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Study of Special Ceramics with a Dilatometer for the Temperature Range up to 2000°C[1]

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Many properties of special ceramic materials, often closely related, such as sintering temperature, shrinkage in firing, mineral reaction, and strength can be studied with thermal analysis. Also, the influence of type, structure, and preparation of raw materials, plasticizers, and binding materials for forming and compressing, as well as the compatibility with protective coatings (glazes, varnishes, metal films), is investigated by thermal analysis. The development of a new dilatometer for the temperature range 25–2000°C with maximum heating rates of 20 $K \cdot min^{-1}$ and samples 25–50 mm in length and 6–12 mm in diameter for measurements in argon armosphere and vacuum has opened up new horizons. Sintering studies at high temperatures are described.

KEY WORDS: ceramics; dilatometry; high temperatures; instrumentation; refractory materials; sintering studies; thermal expansion.

1. INTRODUCTION

The development of high-performance materials for many branches of modern technology favors technical ceramics rather than metals. With the exception of specially developed alloys, the so-called high-tech ceramic materials are–together with polymeric materials—of the greatest importance in terms of the increase in production efficiency, product improvement, energy, and raw materials, as well as decreasing the impact on the environment. Worldwide, enormous efforts are being made to characterize analytically ceramic materials, optimize the production methods, and develop the desired product properties for special applications.

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Thermoanalytical processes indicate the application limits in the range of high temperatures as well as the compatibility with other materials in composites. The temperature stability, corrosion behavior in different atmospheres, and phase transitions are studies by thermogravimetry (TG), differential thermal analysis (DTA), and evolved gas analysis (EGA) with commercial units [1]. Precise measurement of thermal expansion and changes in dimension during structural modifications can be realized with dilatometry in the temperature range up to 2000°C. In the following the technical performance of our instrument is shown, and special application examples in the area of high-tech ceramics are discussed.

2. EXPERIMENTAL

For measurements of technical ceramics and refractory metals a newly developed single push-rod dilatometer was used. The construction of the instrument is shown in Fig. 1.

The sample support, measuring unit, and displaceable furnace are mounted horizontally. Sample support and push rod are made of the same pure graphite material and were subjected to a tempering process higher than the application limit of 2000°C. Reproducible dilatation behavior of these essential construction elements can, therefore, be achieved. Measurement is made by an inductive transducer (LVDT) which has a linear range of 5 mm. This transducer is connected to a carrier frequency measuring amplifier for selection of calibrated measuring ranges. The

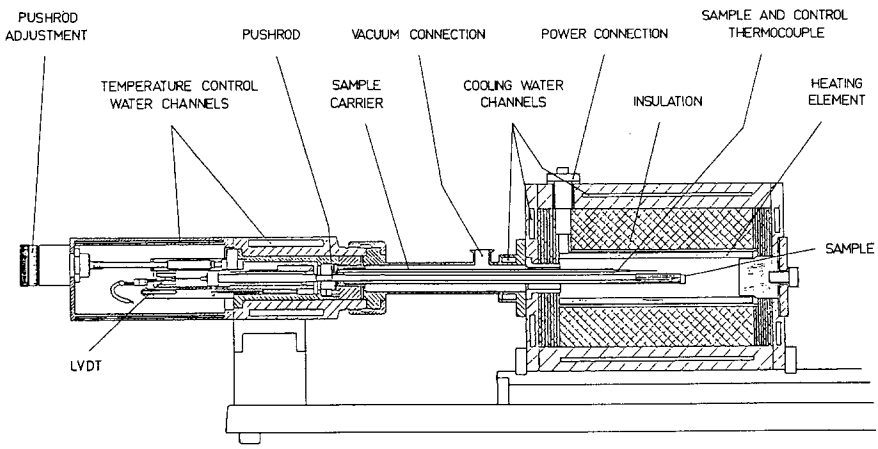


Fig. 1. Schematic diagram of the dilatometer (Netzsch 402 E/7) for thermal expansion measurements to 2000°C.

measurement of temperature is made by a W–Re thermocouple placed directly on the sample. The push rod, which is adjustable to different sample lengths from 0 to 25 mm, applies a small force of 0.2 N on the sample–small enough to ensure no plastic deformation of the sample at high temperatures. Extensive thermostatic control of the mechanical parts and transmission elements prevents the influence of changing ambient temperatures on the measuring results. The high-temperature furnace is heated by a bifilar machined graphite tubular heating element, which is insulated with carbon fiber material against the water-cooled furnace wall. The furnace space is vacuum tight and the sample support is enclosed in a vacuum-tight area. The energy demand of the furnace is very small—on the average, 5 kVA up to 2000°C in an argon atmosphere—with good control performance even at high heating and cooling rates (up to $50\ \mathrm{K} \cdot \mathrm{min}^{-1}$). The instrument design also permits the use of a protective tube in the furnace separating the sample space from the heating element, thereby offering more possibilities for the selection of atmospheres on the sample. Data acquisition and recording can be analog or digital.

3. RESULTS AND DISCUSSION

The measuring results of a push-rod dilatometer are influenced by several factors [2]: the material of the sample support and push rod, sample position, transducer, furnace system, and temperature measurement; therefore, calibration is essential for achieving precise and reproducible results [3]. The exact calibration of a dilatometer with a temperature range above 1600°C is very difficult due to the lack of certified standard reference materials. Using materials which are applicable in the highest temperature range, e.g., tungsten, one has to use the dilation values given in the literature [4]. In this case, efforts are necessary to obtain generally available standards with certified dilatation values. Based on this problem, it is reasonable to test a highest-temperature dilatometer in the range of validity of the usual standard reference materials. Figure 2 shows the comparison of uncorrected dilatation curves of synthetic sapphire (NBS SRM 732) and sintered Al_2O_3 samples (dilatation values according to DIN 51045). These well-known reference materials show very good reproducible results in repeated measurements. This proves the good reproducibility of the graphite sample support in this temperature range.

A promising ceramic material for use in combustion engines, especially diesel engines, is ZrO_2. The high expansion coefficient allows direct combination with metals. The use of pure ZrO_2 causes problems due to the polymorphism of this material, especially because of the crystal transition monoclinic–tetragonal at a temperature of 1100°C. The dotation with

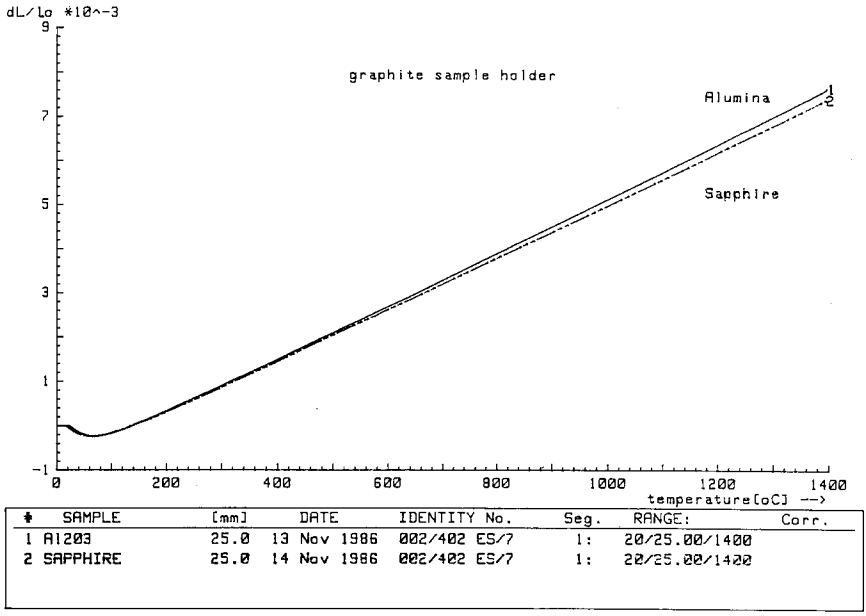


Fig. 2. Thermal expansion of alumina and sapphire; graphite sample holder used.

oxides will result in partial or complete stabilization of the cubic high-temperature form of ZrO_2 so that up to the melting point no transition can be seen. For this practical application, partially stabilized ZrO_2 has proven better suited for several reasons, such as thermal shock resistance, grain structure, stability, and toughness. Dilatometry is, in this case, a reliable method for the analysis of degree of stabilization, i.e., the remaining monoclinic structure.

Figure 3 shows the testing of partially stabilized ZrO_2 in an argon atmosphere with the transition monoclinic–tetragonal in the temperature range of 1092°C up to 1256°C. The average expansion coefficient in the range of 60 to 1010°C is $7.86 \times 10^{-6} x^{-1}$; after transition it is $101 \times 10^{-6} x^{-1}$. The change in length (shrinkage) of the sample during the transition phase is 0.45% with regard to the initial length. The hystereses of the transition during the cooling phase was not tested, as no details regarding the composition of this technical material were available for further interpretation.

Figure 4 shows the application of a dilatometer to the study of sintering processes. Powder compacts of SiC with additives were sintered in a dilatometer (unsintered material) as well as externally (sintered material). The comparison of the samples shown in Fig. 4 indicates the release of additives in the curve of the unsintered material in the temperature range

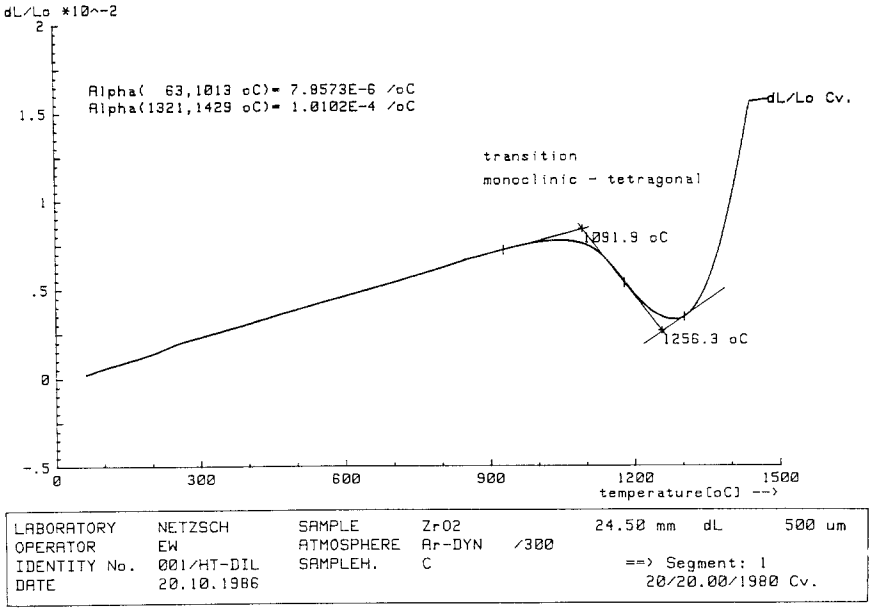


Fig. 3. Thermal expansion of partially stabilized ZrO_2.

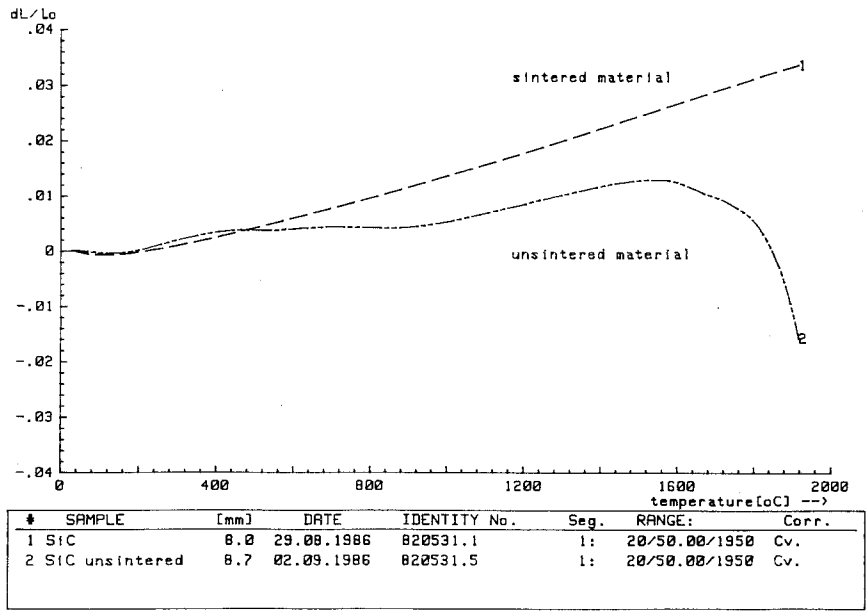
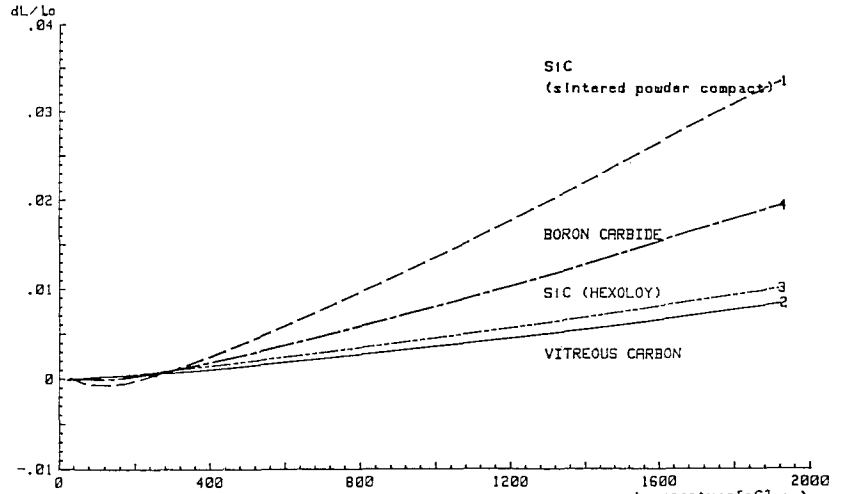


Fig. 4. Comparison of thermal expansion of sintered and unsintered SiC powder compacts (with additives).



#	SAMPLE	[mm]	DATE	IDENTITY No.	Seg.	RANGE:	Corr.
1	SIC	8.0	29.08.1986	820531.1	1:	20/50.00/1950	Cv.
2	VITREOUS CARBON	24.9	01.09.1986	520531.2	1:	20/50.00/1950	Cv.
3	SIC(Hexoloy)	24.8	03.09.1986	820531.7	1:	20/50.00/1950	Cv.
4	B4C	15.0	01.09.1986	520531.4	1:	20/50.00/1950	Cv.

Fig. 5. Comparison of thermal expansion of high-tech ceramic materials.

up to 1000°C as well as the beginning of sintering at 1533°C and the acceleration of the shrinkage at 1812°C. The selected maximum temperature of 1950°C is not sufficient for completion of the sintering process of this material.

The wide range of dilatation values of crystalline and amorphous high-tech ceramic materials and, therefore, also the wide range of application of dilatometry are shown in Fig. 5.

With the exception of possible contact reactions between sample support and sample, which can be prevented in many cases by selecting inert liners, there are no restrictions for the use of the instrument up to a maximum temperature of 2000°C. The components of the sample support and the thermocouple are easily and quickly replaceable, low-cost spare parts. Alternative materials are being investigated.

4. CONCLUSION

In the field of technical ceramics, material analysis is of great importance. Dilatometry determines two important thermophysical parameters with great exactitude, the thermal dilatation and the coefficient of expansion. This means that the application possibilities of materials can be

exactly determined, especially in composite systems with other materials. The newly developed dilatometer with a temperature range up to 2000°C covers the highest temperature range for high-tech ceramic materials.

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