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Pyroceram 9606, A Certified Ceramic Reference Material for High-Temperature Thermal Transport Properties: Part 1—Material Selection and Characterization

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Abstract A three-year program of work supported by the European Commission (EC) involving eleven partners from six countries has been carried out to select, procure, characterize, and certify the thermal transport properties (thermal conductivity, λ, and thermal diffusivity, a) of Pyroceram 9606, a polycrystalline glass ceramic identified as the most suitable reference material for use up to at least 1000 °C. For the initial calibration, six blocks were chosen from a batch of 30 blocks purchased for the project. Measurements of the following properties were undertaken: chemical analysis and microstructure, density and porosity, homogeneity, anisotropy, thermal cycling between 20 °C and 1000 °C, and long-term stability and reproducibility. In addition, specific heat capacity, linear thermal expansivity, and thermal transmissivity measurements were carried out so that the thermal conductivity could also be determined from thermal-diffusivity values obtained from the certification measurements. As a result of a successful characterization program, the partners had no hesitation in recommending to the European Commission that full certification of the thermal conductivity and thermal diffusivity of Pyroceram 9606 should be undertaken.

Keywords Certified reference material · High temperatures · Material characterization · Pyroceram 9606 · Thermal conductivity · Thermal diffusivity · Thermal properties

1 Introduction

The present authors have drawn attention to the lack of sufficient numbers and types of reference materials currently required to provide reliability and confidence in

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measured thermal properties [1–3]. In addition, they have identified the gaps that exist, possible candidate reference materials to fill them, and also the need for more international cooperation to help solve the existing problem. Furthermore, they have recently outlined the additional needs of those working with multiproperty transient methods where the requirements are for certified reference values for several thermal properties.

One particularly urgent need, especially for the refractory and ceramic products industries, is for a low to moderate thermal conductivity material ($1 < \lambda < 10\,\mathrm{W \cdot m^{-1} \cdot K^{-1}}$), which is stable and reproducible at temperatures up to at least 1000 °C. Heavy reliance is placed on thermal-conductivity values in the marketing of these products. However, different organizations in different countries measure or derive the property by different methods including some form of the line-source hot-wire method, the guarded hot plate, and the laser flash method; these are described in detail in Ref. [4].

It is well known that there can be significant differences in the thermal-conductivity values obtained by different techniques (including three versions of the hot wire, i.e., resistive wire, cross wire, and parallel wire). As a consequence, a product type is often sold finally on the lowest thermal conductivity quoted. On many occasions there is an unfair advantage between European manufacturers and those from other geographical areas due solely to these measurement differences.

Without an isotropic standard reference material it is not possible to compare thermal conductivity values measured by different test methods. Therefore, all producers of refractory products, which are traded worldwide, face a significant expense in having products tested by the different measurement methods. A certified reference material based on the values obtained by the three basic techniques will help to both reduce the testing expenses and also to remove trade barriers.

To meet this need, the European Commission funded a cooperative investigation under its Standards Measurements and Testing program to identify and purchase a suitable material and undertake the necessary characterization and measurements to provide certified reference values of the thermal conductivity and thermal diffusivity. After completion of the certification measurements by the group, the stock of material and measurement data was given over to the Institute of Reference Materials and Measurements (IRMM), Geel, Belgium for completion of the certification process and organization of the sale of the Certified Material [5].

The present article contains details of the characterization measurements, which justify the choice of Pyroceram 9606 as the proposed reference material. A supplementary article [6] contains details of all the steady-state and the transient measurements of thermal conductivity and thermal diffusivity undertaken for the certification requirements.

2 Participants and Material Selection

The 11 project participants are listed in Table 1. The table contains the acronym for the partner, the full name and address of the organization, the department where the work was carried out, and the technical person responsible for the delivery of results.

Table 1 Details of partners in the EC funded certification program

Abbreviation	Institution	Laboratory/department	Country	Name
ARCS (OFZS)	ARC Seibersdorf Research GmbH, (formerly OFZS) A-2444 Seibersdorf	Materials Technology	Austria	Ing. G. Groboth
CERAM	CeramRes Queen's Road Penkhull, Stoke-on-Trent ST4 7LQ	Thermal Conductivity Testing	UK	Sarah Baxendale
CORUS	Corus R and D (formerly Hoogovens) Wenckebachstraat 1 1970 CA Ijmuiden	Ceramics Research Centre	The Netherlands	Dr. S. Sinnema
FIW	Forschungsinstitut fuer Waermeschutz Lochhamer Schlag 4 D-82166 Grafelfing	Postfache 1525	Germany	R. Schreiner
INSA	Institute Nationale des Sciences Appliquées 20 avenue Albert Einstein F-69621 Villeurbanne cedex	Centre de Thermique de Lyon	France	Dr. D. Baillis
KE	Forschungsinstitut für Kerntechnik und Energiewandlung e.V. Pfaffenwaldring 31 D- 70569 Stuttgart	Energiewandlung und Wärmetechnik	Germany	Dipl.-Ing. R. Brandt
LNE	Laboratoire National d'Essais 29, avenue Roger Hennequin F - 78197 TRAPPES CEDEX	Division Optique et Propriétés Thermiques des Matériaux	France	Dr. B. Hay
Netzsch	Netzsch Geratebau GmbH Wittelsbacherstrasse, 42 D-95100 Selb/Bayern	Thermische Analyse	Germany	Dipl-Phys. J. Blumm
NPL	National Physical Laboratory Queen's Road Teddington TW11 0LW	CBTLM	UK	D. Salmon
PTB	Physikalisch-Technische Bundesanstalt Bundesallee 100, D - 38023 Braunschweig	Dept. 3.102	Germany	Dr. U. Hammer-schmidt
SFC	Societe Francais de Ceramique 23 rue de Cronstadt F - 75015 Paris	Ceramique Industrielles	France	G. Bisson

At the kick-off meeting, the partners considered cordierite, zirconia, a very high-density calcium silicate, and Pyroceram 9606 to be the most promising materials available. The cordierite material has the main advantages of being a commercial material that is relatively cheap and readily available. It was also manufactured by a company whose staff were very familiar with the overall aims of the project and could ensure that the manufacturing process was well controlled so that a good batch of material could be produced. Preliminary investigations of the thermal diffusivity by four different laboratories looked very promising [7]. Unfortunately, the material was found to be potentially unstable due to phase changes during thermal cycling from room temperature to temperatures around 1000 °C. In particular large specimens, such as those required for hot-wire tests, showed evidence of cracking due to differential expansion and contraction within the body of the material. Zirconia and calcium silicate were rejected for being potentially unstable over the temperature range or for having values of thermal conductivity outside the required range.

Pyroceram 9606 had the major advantage of a long history of use in thermal properties measurement. Corning Glass Works (now Corning Inc.) developed the material in the mid 1950s and, because of its excellent mechanical and dielectric properties at high temperatures, it was used for the manufacture of missile radomes. Very detailed specifications and procedures for the manufacture of the material were established by Corning to ensure that consecutive batches of the material had reproducible mechanical and dielectric properties; this is an essential quality factor for its intended application as a reference material. Many laboratories around the world, including Corning and the National Bureau of Standards, NBS (now NIST), have extensively measured the thermal properties of the material. Despite much experimental work to produce a reference material [8], no certified values for its properties have been established. Over the past 30 years or so the material has been very widely used as an unofficial (or historical) reference material having recommended values developed by the Thermophysical Properties Research Center, Purdue University and published by NIST [9].

In general, the earlier work has shown the material to be extremely stable and reliable. The major disadvantages are its relatively high initial and machining costs but these are outweighed by the other very positive attributes. As a result, the partners decided to purchase a batch of the material and established a program to characterize all the properties of a sample from that batch to confirm its suitability as a candidate reference material.

Thirty blocks of the material having approximate dimensions 300 mm × 75 mm × 93 mm were purchased from Corning Inc. and delivered to NPL in March 1999 for subsequent documentation and machining by CERAM and NPL.

3 Characterization Program

Six blocks were chosen randomly from the batch to provide enough specimens for all the characterization measurements by the different partners. Figures 1 and 2 contain details of the cutting plan for the blocks and the individual specimens for the appropriate tests, respectively. The 20 % sample size was considered to be more than adequate to be representative of the batch.

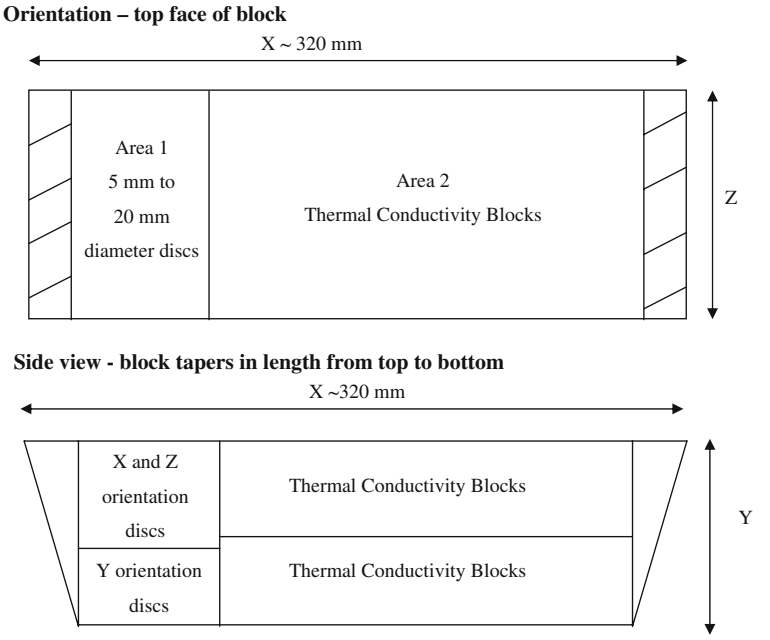


Fig. 1 Cutting plan for blocks 1–4

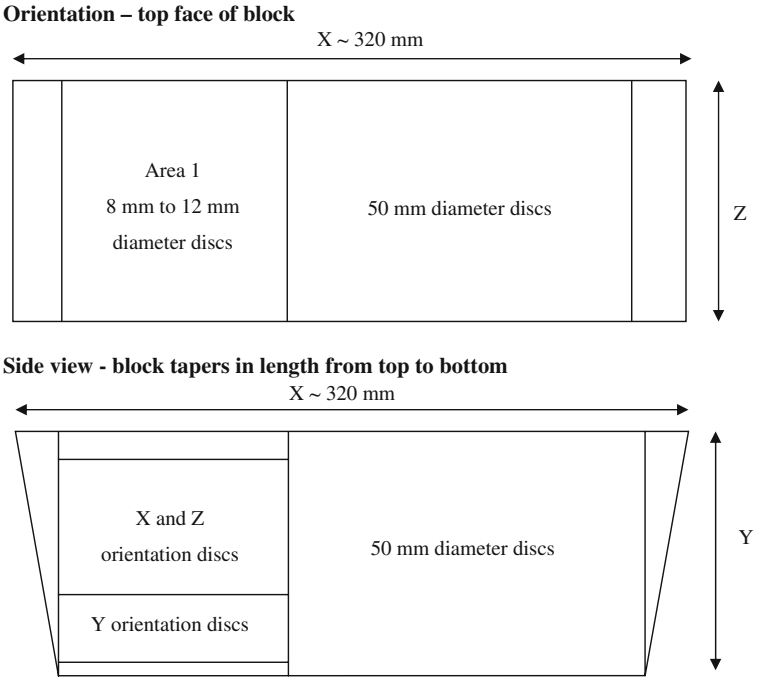


Fig. 2 Cutting plan for blocks 5 and 6

To confirm its suitability as a reference material, the following material parameters were investigated:

- Chemical analysis and microstructure
- Density and porosity
- Homogeneity
- Anisotropy
- Stability on thermal cycling between room temperature and 1000 °C
- Long-term stability and reproducibility of thermal property measurements

In addition, it was seen as essential to fully characterize the material by measuring the following properties in order to be able to derive the thermal conductivity of the material from thermal diffusivity results measured during the certification:

- Specific heat capacity
- Thermal expansion
- Thermal radiation transmission and emissivity

4 Characterization Measurements

4.1 Composition and Microstructure

ARCS and Corus undertook this analysis using different techniques. ARCS used a combination of inductive coupled plasma and atomic emission spectroscopy (ICP/AES) and X-ray diffraction to identify and determine the constituents and phases, respectively. In addition, Corus analyzed the microstructure by the use of scanning electron microscopy (SEM). Quantification of the SEM images to give the mean elemental distribution was carried out by the use of electron probe microanalysis (EPMA) at about 25 to 27 locations within each specimen. Pore size and grain size distributions were determined by use of filter techniques (e.g., false color imaging).

4.2 Density

Corus and NPL carried out room-temperature measurements again using different techniques. The former measured the apparent density in accordance with the ISO 5017 standard. This involved weighing 20 mm diameter, 20 mm thick specimens (MS) dry, impregnated with water, and immersed in water. The density and porosity were obtained by applying Archimedes' principle. NPL used the hot-wire thermal-conductivity specimens (identified by the prefix HW) and measured the dry mass and all dimensions accurately including estimates for small chipped areas, and calculated the density or mass per unit volume in the dry state. Measurements were made on the specimens of the virgin material and on the same specimens after heating to 1000 °C and cooling to room temperature.

4.3 Homogeneity and Anisotropy

Several techniques were used to examine the homogeneity of the material. These included measurements on the specimens cut in the three orthogonal directions from the blocks to evaluate the extent of any anisotropy in the properties.

4.3.1 Ultrasonic Velocity

Measurements were undertaken by Ceram using a portable nondestructive digital indicating tester (PUNDIT) with a 200 kHz transducer. This measures the time taken for a pulse to travel between a transmitter and receiver. One or two determinations were made across the major dimension and three across each of the two minor directions.

A first series of measurements was made on six blocks in the as-received condition with the surfaces in the as-cast state. Following this, a similar series of tests was made on the machined large rectangular brick specimens prepared from three blocks for hot-wire measurements of thermal conductivity.

4.3.2 Thermal Diffusivity

In the overall characterization testing, three organizations measured this property. The major study to investigate possible anisotropy was carried out by KE using the modulated beam technique. Specimens were prepared in three orthogonal directions from blocks 4, 5, and 6. In the case of block 5, three specimens in each orientation were measured and, in all cases, measurements were made on heating to and cooling from 1000 °C.

LNE and NPL carried out measurements using the laser-flash method on specimens cut in the *y*-orientation essentially to investigate the stability of the material as described later. However, the results for this direction could be compared with those from KE. The possible effect of surface coatings was also examined during this series of measurements. NPL and LNE had duplicate specimens. One set was coated with tungsten, the normal coating used by KE. The other set was coated with graphite by NPL and with gold by LNE.

4.3.3 Thermal Expansion

ARCS measured duplicate 25 mm long specimens cut in three orthogonal orientations from blocks 1, 2, and 3. The measurements were carried out in duplicate runs using a push rod dilatometer system on heating at $5\,\mathrm{K}\cdot\mathrm{min}^{-1}$ to 1000 °C and on cooling back to room temperature. Measurements were made in a similar manner (but at $2\,\mathrm{K}\cdot\mathrm{min}^{-1}$) by LNE on specimens cut from block 3.

4.3.4 Specific Heat Capacity

Five partners measured the specific heat of three specimens from three different blocks. All the specimens were prepared in the *x* direction for convenience since the specific heat is not affected by orientation. Details of the procedures and results are provided

in the accompanying article since they are more relevant to the analysis of the thermal transport properties.

4.4 Stability

4.4.1 Short-Term Stability Due to Thermal Cycling

This behavior was studied by CORUS based predominantly on measurements of sound velocity and acoustic attenuation before and following a number of heating cycles. The partners defined a thermal cycle for this test as heating a hot-wire specimen (thickest specimen available) from room temperature to 1100 °C at $5\,\mathrm{K}\cdot\mathrm{min}^{-1}$; hold for 1 h and cool to room temperature at the same rate. A sequence of measurements was then developed as follows:

1. Measure ultrasonic speed and thermal conductivity,
2. Cycle three times to 1100 °C,
3. Re-measure the sound velocity and attenuation,
4. Repeat steps (2) and (3) five times so that the specimens had been cycled 15 times from room temperature to 1100 °C, and
5. Re-measure the thermal conductivity (or earlier than 15 cycles if the sound velocity and attenuation change vary significantly).

Sound velocity and attenuation were measured in three perpendicular directions on the specimen to measure all possible orientation of cracks. The acoustic measurements are performed using a Sonic FTS Mark IV tester with a thickness measurement adaption. Using a combined emitter/receiver sensor, an acoustic pulse is generated in the examined material, reflected at the end of the material, and received back at the sensor. The frequency of the sensor is 7.5 MHz. By measuring the pulse height of the reflection peaks, the attenuation produced by the material is calculated. In addition, the sound velocity is measured by recording the position of the reflection peaks on the time axis. A change in velocity and attenuation indicates a degradation (crack formation) in the examined material.

Measurements of thermal conductivity had been planned at each stage but unfortunately after the first cycling, it was discovered that one of the brick pieces had cracked and broken along the groove in the longer direction. Although the groove had been machined very carefully, micro-cracks had probably been introduced in the material causing an induced thermo-mechanical stress of sufficient magnitude to cause critical crack growth. This failure did not affect the sound velocity tests. However, the hot-wire specimens used by the other participants have not shown similar susceptibility to cracking.

4.4.2 Long-Term Stability

This was monitored by LNE by measuring the thermal diffusivity of a set of four specimens cut from one block initially and then after periods of (3, 6, 12, and 24) months. All measurements were carried out at temperatures of 23 °C, 400 °C, and 800 °C on tungsten-coated specimens in argon and in a vacuum of 1.4×10^{-3} torr.

Table 2 Chemical analysis of Pyroceram 9606 batch

Substance	% Content	
	Corus	ARCS
SiO_2	56.0	56.8
Al_2O_3	19.62	19.4
MgO	14.85	13.9
TiO_2	8.58	8.8
K_2O	0.02	0.08
As_2O_3	–	0.4
Fe_2O_3	–	0.04
SnO_2	–	0.04
CaO	0.16	0.2
Na_2O	0.07	0.2
Other	0.3	–
Total	99.6	99.9

Corus values are means of measurements taken from 25 to 27 locations within a specimen

4.5 Thermal Radiation Transmissivity and Emissivity

The measurements of the thermal radiation transmissivity were undertaken by PTB and INSA, while the emissivity measurements were carried out by NPL. As for the specific heat, details of the measurements and results are provided in the accompanying article.

5 Results

5.1 Composition and Microstructure

Table 2 summarizes the very similar chemical analysis obtained by the two organizations. The chemical composition consists primarily of the oxides of silicon, aluminum, magnesium, and titanium, with less than 1 % of other minor oxides. The fully cerammed material consists primarily of a cordierite phase ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), with smaller amounts of cristobalite (SiO_2), rutile (TiO_2), and magnesium aluminum titanate ((Mg,Al) $(Ti,Al)_2O_5$) as well as some residual glassy phase. No significant differences were observed between specimens from different blocks.

5.2 Density

The results of the NPL density measurements are shown in Table 3, and Table 4 summarizes the results for Corus and NPL. Table 5 also shows the apparent porosity of the Corus specimens. The results show a remarkable agreement and homogeneity indicating an average density of all specimens of 2602 $kg \cdot m^{-3}$ with a standard deviation of 0.25 %. The largest difference is shown for block 4, which has a standard deviation

Table 3 NPL density measurements showing change due to expansion on heating to 1000 °C

	Density ($kg \cdot m^{-3}$)			
Specimen	HW1.1	HW1.2	HW3.1	HW4.1
Block number	1	1	3	4
Prior to testing	2591	2599	2600	2597
Heated to 1000 °C	2571	2580	2571	2578
Permanent expansion (%)	0.26	0.24	0.37	0.24

Table 4 Summary of NPL and Corus density measurements before heating to 1000 °C

Specimen number	Density ($kg \cdot m^{-3}$)	Mean density ($kg \cdot m^{-3}$)	SD ($kg \cdot m^{-3}$)	SD (%)
HW1.1	2591			
HW1.2	2599			
MS1.3	2600	2597	4.03	0.16
MS2.1	2612	2612	0	0
MS3.1	2608			
HW3.1	2600	2604	4.0	0.15
HW4.1	2597			
MS4.1	2611			
MS4.2	2598			
MS4.3	2608	2604	6.10	0.23
Mean of all data	2602		6.56	0.25

Table 5 Corus porosity measurements

Specimen number	Apparent porosity (%)
MS 1.1	0.48
MS 2.1	0.16
MS 3.1	0.32
MS 4.1	0.16
MS 4.2	0.48
MS 4.3	0.16

of 0.23 % from its mean value. Similarly, the porosity measurements indicate that it is less than 0.48 %, which tends to substantiate the claim of zero porosity made by the manufacturer. This attribute is a significant one for a reference material, especially one for use at high temperatures, since it minimizes the possibility of any significant radiative heat transmission within the bulk material so that the predominant mode of heat transfer is by solid conduction.

It should be noted, however, that the NPL results, Table 3, indicated that while there was no increase in mass, the specimen volume had changed due to a permanent

Table 6 Summary of results of ultrasonic velocity tests

Specimen	Direction	Velocity ($m \cdot s^{-1}$)	SD ($m \cdot s^{-1}$)	SD (%)
Original block	Length (321 mm)	7264	55	0.76
	Depth (71–78 mm)	7622	75	0.98
	Width (95–100 mm)	7362	75	1.02
Machined HW specimen	Length (230 mm)	7516	25	0.33
	Depth (34–49 mm)	7639	73	0.96
	Width (91–93 mm)	7507	36	0.47

expansion of about 0.28 % following the first heating of the material to 1000 °C and cooling to room temperature.

5.3 Homogeneity and Anisotropy

5.3.1 Ultrasonic Velocity

The results for the two series of measurements are summarized in Table 6. The initial measurements on the unmachined blocks appear to indicate some difference with v_y (depth) $>$ v_z (width) $>$ v_x (length). However, the results for the specimens machined from three blocks, while indicating a similar but much smaller trend, show that there is no significant difference in the values obtained with this type of test. These results can be explained by the fact that the surfaces of the original blocks were not smooth and could affect contact with the probes.

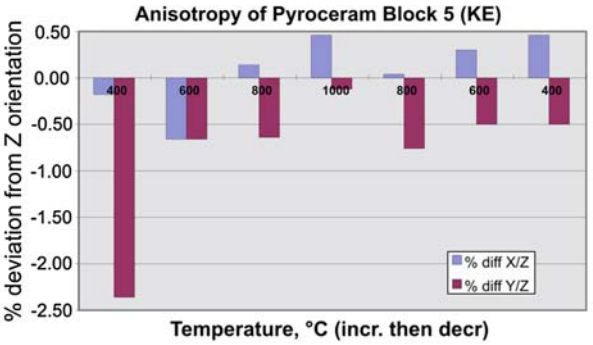
5.3.2 Thermal Diffusivity

Figure 3 summarizes the results of the measurements on the triplicate specimens from blocks 4, 5, and 6. For the complete series, the scatter, although lower on the cooling runs, was found to be less than ±2 % and no significant differences were seen between the heating and cooling runs. The results on the single specimens from blocks 4 and 6 confirmed those for block 5 although the scatter at temperatures below 400 °C increased to ±3 %. Overall, any differences seen in the values are within the experimental uncertainty and show conclusively that there is no anisotropy within the material.

5.3.3 Thermal Expansion

The results obtained by ARCS are summarized in Table 7. This shows the percentage difference from the overall mean value for each orientation for the separate runs on specimens cut from one block. Very similar results were obtained for those specimens cut from the other blocks. Results of the measurements by LNE confirmed those of ARCS although they exhibited more scatter particularly in the temperature range below 300 °C.

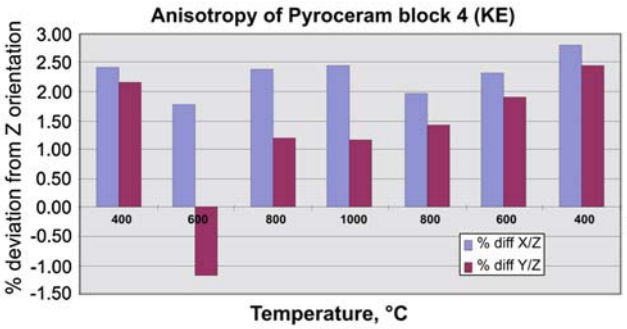
One particular point was that both organizations observed a permanent change of the order of 0.28 % in the expansion between the first and second runs. Further details of



Orientation effects in Block 5

Temp	X/Z % diff.	Y/Z % diff.
400	*-0.18*	*-2.36*
600	*-0.66*	*-0.66*
800	*0.14*	*-0.65*
1000	*0.46*	*-0.12*
800	*0.04*	*-0.75*
600	*0.30*	*-0.50*
400	*0.45*	*-0.51*

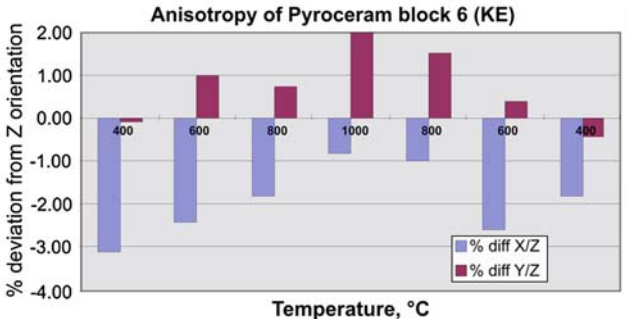
3 specimens per orientation



Orientation effects in Block 4

Temp	X/Z % diff.	Y/Z % diff.
400	2.42	2.15
600	1.78	-1.19
800	2.38	1.19
1000	2.43	1.16
800	1.95	1.41
600	2.32	1.92
400	2.81	2.45

One specimen per orientation



Orientation effects in Block 6

Temp	X/Z % diff.	Y/Z % diff.
400	-3.09	-0.09
600	-2.40	1.00
800	-1.83	0.75
1000	-0.81	1.97
800	-0.98	1.52
600	-2.61	0.40
400	-1.80	-0.45

One specimen per orientation

Fig. 3 KE thermal diffusivity results investigating anisotropy in blocks 4–6

the thermal expansion results will be discussed in the second part of this article when the results are used to make corrections for changes in specimen thickness during thermal diffusivity measurements.

5.4 Stability

5.4.1 Short-Term Stability Due to Thermal Cycling

Table 8 contains the results for the acoustic velocity and attenuation for the different orientations and before and after thermal cycling three times between 1100 °C and

Table 7 Thermal expansion results on specimens of different orientations cut from Block 3 ($\Delta L/L \times 10^3$)

Block 3 mean		% difference from the mean in each orientation		
T (°C)	TE3 first	x-	y-	z-
20				
100	0.62	1.37	−2.60	1.22
200	1.34	0.76	−1.58	0.82
300	1.74	0.96	−1.56	0.60
400	2.13	1.19	−1.56	0.37
500	2.54	1.40	−1.49	0.09
600	2.96	1.46	−1.35	−0.11
700	3.43	1.62	−1.36	−0.26
800	4.03	1.59	−1.17	−0.42
900	4.65	1.67	−1.29	−0.38
1000	5.25	1.87	−1.38	−0.49
1100	5.83	2.15	−1.37	−0.78
	TE3 second			
20				
100	0.58	1.59	−1.25	−0.34
200	1.34	0.34	−0.60	0.26
300	1.73	0.49	−0.33	−0.16
400	2.11	0.47	−0.21	−0.26
500	2.52	0.66	−0.30	−0.36
600	2.95	0.83	−0.36	−0.47
700	3.39	1.07	−0.31	−0.76
800	3.90	1.04	−0.26	−0.49
900	4.40	1.05	−0.37	−0.67
1000	4.82	1.27	−0.60	−0.66
1100	5.23	1.54	−0.89	−0.65

room temperature. The tests were expected to be carried out with a minimum of five sets of three cycles to 1100 °C but the specimen broke along the thermocouple groove as described earlier (Sect. 4.4.1) and the tests were stopped.

In order to obtain the best operating conditions for the measurement of thermal conductivity, NPL has cycled 35 mm and 50 mm thick hot-wire specimens from room temperature up to 1000 °C and back several times in carrying out measurements using the parallel wire and resistive wire mode with no visible detrimental effect to the specimens. However, Corus found that after one thermal cycle of their 35 mm thick hot-wire specimens that one of them cracked along the groove machined in the specimen surface for the thermocouple. This was unfortunate but it is thought that the crack was initiated by micro-cracks introduced during the machining of the specimen.

Table 8 Ultrasonic velocity and attenuation in three orientations in a hot-wire specimen of Pyroceram 9606

Condition	Velocity ($m \cdot s^{-1}$)	Peak	Attenuation (dB)		
			34 mm thick direction	92 mm width direction	230 mm length direction
Initial	7479	1st	45	64	81
		2nd	61	88	Weak
3 cycles to 1100 °C	7370	1st	42	59	NA
		2nd	59	70	NA

Table 9 Stability of four specimens of Pyroceram 9606 after repeated measurements over a two-year period

Specimen	Temp (°C)	Jan 2000	April 2000	August 2000	Jan 2001	Jan 2002	Mean value	SD	SD (%)
		Thermal diffusivity ($10^{-6} m^2 \cdot s^{-1}$)							
TD5.3	23	1.905	1.912	1.912	1.923	1.898	1.910	0.009	0.5
	400	1.125	1.121	1.125	1.119	1.106	1.119	0.008	0.7
	800	0.940	0.934	0.930	0.926	0.912	0.928	0.010	1.1
TD5.4	23	1.939	1.947	1.946	1.964	1.950	1.950	0.010	0.5
	400	1.159	1.142	1.147	1.152	1.146	1.146	0.011	0.9
	800	0.968	0.953	0.949	0.961	0.954	0.954	0.012	1.2
TD5.10	23	1.907	1.956	1.940	1.931	1.920	1.931	0.018	1.0
	400	1.130	1.122	1.125	1.124	1.124	1.124	0.003	0.3
	800	0.958	0.932	0.933	0.962	0.936	0.944	0.014	1.5
TD5.11	23	1.956	1.947	1.928	1.961	1.935	1.945	0.014	0.7
	400	1.132	1.132	1.126	1.135	1.116	1.128	0.008	0.7
	800	0.944	0.933	0.952	0.953	0.917	0.940	0.015	1.6

5.4.2 Long-Term Stability

Table 9 shows the thermal-diffusivity measurements carried out by LNE over the final 2 years of the project after the acquisition of the batch of Pyroceram 9606 and the manufacture of all the specimens required for the characterization tests. Over the 2 years the results show no drift to higher or lower values and the standard deviation of the measured values from the mean value is 1 % or less at 23 °C and 400 °C and less than 1.5 % at 800 °C.

6 Conclusions

6.1 Anisotropy

The results from ultrasound velocity, thermal expansion, and thermal diffusivity measurements show that, within the limits of measurement uncertainty for the respective

apparatus, the Pyroceram 9606 batch is isotropic and that the thermal properties do not vary with orientation by more than 1 %.

6.2 Homogeneity

All the results obtained by the partners on density, thermal expansion, thermal diffusivity, and specific heat show that the batch of Pyroceram 9606 is homogeneous both within blocks and between blocks taken at random from the batch of material. Of the 30 blocks of material acquired, six blocks have been tested which is considered to be a more than sufficient sample to represent the properties of the entire batch.

6.3 Porosity

The material is claimed by the manufacturer to have zero porosity, and measurements by Corus have shown that the porosity is less than 0.48 %. This virtually negligible porosity is an advantage to reference materials for use at high temperatures as it reduces the possibility of radiative heat transfer within the bulk of the material so that the predominant mode of heat transfer is conductive.

6.4 Chemical Analysis and Microstructure

Pyroceram is an opaque glassy ceramic with high strength and elastic modulus and an operational temperature covering the range from −200 °C to 1000 °C; the material starts to soften at 1350 °C. The chemical composition consists of refractory oxides of aluminum, magnesium, titanium, and predominantly silica. These are present in amorphous phases of cordierite, armarcolite, and cristobalite.

6.5 Stability on Thermal Cycling

There is some evidence from the thermal expansion and density measurements of a small, 0.28 %, permanent expansion that takes place on heating the material to 1000 °C and cooling to room temperature. This effect is very small and is extremely unlikely to have any effect on the thermal properties of the material. It may be that the material will have to be heat treated by taking it up to 1000 °C and holding it there for a couple of hours before cooling to room temperature.

During their initial hot-wire measurements NPL cycled 35 mm and 50 mm thick specimens from room temperature up to 1000 °C and back several times with no visible detrimental effect to the specimens. However, Corus found that after one thermal cycle a hot-wire specimen cracked along the groove machined in the specimen surface for the thermocouple (Sect. 5.4.1).

6.6 Long-Term Stability

These tests were carried out during the lifetime of the project by LNE measuring the thermal diffusivity of a set of four tungsten-coated specimens in argon and in vacuum. The consistency of the results on individual specimens and within the set of four specimens indicates that there are no effects due to aging and repeated cycling to and from 800 °C.

6.7 Summary

The results of the characterization phase of the project are as follows:

- The composition of the material is predominantly silica with some refractory oxides of aluminum, magnesium, and titanium.
- The material is homogeneous, having a density of $(2600 \pm 1)\ \mathrm{kg \cdot m^{-3}}$ and a porosity of less than 0.5 %, both within and between blocks.
- Sound velocity, thermal expansion, and thermal diffusivity results showed that the material is essentially isotropic since these properties varied with orientation by less than 1 % for the first two properties and 3 % for the thermal diffusivity, well within the experimental uncertainty.
- Some evidence of a small (0.28 %) permanent change in thermal expansion and density after heating to 1000 °C and cooling to room temperature and of a minor phase change in the range from 150 °C to 180 °C was observed. However, these very small effects are unlikely to affect the thermal transport properties to any extent.
- Cycling of the material between 20 °C and 800 °C and aging over a two-year period have no visible or significant detrimental effect on the material or its thermal diffusivity.
- Thermal transmissivity measurements of thin specimens from 1 mm to 5 mm thick indicate that the material is essentially opaque to thermal radiation of wavelengths in the range of 1.25 μm to 20 μm, confirming that the predominant heat transmission mode over most of the temperature range is by conduction.

7 Recommendation

All the above evidences collected by the partners show that Pyroceram 9606 has excellent characteristics that make it an ideal candidate for a Certified Reference Material. The batch of material has been shown to be very uniform and isotropic. It is also stable in the short term; and the long-term stability is being investigated throughout the project but this is thought to be a low-risk factor in the light of other studies with the material.

The partners therefore had no hesitation in recommending to the Commission that the project should progress to the next stage, i.e., full certification of the thermal diffusivity and thermal conductivity of Pyroceram 9606 over the temperature range from 100 °C to 1000 °C.

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