1730 °C using Y_2O_3 as a sintering additive. In this study XRD and SEM methods were used. XRD method showed that SiAlON-S is pure aluminum silicon nitride oxide, while sample from natural pyrophilite is composed of two aluminum silicon nitride oxides and corundum. Hardness and fracture toughness values were measured for all samples, the average values (means of 10 measurements) of SiAlON-S and SiAlON -N were H_V = 12.28 GPa and 12.34 GPa, K_{IC} = 4.11 MPa $m^{1/2}$ and 3.77 MPa $m^{1/2}$ respectively. A new testing method was used to assess the resistance of SiAlON samples to repeated thermal shocks. Samples with initiated cracks by Vickers's indentor were cyclically heated to 1000˚C and cooled to 500˚C. Apart from phase composition, the source of raw materials has a little influence on the properties of ceramic samples. Therefore, pyrophilite could be a potential natural source to synthesize SiAlON ceramics.

Keywords: SiAlON ceramics, starting materials, hardness, fracture toughness, thermal shock resistance.

Introduction

SiAlON ceramics are solid solution of silicon nitride (Si_3N_4) and alumina (Al_2O_3), forming thus composite non-oxide and oxide structural ceramics. They are known in two modification forms α- and β- SiAlON according to the initial silicon nitride used (Jack 1996). For example β- SiALON, represented by the general formula $Si_{6-z}Al_zO_zN_{8-z}$ ($0<z<4.2$), is a solid-solution phase with a structure similar to hexagonal β -Si_3N_4 (Pettersson, Johnsson and Shen 2002). They are generally synthesized from commercial finely ground powder of Si_3N_4, AlN and Al_2O_3 by different synthesis method. One of the factors making ceramic materials based on SiALON attractive is their potential application at high temperatures. These application conditions require high hardness, superior wear and corrosion resistance, and excellent thermal shock resistance.

The thermal shock properties of a material depend on many parameters such as tensile strength, fracture toughness, 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 behavior of a material. Due to the many parameters influencing thermal shock behavior of materials, it is difficult to model this property, especially for composite materials.

Materials that are prepared for high temperature applications are often exposed to rapid temperature changes, which cause thermal stresses and risks for thermal shock damage. Good thermal-shock resistance is an advantage, since the use of SiAlON ceramics at high temperatures always involves repeated heating and cooling of the materials (Pettersson, Johnsson and Shen 2002).

Various methods have been developed over the years in order to measure the thermal shock resistance of materials. Most of those methods are based on test bars of specified dimensions and geometries which are heated to thermal equilibrium in a furnace and then quenched into a water bath and subsequently subjected to mechanical testing, for example by determining their three- or four-point bending strength (Buessem 1955).

In recent years, some methods have been invented to test resistance to repeated thermal shock. Indentation-quenching method is the most one widely used. A specimen with initiated cracks is heated to a certain temperature in an oven and then rapidly quenched, usually by falling into water (Andersson, Rowcliffe 1996, Glandus, Tranchand, Koh, Kim

Kim and Halloran 2004). By this way the specimen is subjected to repeated thermal shock. Several modifications of this method have been introduced, for example a modification that allows a more rapid thermal shock by avoiding phase changes of the quenching medium. Also, Absi and Glandus (Absi and Glandus 2003) proposed a new experimental technique which minimizes the water phase changes in order to perform severe thermal shocks. The sample, uniformly heated at a temperature higher than the boiling water temperature, is then suddenly cooled in periphery by a system of water jets at room temperature.

A new testing method has been developed (Gondar, Pulc, Krizanska 1995; Gondar 1998) and optimized (Gondar, Hlava and Roshko 2006) to assess the resistance of technical ceramics to repeated thermal shocks. The principle of it is shown in Fig. 1. Specimens of circular cross-section with cracks formerly initiated by Vickers's indentor are used in this test. The specimen is placed with its damaged side facing downwards and this side is constantly (without interruptions) cooled by water. Its opposite side is cyclically heated using a punch. The punch is heated by an induction coil and is loaded by a 6 kg weight.

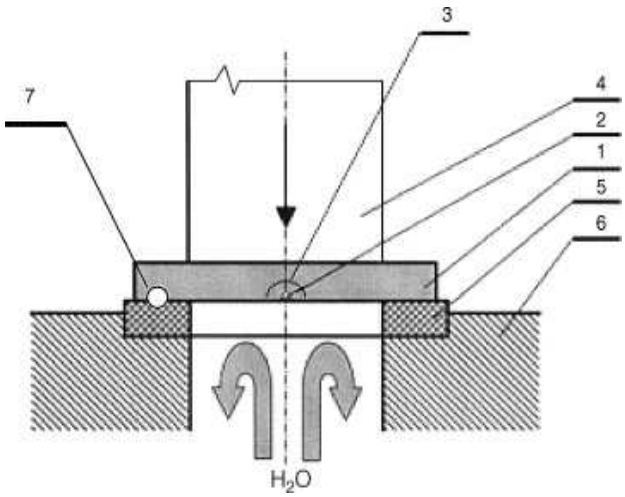

Fig.1. Principle of the new method of testing the resistance of technical ceramics to repeated thermal shocks. 1-Specimen; 2- indent; 3- crack; 4- punch; 5- sealing; 6- support; 7- position of thermocouple (Gondar, Hlava and Roshko 2006).

This weight prevents the cooling water from leaking under the sealing. The diameter of the punch is equal to the whole diameter of the sealing. This way, the only mechanical loading of the specimen is shear acting under the perimeter of the punch. Mechanical loading acting on the indent and the cracks is negligible. Modifying the punch diameter can change the type of mechanical loading.

The aim of present paper is to test the thermal shock resistance of two types of β-SiAlONs by new test method, the first prepared from commercial powders (SiAlON-S), and the second one from precursors synthesized by carbothermal nitridation of pyrophilite (SiAlON-N).

Materials and Methods

Sample preparation

Two types of β-SiAlON ceramics with the same *z* value were prepared from different starting raw materials. Samples of series N (natural) and S (synthetic) were designed to give β-SiAlON ceramics with z value of 4.2. The starting powder materials used in this work were precursor powder (Si_3N_4+Al_2O_3); α-Al_2O_3(Martoxide PS-6, Martinswerk, FRG), β-Si_3N_4 (Tschernogolovka, Russia), AlN (Grade C, H.C. Starck, Germany) and corrections were made for the small amounts of oxygen present in the Si_3N_4 and AlN raw materials. The powder products of carbothermal reduction and nitridation (CRN) process were pressed into pellets in a steel die at 100 MPa after adding Y_2O_3 as a sintering additive. The compacted samples were then sintered by hot pressing (HP) in a graphite die in order to ensure full density at 1730 °C for 2 h in 0.1 MPa of nitrogen and mechanical load of 30 MPa. Likewise, samples of SiAlON ceramics were prepared by carbothermal reduction and nitridation of natural aluminosilicate raw material, pyrophilite with ideal composition $Al_2Si_4O_{10}(OH)_2$. The prepared specimens were of 12 mm diameter and a thickness of 4 mm. For thermal shock test specimens were cut to a thickness equal to 2 mm. Number of samples were 10 for each kind of material.

Indenting

After metallographic preparation of the specimens, they were submitted to a series of Vickers indentations with parameters: loading force, F = 294.3 N; loading time, τ = 15 s; temperature, T = 20 °C. Each Vickers indentation generates four cracks (Fig.3). The initial dimensional parameters of crack surface were measured for each specimen using an optical microscope (Olympus PMG3).

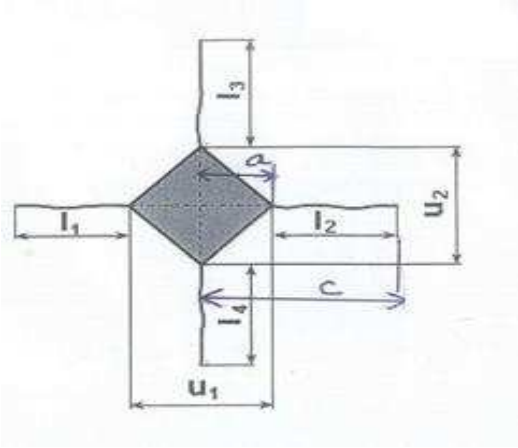

Fig.3 Dimensions of indents and cracks (Menčík, 1990)

Thermal cycling

The specimens were cyclically heated to 1000 ˚C and cooled to 500 ˚C (temperature differential ΔT= 500 °C). The duration of the heating and cooling cycle was 16 seconds and 5 seconds, respectively using a new testing method. The temperatures were controlled by using a thermocouple situated between the punch and the sample and by pyrometer. Crack propagation was optically examined after each cycle and the critical number of cycles to cause crack running was determined. Crack extension was calculated from initial crack length c_0 and final crack length after the critical number of cycles causing crack propagation.

Mechanical properties

Hardness H_v and fracture toughness K_{Ic} of the specimens were calculated from the crack dimensions caused by hardness indentation as illustrated in Fig.3. The indent crack geometry so-called Vickers indentor is characterized by its dimensions such as indentation diagonal (U_1, U_2) and radius or indent half diagonal a. Furthermore one can determine the length of lateral cracks (l_1, l_2, l_3, l_4) produced by indentation force and radial surface crack c measured from the center to the tip of the crack (Fig. 3)

Results and Discussion

XRD patterns depicted in Figs. 4 and 5 show that the phase composition of SiALON ceramics is not similar after sintering. As it can be seen from these figures, sample synthesized from commercial powders is a single phase of pure Aluminum Silicon Nitride Oxide with ICDD File No number 76-598 (Fig.4). In this figure the absolute intensity of

diffraction peak is plotted against 2 Theta. The first above X-ray diffraction pattern characterizes the synthesized sample and the second below is for standard SiAlON.

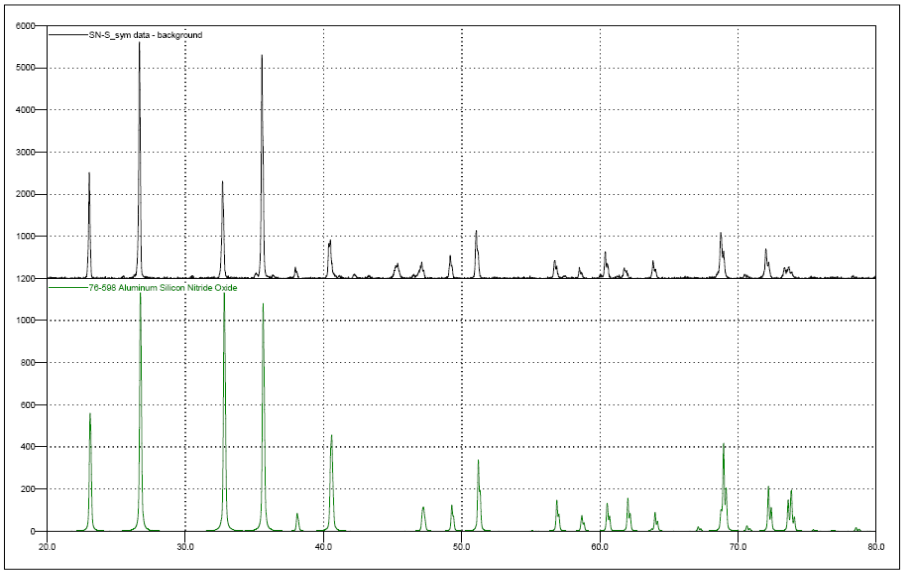

Fig. 4 XRD-pattern of β-SiAlON-S sample synthesized from commercial raw materials compared with that of standard β-SiAlON. Absolute intensity (Y-axe) of diffraction peak is plotted against diffraction angle (2 Theta).

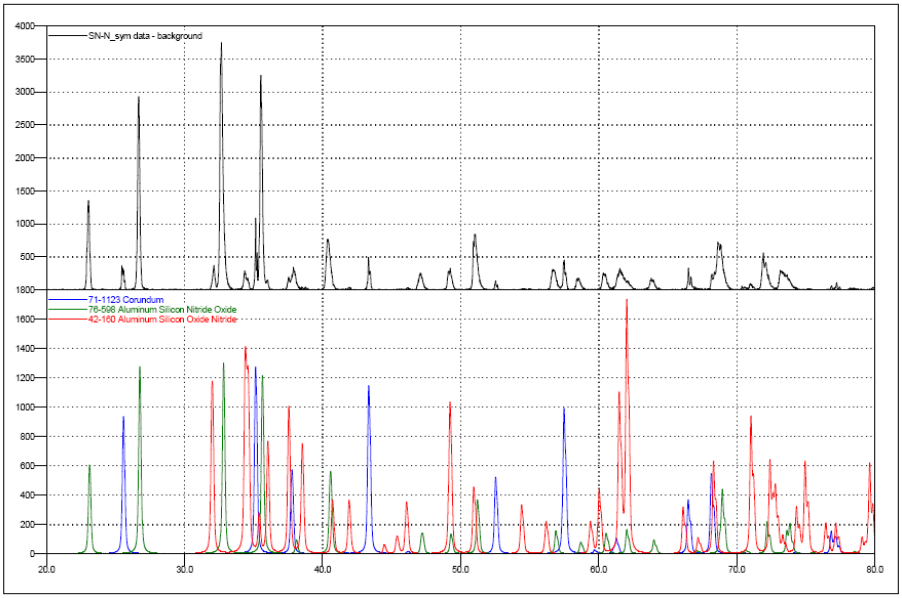

Fig.5 XRD-pattern of β-SiAlON-N sample synthesized from natural raw materials. Absolute intensity (Y-axe) of diffraction peak is plotted against diffraction angle (2 Theta).

The X-ray pattern of sample synthesized from natural raw materials is reported by Fig. 5, in which, it clear that the sample obtained by CTRN of natural raw materials is composed not only by unique phase of SiAlON, but by two types of Aluminum Silicon Nitride Oxide with ICDD File No. 76-598 and 42-160, and a residual of Alumina (ICDD No 71-1123).This result suggested some difficulties to obtain pure β- SiAlON because of reactivity of natural raw materials.

The microstructure of samples are shown in Figs 6 a and b. There is some visible difference on the surface of synthesized β-SiAlON materials. Some porous characteristics are seen on the surface of β-SiAlON from synthetic raw materials, while the second sample presents a dense structure. The bulk density measured by Archimedes method in Hg (3.035 $g.cm^{-3}$ for β-SiAlON-N and 3.092 $g.cm^{-3}$ for β-SiAlON-S) for both samples is closely related to the density values of β–SiAlON prepared by the conventional dry processing and reported by (Ganesh, Thiyarajen, Jana, Barick, Sundarajana and Ferreira 2008), indicating that these β-SiAlON samples were fully densified. The slight difference between them can be due to number of phases present in samples.

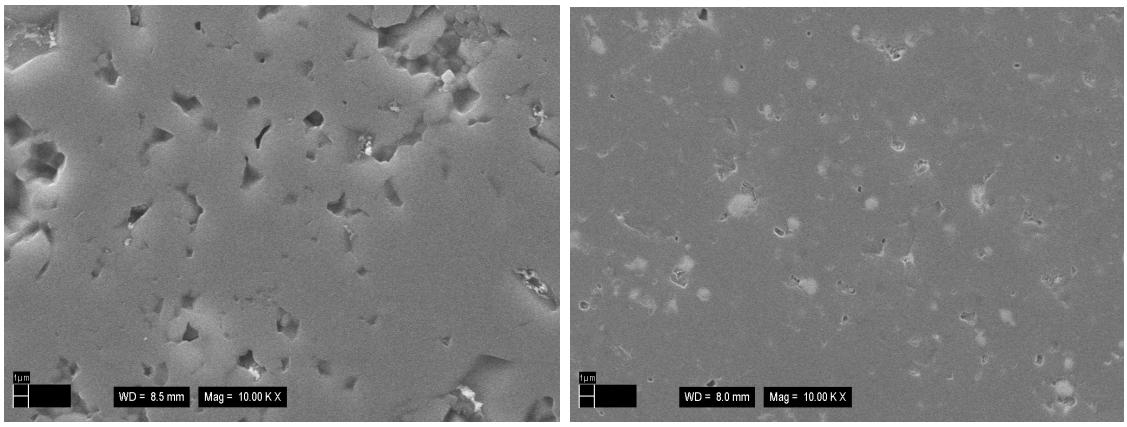

Fig.6 SEM of samples synthesized from a) commercial raw materials and b) from natural raw materials

Thermal cycling

Figs. 7 and 8 show typical crack profile and lateral crack propagation from corner of Vickers's square after repeated cycling. All specimens were cycled with condition mentioned before. During practical experiment, the specimens (S-1, S-2) were first subjected to 3 and 5 thermal cycles respectively, and duration time 16/6 seconds at maximum temperature 1100 °C and minimum 600 °C (ΔT = 500 °C), but these conditions result in broken samples. Then, the

maximum and minimum temperatures were decreased to 1000 °C and 500 °C (ΔT = 500 °C), and time duration to 14/6 seconds to determine the lowest number of cycles, at which crack growth occurred.

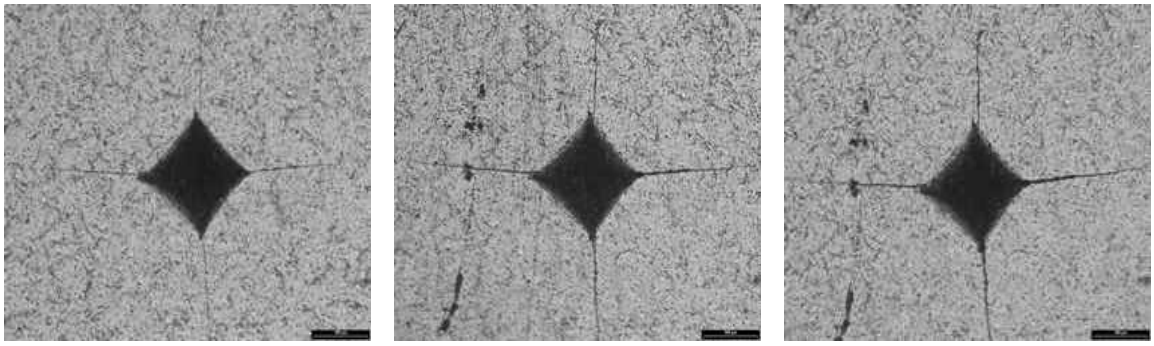

Fig. 7 a) S-7 before cycling b) S-7 after 4 cycles c) S-7 after 5cycle

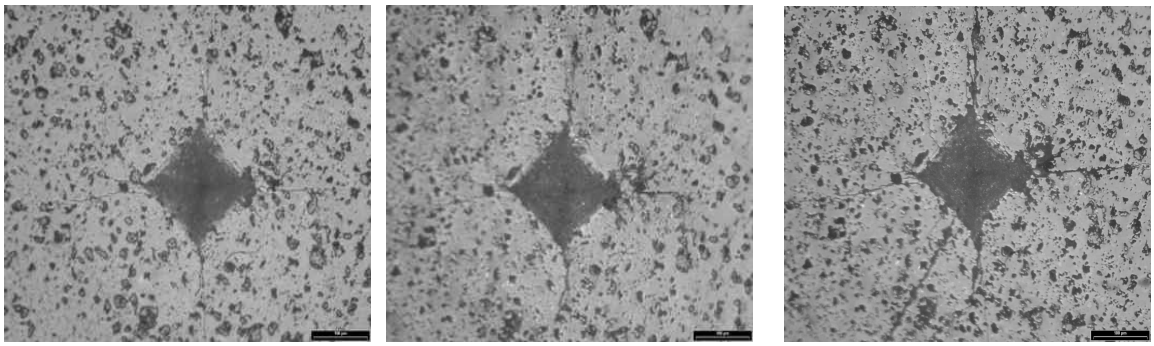

Fig. 8 a) N before cycling b) N after 4 cycles c) N after 5cycle

Mechanical properties

The hardness of the specimens was calculated from the length of the cracks using Equation (1)

$$H_V = 1854\frac{F}{U^2} \qquad (1)$$

Applying the central model of crack growth with a/c > 2.5 (Fig.3), the fracture toughness can be determined from the as-indented crack dimensions as follows in Equation (2) (Anstis, Chantiklul, Lawn and Marchall 1981)

$$K_{IC} = 0.16H_v a^{\frac{1}{2}}\left(\frac{a}{b}\right)^{\frac{-1}{5}} \qquad (2),$$

where H_V is Vickers's hardness [GPa]; F is the loading force [N]; U is the total surface crack length in damage zoom [μm^2]; K_{IC} is the fracture toughness [MPa $m^{1/2}$]; (*U, c, a* and l are illustrated in Fig.2). The calculated values of Vickers's hardness and fracture toughness of individual measurements, as well as their average are listed in Table 1.

Table 1 Experimental values of Vickers hardness and indentation fracture toughness

Samples	H_V [GPa]		K_{Ic} [MPa. (m) $^{1/2}$]	
	β-SiAlON-S	β-SiAlON-N	β-SiAlON-S	β-SiAlON-N
1	12.79	12.48	4.00	4.00
2	13.45	13.08	4.05	3.69
3	11. 89	12.31	4.03	3.88
4	12.79	12.58	4.19	3.20
5	12.69	12.33	4.42	3.99
6	12.31	12.85	3.94	3.68
7	12.08	11.23	4.10	4.58
8	11.63	12.33	3.80	3.55
9	11.94	12.62	4.47	3.60
10	12.48	11.27	4.13	3.60
Average	12.29	12.34	4.11	3.77

The results evidently show that both samples of β-SiAlON ceramics are similar in term of Vickers's hardness and fracture toughness.

The growth of thermal shock cracks

One of the objectives of the present work is to determine the minimal or critical number of cycles that initiate crack growth from initial indentation load flaws and the extension of crack. Tables 2 and 3 report the results obtained with both samples. It can be noted that both samples undergo the same critical number of cycles, but with different extension. The average extension of crack after critical number of cycles is higher with sample from synthetic raw materials than that of sample from natural raw materials. Taking into consideration the result of Vickers hardness, it is evident that β-SiAlON –S are harder than β-SiAlON-N. But, submitted to repeated thermal shock test, the resistance to crack extension of β-SiAlON-N is higher than that of β- SiAlON-S.

Table 2 Critical numbers of heating cycles and extension of β-SiAlON-S samples

β-SiAlON-S.	Cycles applied	Results	Initial length of lateral crack [μm]	Propagation [μm]	Extension [%]
1	4	Crack growth	297.47	89.88	43.29
2	4 5	Crack length unchanged. Crack growth	304.45	105.97	53.39
3	4 5	Crack length unchanged. Crack growth	287.95	75.27	35.38
4	4 5	Crack length unchanged. Crack growth	270.45	89.37	49.36
Average				90.13	45.36

Table 3 Critical numbers of heating cycles and extension of β-SiAlON-N samples

β-SiALON-N	Cycles applied	Results	Initial length lateral crack [μm]	Propagation [μm]	Extension [%]
N-1	4	Crack growth	205.26	63.16	30.77
N-2	4	Crack growth	210.83	71.96	34.13
N-3	4	Crack length unchanged	215.92	65.45	31.40
	5	Crack growth	205.47	59.51	28.96
N-4	4	Crack growth	224.39	59.31	26.43
Average				63.48	30.07

According to the results reported in Tables 2 and 3, the critical number of cycles was found about 4 or 5 indicating possibility of use low-price and abundant natural raw materials

Conclusion

Two samples of β-SiAlON ceramics were synthesized from commercial (SiAlON-S) and natural (SiALON-N) raw materials by hot-pressing method using Y_2O_3 additive. Sample of β-SiAlON-S is a pure β-SiAlON while two kinds of SiAlON and Al_2O_3 were identified in sample β-SiAlON-N. A new method of thermal shock resistance test has shown that both samples have the same critical numbers of cycles to cause crack growth from the initial indentation flaws. Crack extension caused by critical number of heating cycles is lower with β-SiAlON-N than β-SiAlON-S. Vickers hardness and fracture toughness both samples are nearly similar and comparable with other structural ceramics.

Acknowledgment

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References

Absi J, Glandus C (2003): J. Eur. Ceram. Soc. 24: 2835- 2845;

Anstis G R, Chantiklul P, Lawn B R and Marchall D D (1981): J. Am. Ceram. Soc. 64: 533-538;

Andersson T, Rowcliffe D J (1996): J. Am. Ceram. Soc. 79: 1509–1514;

Buessem W R (1955): J. Am. Ceram. Soc. 38:15- 17;

Davidge R W, Tappin G (1967): Trans. Br. Ceram. Soc. 66: 405- 422;

Ganesh G, Thiyarajen N, Jana D C, Barick P, Sundarajana G and Ferreira J M F W(2008): J. Eur. Ceram. Soc. 2879-885;

Glandus J.C., Tranchand V.: Thermal shock by water quenching, numerical simulation, thermal shock and thermal fatigue behavior of advanced ceramics. Nato ASI Series, Series E: Applied Sciences, Vol. 241, 1993, pp. 307–316.

Gondar E., Pulc V., Krizanska M (1995). In: Technologia 95, (pp 34- 40). STU Bratislava;

Gondar E.: The testing method of resistance of silicon nitride based technical ceramics to thermal loading (1998): Conferment Project, SjF STU Bratislava

Gondar E, Hlava T, Roshko M (2006): J. Eur. Ceram. Soc. 26:1743- 1752;

Hasselman D PH (1970): J. Am. Ceram. Soc. 53: 754-760;

Jack K H, (1996): J. Material Science 11: 1135-1137;

Kingery W D (1995): J. Am. Ceram. Soc. 38: 3- 15;

Koh YH, Kim H W, Kim H E, Halloran J (2004): J. Eur. Ceram. Soc. 24: 2339–2347;

Manson S S, Smith R W (1955): J. Am. Ceram. Soc. 38: 18- 27;

Menčík J (1990): Strength and fracture of glass and ceramics, SNTL, Prague;

Pettersson P, Johnsson M, Shen Z (2002): J. Eur. Ceram. Soc. 22: 1357–1365;

Yabuta K, NISISHIO H, Kitamura A (1991): J. Mat. Sci. Lett. 10: 1144- 1145;