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RECENT RESEARCH AND PROSPECTS OF THERMAL EXPANSION STUDIES. STANDARD MANERIALS

T. Kompan, S. Kondratiev, N. Pukhov
D. I. Mendeleyev Institute for Metrology, Saint-Petersburg, Russia
Laboratory of State Standards in Thermal Expansion
Saint-Petersburg,
190005, Russia
E-mail: T.A.Kompan@vniim.ru

ABSTRACT

The paper describes the metrological activity of the D.I. Mendeleyev Institute for Metrology (S.-Petersburg, Russia) in the field of dilatometric research of solids. The measurement ability nowadays are as follows: from 90K up to 3000K, the TEC value can be determined with accuracy up to 0,2 10^{-8} K^{-1}. Also the attention is paid to the standard reference materials and the standard samples of Thermal Expansion.

INTRODUCTION

Thermal expansion of solids is a general property of condensed materials. It is based on the fundamental principle of condensed matter structure: on the asymmetry of attractive and repulsive forces between particles (atoms, ets) constituting macroscopic bodies. Whereas the distance between the particles is determined by force balance, potential minimum in the balance point stays asymmetric, therefore, with the temperature increase, the particles are displaced towards the flat side of the potential well.

The thermal expansion is usually described by Thermal Expansion Coefficient (TEC). TEC in turn can be formalised in one of the following ways:

$\alpha = dL / L\,dT$ (differential)

$\alpha_{av} = \Delta L / L\,\Delta T$ (averaged over temperature interval)

$\beta = dV / V\,dT$ (volume expansion coefficient)

First expression is used predominantly in scientific research, the second option is more convenient for practical purposes, e.g. in industry, and the last one is mostly used for the relative volume expansion of liquids. The physical dimension of TEC is K^{-1}. Different authors may assume different type of TEC formalisation and this should be take into account.

Coefficient of thermal expansion is related to the other thermodynamic parameters, including heat capacity, that follows from the Gruneisen's relation [1]

$$\beta = \gamma \frac{C_v}{V} \chi_T \qquad (1)$$

where β – is volumetric coefficient of thermal expansion;

γ - Gruneisen parameter, describing Debye temperature variation with volume change;

V - molecular volume

C_v - heat capacity at constant volume

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (2)$$

where χ_T - is isothermal compressibility.

Temperature dependence of thermal expansion coefficient can be determined from the expression above. In Gruneisen approximation γ does not depend on temperature, whereas χ and V vary slowly with temperature, which means that TEC dependence on temperature is mostly determined by heat capacity dependence on temperature. Therefore, coefficient of thermal expansion tends to zero as $T \rightarrow 0$ K, and tends to a constant value for higher temperatures. In some cases, structural and phase transitions can cause a sharp change of sample dimensions.

For the most materials TEC at room temperature lies within a narrow range – less then one order of magnitude. Closeness of TEC values of various materials and their weak dependence on history and purity of material emphasize the fundamental character of this quantity and also its relation to

general material parameters and the structure of material. Therefore, thermal expansion is an important and informative parameter of the solid, which is related to the thermodynamic parameters (Helmholtz energy, enthalpy) and the structural parameters (phonon spectrum, lattice unharmonicity, defects) of the material.

On the other hand TEC should be taken into account whenever one deals with wide range of temperatures: from cryogenics to solid state technology. For instance, coefficient of thermal expansion of the material for a telescope mirror has to be controlled up to 10^{-9} K^{-1}. Dilatometer data is also required for vacuum and solid state electronics, where different materials junctions are used, for building heterojunctions in optoelectronics, because normal operation of heterojunction devices are limited by strain accumulation due to materials TEC mismatch. These and other applications require high precision TEC determination in a wide range of temperatures.

Coefficients of thermal expansion for modern artificial materials, including custom made ones, in contrast, can vary over a wide range between $0.01 \cdot 10^{6}$ and $50 \cdot 10^{-6}$ K^{-1}. There are many types of dilatometers dealing with different scientific and practical problems of materials. Any of those dilatometers have their constructive and operating features. Different TEC determination techniques are used for different purposes.

It can be problematic to take into account all of the entities that influence the TEC measurement precision. Therefore, special standard reference materials (SRM) with different physical properties are used for calibration of dilatometers.

Typically, a dilatometer should be calibrated using materials similar to those to be studied in specific measurements. The usage of similar kinds of materials provides realistic examination under near-real conditions in order to minimise possible side effects contributing to the measurement uncertainty. That explains the necessity to find suitable reference materials for TEC standards with different TEC values and various physical properties.

The TEC measurement includes measurements of sample length, elongation and interval of the temperature change. Methods of measurements for SRM certification have to provide accuracy, comparable with the highest accuracy achievable for every kind of included measurements.

In Russia TEC values of SRM materials have been obtained using high precision interference dilatometers from "D.I.Mendeleyev Institute for Metrology", that provide standard deviation of the TEC value of up to $0.5 \cdot 10^{-9}$ K^{-1} in 100 degree temperature range [2]. Stability of the properties of the reference materials and standards is given special attention, with highest priority to the TEC values stability.

Measurements on VNIIM dilatometers are based on the analysis of the interference fringe pattern. Special algorithm is used for interferogram processing, that provides detection of phase shift value with precision of up to 10^{-3} part of a fringe [3]. In the fig 1 a test sample with the interference plates is shown along with the experiment monitor screenshot, displaying current interference pattern and experiment data record.

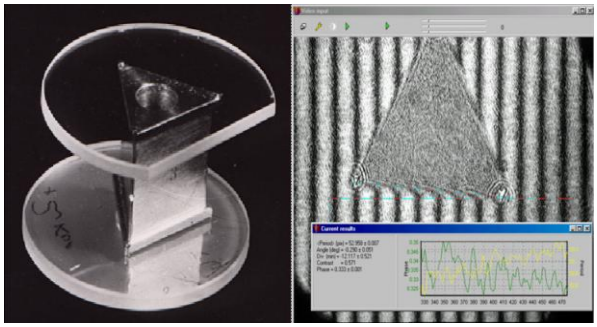
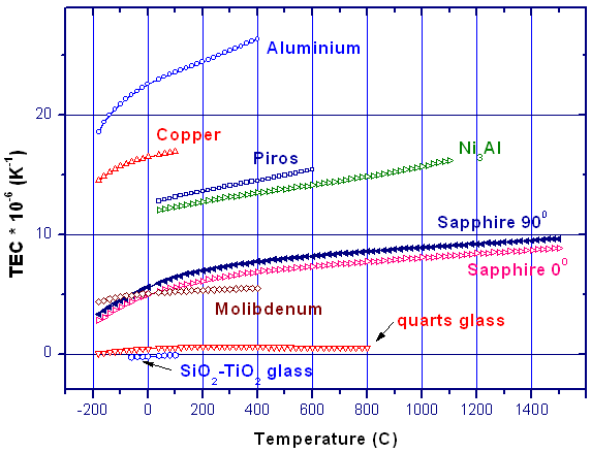


Figure 1 Left: sample under investigation with interferometric plates; Right: Experiment monitor showing interference pattern and the real-time plot of experiment parameters

The technique mentioned above allowed to develop a set of standard samples with different physical properties for use in a wide range of temperatures between 90 and 1800 K to meet all customer requirements. Platinum, copper, single crystalline aluminium oxide, molybdenum, aluminium, various sorts of fused silica, and alloys are used for that purpose. The TEC values of those



materials, depending on the temperature, are shown in fig 2.

Figure 2 TEC values for various materials as a function of temperature

Samples, made of specially oriented single crystalline sapphire, imitating the LEC of corundum ceramics, are the most popular [4].

Single crystal sapphire is an anisotropic crystal. The crystal belongs to a trigonal syngony, to a space group 3m. The TEC value along the crystal axis of Al_2O_3 differs from that for the transverse direction ($\alpha_{\perp}$ = 5.62 10^{-6} K^{-1}; $\alpha_{\parallel}$ = 6.44 10^{-6} K^{-1} in the temperature range 20-100^{0}C). Length gauge made of sapphire do not change their dimensions during thermal cycling.

Nowadays the push-rod dilatometers for high temperature TEC measurement are used worldwide.

Those dilatometers are produced by the world's leading corporations. They have a kinematics system made of aluminium oxide ceramics. To determine the uncertainty of the dilatometer's self extension, TEC reference materials should be the same as that of the kinematics system or to have TEC value as close as possible. However ceramic length standards do not meet requirements on accuracy, because their properties are less repeatable than those of a single crystal. Single crystal standards with their length axis aligned at the angle of 59^0 to the crystal C axis are the best for this purpose, as their TEC value is close to TEC of corundum ceramics.

On the other hand that kind of orientation place more severe requirements for the sample orientation with respect to the crystal C axis. Alignment accuracy of ± 2^o is required for 59° alignment to achieve TEC standard uncertainty value of 5.10^{-8} K^{-1}. Production and distribution of those standards became possible because of the successful cooperation with the material scientists from Russian Academy of Sciences who developed the growth method of profiled sapphire single crystal.
The figure 3 shows the investigation results. The data shown are the TEC values of single crystal sapphire for various orientations. NIST [5] data is shown along with the data from D.I.Mendeleyev institute for comparison. The uncertainty of measurements does not exceed $2{\cdot}10^{-8} \div 5{\cdot}10^{-8}$ K^{-1} throughout temperature range.

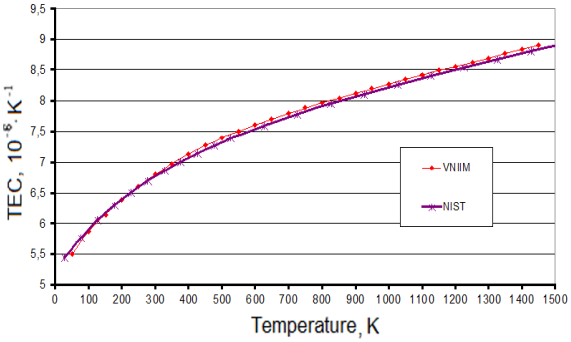


Figure 3 Dependence of TEC of single crystal sapphire for different orientations. The two curves for 59^0 orientation are the data from NIST and from D.I.Mendeleyev Institute.

It can be seen that data on single crystal TEC scattering presented in this paper as well as data from other authors falls within the uncertainty range of the dilatometer used.

Alumosilicate based pyroceramics sitall CO-115M (Lytcarino, Russia), can be provided as another example of thoroughly studied ultralow TEC material. This ceramics include the nanocrystals of β - spodumene, β - silica and β - eucryptite as the constituting phases. Transparency of alumosilicate is achieved by thermal treatment, when crystallite dimensions become significantly smaller than the wavelength.

TEC measurements of sitall CO115M were performed using the Institute's high precision interference dilatometers according to the measurement technique, and gained average TEC measurement standard deviation in the hundred degree range of $0{,}2.10^{-8} \div 0{,}5.10^{-8}$ K^{-1} [6]. Fig. 4 shows typical temperature dependencies of TEC for – 60 ÷ 100 °C temperature range. One can see that the material almost does not change its size at around room temperature.

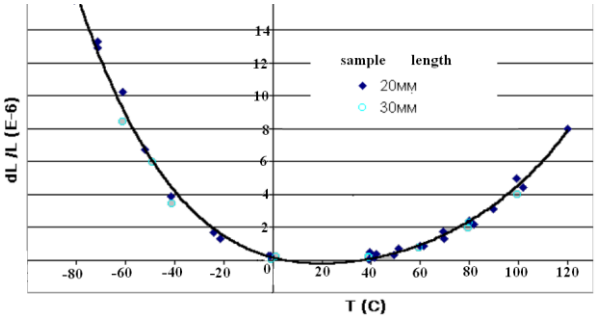


Figure 4 Temperature dependence of expansion of CO115-M sitall samples

Special attention was given to homogeneity of the material. Figure 5 illustrates TEC scattering within the slab.

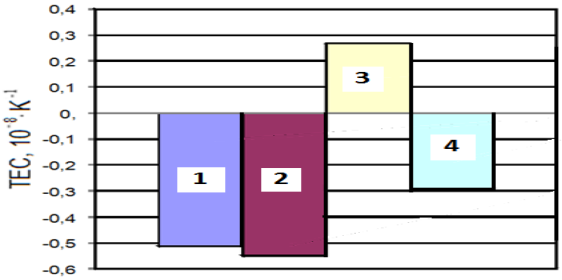


Figure 5 Homogeneity of TEC inside the CO115-M alumosilicate slab. 1,2,3,4 – side, bottom, upper and middle parts of slab.

Low TEC value and time stability of sitall CO115M allowed for use of the material for production of the mirror for the Southern African Large Telescope, and also in metrology as low TEC reference material [7] (Fig.6).

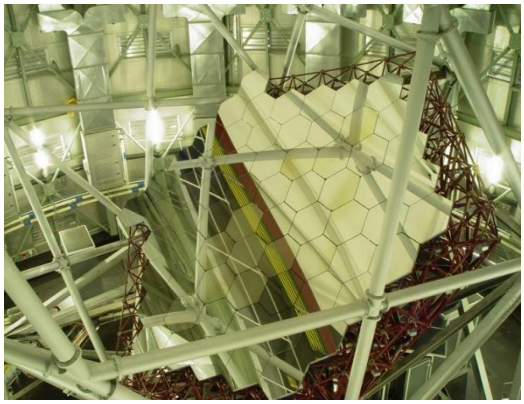


Figure 6 10-meter mirror of SALT assembly. Mirror elements made of ultralow TEC material. TEC value and material inhomogeneity was supervised by D.I.Mendeleyev institute for Metrology.

Quite recently a new dilatometer for extra-high temperatures, up to 3000 K, was made and was added to the set of standard dilatometers of D.I.Mendeleyev Institute [8, 9]. The new dilatometer uses the comparator method of elongation measurement and two parallel system of distant temperature measurement. The uncertainty of elongation measurement of a new device is about 1 – 2 μm. The result of a test TEC measurement for various high temperature materials can be seen in the Fig. 7.

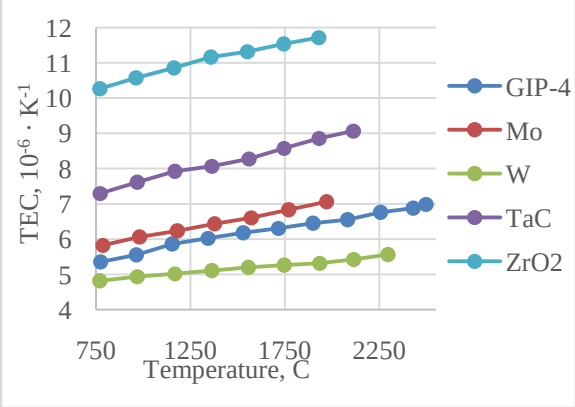


Figure 7 TEC value for various materials as a function of temperature

SUMMARY

D. I. Mendeleyev Institute for Metrology has resources for precise TEC measurements, develops and supplies reference materials with certified properties.

Everybody is welcome for collaboration.

REFERENCES

[1] E. Gruneisen, Handbuch der Physik, 1926,10, 1.
[2] A. I. Pokhodun, T. A. Kompan, N. A. Sokolov, et al "The Upgraded State Primary Standards for Units of Thermophysical Quantities", *Measurement Techniques*, No. 8, 55 (2009)
[3] T.A. Kompan, A.S. Korenev, A.Ya. Lukin, "An automatic system for dilatometric measurements with the multiparametrical data processing from the of interference pattern field*", Measurement Techniques*, No. 6, 31 (2001)
[4] Kompan T., Korenev A., Lukin A., Antonov P.,V. Krymov "Profiled single cristal sapphire – new reference material dilatometry " Bulletin of the *Russian Academy of Sciences*: Physics, 2004, v. 68, № 6, p.895-898
[5] T.A. Hahn "Thermal expansion of single crystal sapphire from 293 to 2000 K. Standard reference material 732",// Thermal Expansion – 6,p. 191–201, (1978)
[6] Kompan T., Korenev A., Lukin A. **"**Investigation of Thermal Expansion of a Glass-Ceramic Material with an Extra-low Thermal Linear Expansion Coefficient", International Journal of Thermophysics 2008, Volume 29, Number 5, p. 1896-1905.
[7] O. Ponin, A. Sharov, I. Galyavov, T. Kompan, J. Swiegers, A. Swat, in *Proc. of SPIE "Large Ground-Based Telescopes"*, SPIE, Bellingham, 2003 v.. 4837, part 1, pp. 795-804.
[8] T. A. Kompan, S. V. Kondrat'ev, A. S. Korenev, N. F. Pukhov, F. M. Inochkin, S. K. Kruglov, and I. G. Bronshtein "Extending the temperature range of the National primary standard for the unit of the thermal linear expansion coefficient", *Measurement Techniques*, Vol. 58, No. 12, March, 2016
[9] I. G. Bronshtein, F. M. Inochkin, S. K. Kruglov, T. A. Kompan, S. V. Kondrat'ev,3 A. S. Korenev and N.F. Pukhov "Optoelectronic measurement system for a high-temperature dilatometer", Measurement Techniques, vol. 58, No.12, p. 1347-1353 (2016).