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Study of Special Ceramics with a Dilatometer in the Temperature Range 25–2000°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 and, of plasticizers and binding materials for forming and compressing, as well as the compatibility with protective coatings (glazes, varnishes, metal films), are 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 sample sizes 25–50 mm in length and 6–12 mm in diameter for measurements in an argon atmosphere and vacuum has opened up new horizons. Sintering studies at high temperatures are described.

KEY WORDS: ceramics; dilatometry; high temperatures; 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 great importance in terms of the increase in production efficiency, product improvement, and energy and raw material savings, as well as decreasing the load on the environment. Worldwide, significant efforts are being made to characterize analytically ceramic materials, optimize the production methods, and develop the desired product properties for special applications.

Thermoanalytical processes indicate the application limits in the range of high temperatures as well as the compatibility with other materials in

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composites. The temperature stability, corrosion behavior in different atmospheres, and phase transition are studied by thermogravimetry (TG), differential thermal analysis (DTA), and gas analysis (EGA) with commercial units [1]. Precise measurement of thermal expansion and change in dimension during structural modifications can be realized with dilatometry at temperatures up to 2000°C. In this paper, the technical performance of the instrument is shown and special examples of its application in the area of hightech ceramics are discussed.

2. EXPERIMENTAL

For measurements of technical ceramics and refractory metals a newly developed push-rod dilatometer was used. The schematic of the instrument is shown in Fig. 1. The sample support, the measuring unit, and the displaceable furnace are mounted horizontally. The sample holder (tube) and the 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 (with an accuracy of 0.4%) 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 temperature is measured by a 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 prevent the influence of changing ambient temperatures on the measuring results.

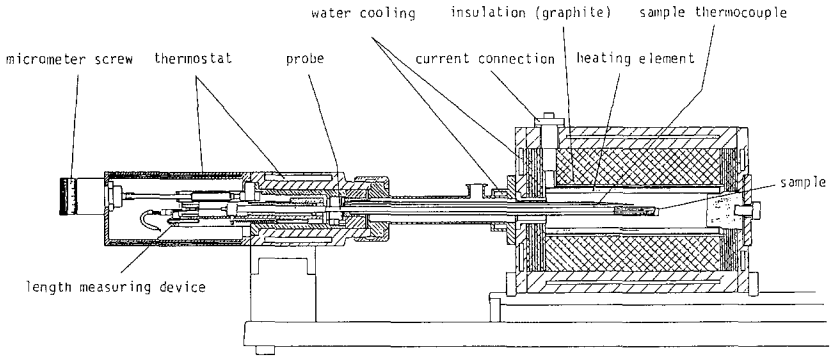

Fig. 1. Schematic diagram of dilatometer for operation in the range 25–2000°C.

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. Both the furnace insulation space and the sample support are enclosed in vacuum-tight areas. The energy demand of the furnace is very small (on average 5 kVA up to 2000°C in argon atmosphere), and good temperature control, even at high heating and cooling rates (up to $50\ K \cdot min^{-1}$), ensures positive results from the tests.

The instrument design also permits the use of a protective tube in the furnace separating the sample space from the heating element, thereby making it possible for the selection of different atmospheres in which to heat the sample.

Data acquisition and recording can be analog or digital. Multichannel recorders or point printers are available for analog recording, with which amplification factors up to 100,000 can be reached. The resolution using an analog recorder is 10 nm. The digital data acquisition ensures a fast data transmission to the coupled computer. The acquisition rate is adjustable (up to 4 bytes/s for each channel). The parallel acquisition of data (an intermediate data storage of up to 16 kbytes), together with the inherent intelligence of the data acquisition system, guarantees coordination of the signals. The selection of the temperature program is also controlled by the computer via the data acquisition system. The resolution of the measuring ranges of the preamplifiers is 20,000 digits (14 bits with sign), so that with this acquisition system a resolution of 2.5 nm per digit can be achieved, which is very high for push-rod dilatometers. The performance of the general basic software is summarized in the following application examples.

3. RESULTS AND DISCUSSION

The applications of a high-temperature dilatometer for hightech ceramics can be listed as follows:

(a) precise determination of the thermal expansion (determination of the relative change of length, the linear coefficient of expansion, and the determination of crystalline phase changes and their transition temperature) and

(b) determination of the sintering range (densification temperature, total shrinkage, sinter kinetics, and relative increase in density [2]).

The results indicated in a describe the general suitability and the application possibilities of a material, while the information given in b is the basis

for the most important step in the manufacturing process of a ceramic product.

The results of the measurements with a push-rod dilatometer are influenced by several factors [3]: the material of the sample support and push-rod, sample position, transducer, furnace system, and temperature measurement. Therefore, calibration is essential for achieving accurate results [4].

The exact calibration of a dilatometer with an upper temperature above 1600°C is very difficult due to the lack of certified reference materials. To obtain reference materials which are applicable in the highest temperature range, e.g., tungsten, one has to refer to dilatation values given in the literature (variation of about 10%) [5]. In the range below 1600°C, however, certified reference materials are generally available. It is therefore reasonable to test the high-temperature dilatometer in the range of validity of these reference materials. Figure 2 shows the comparison of uncorrected dilatation curves of synthetic sapphire (NS SRM 732) and sintered Al_2O_3 (dilatation values according to DIN 51045). These reference materials demonstrate 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. Additional power and improved efficiency are expected by insulation of the high-temperature components of the engine, such as piston, cylinder head, valves, and exhaust parts. The high expansion of ZrO_{23} allows direct combination with metals, e.g., the shrink fit of

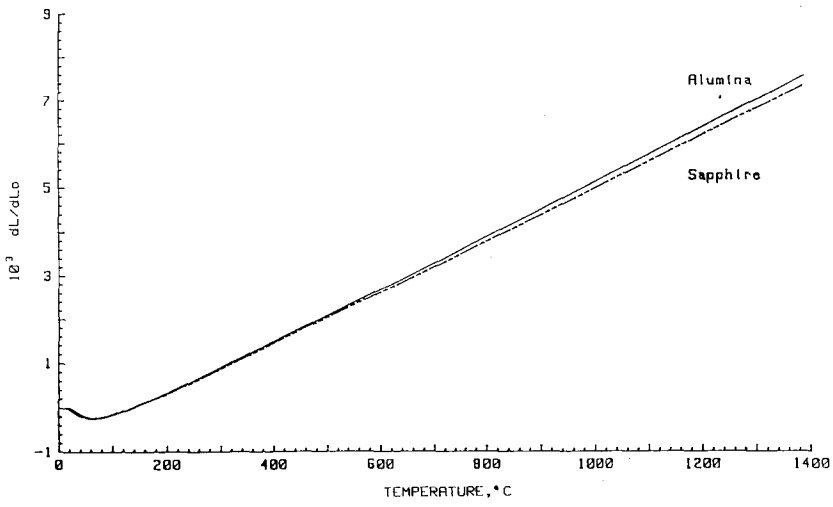

Fig. 2. Comparison of expansion of alumina and sapphire in graphite sample holder.

a ZrO_2 liner in a cast iron block will be maintained at operating temperatures. The use of pure ZrO_2 causes problems due to the polymorphism of this material, especially because of the crystal transition (monoclinic to tetragonal) at a temperature of 1100°C. The addition of other 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 phase transition will occur. For this practical application, partially stabilized ZrO_2 has proven better suited for several reasons (thermal shock resistance, grain structure, stability, and toughness). Dilatometry is, in this case, a reliable method for the analysis of the degree of stabilization, i.e., the remaining monoclinic structure.

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

The suitability of the newly developed dilatometer for precise determinations of dilatation up to 2000°C is shown in Fig. 4. Dense SiC material (hexoloy SA) was heated in a pure argon atmosphere with a heating rate of $50\,K \cdot min^{-1}$ up to 1950°C. The measured values were

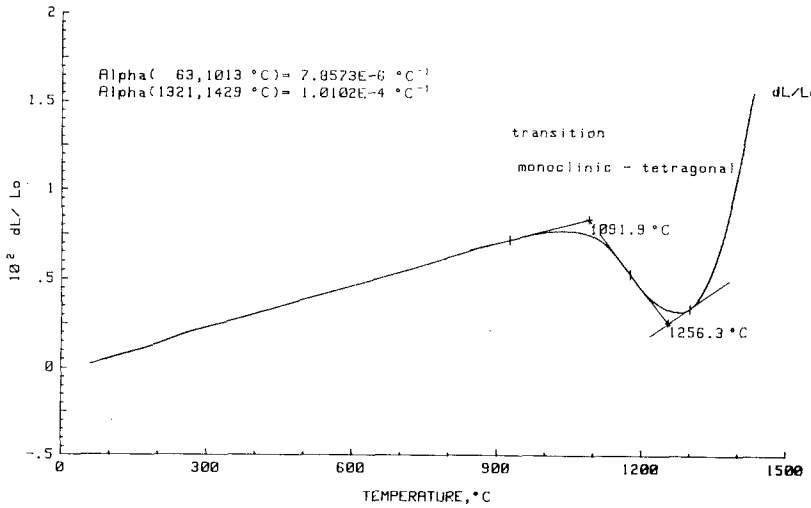

Fig. 3. The heating curve of partially stabilized ZrO_2.

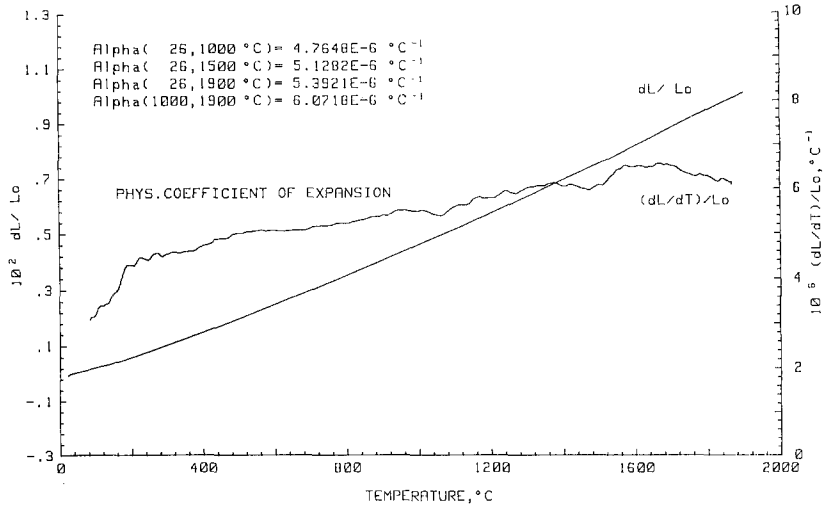

Fig. 4. Evaluation of expansion and expansivity of SiC.

corrected with the curves from the calibration with tungsten (NBS SRM 737). A table indicating the average coefficient of expansion over a wide temperature range, "alpha," and curves indicating the dilatation and the coefficient of dilatation are shown in Fig. 4. The scaling on the right (ordinate) indicates the numerical values for the coefficient of dilatation $[\alpha = (1/L_0)(dL/dT)]$. Using the evaluation program (off-line) of the

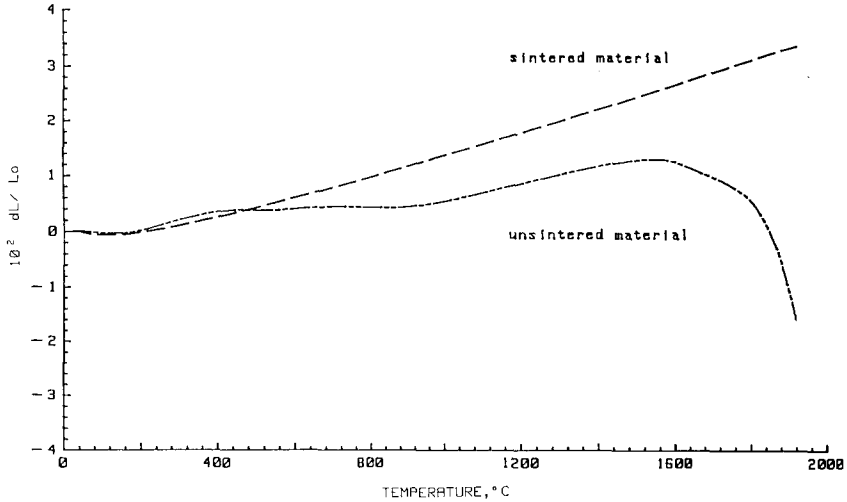

Fig. 5. Comparison of curves of sintered and unsintered SiC powder compacts (with additives).

available software it is also possible to indicate the coefficient of dilatation in tabular form. The average coefficient of expansion can be indicated only in tabular form.

Figure 5 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. 5 (two successive measurements) indicates the release of additives from the unsintered material at temperatures up to 1000°C, as well as 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. To complete the sintering the sample should be maintained isothermally at 2000°C. The wide range of dilatation values of crystalline and amorphous high-tech ceramic materials and therefore the wide range of application of dilatometry are shown in Fig. 6. In addition to the SiC powder compacts from Fig. 5, sintered parts of B_4C, dense SiC, and vitreous carbon are compared.

With the exception of possible contact reactions between the sample support tube and the 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 for ceramics and refractory metals. The components of the sample support and the thermocouple can easily and quickly be replaced.

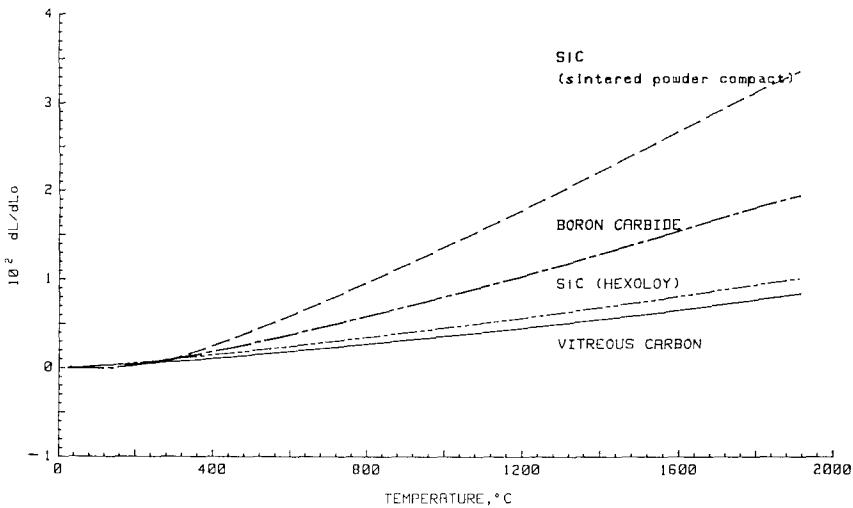

Fig. 6. Comparison of the expansion curves for high-tech ceramic materials.

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 determined, especially in composite systems with other materials. The newly developed dilatometer with a temperature range from 25 to 2000°C covers the highest and increasingly important temperature range for high-tech ceramic materials. The performance of the hardware and software was demonstrated on samples of SiC, ZrO_2, B_4C, and vitreous carbon and with selected reference materials.

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