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A METHOD FOR THE TEMPERATURE CALIBRATION OF PUSHROD DILATOMETERS

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A method for the temperature calibration of pushrod dilatometers and thermomechanical analysis systems using the melting points of metal standards has been established. With this technique, the measured melting temperatures of high-purity metal standards are determined from the sharp change in the length curve which accompanies melting. This procedure was used for the absolute temperature calibration of a pushrod dilatometer capable of operation up to 2000 °C. The results of this calibration show that the technique can be used with a high degree of accuracy and confidence.

During the past several years, there has been an increasing demand for materials which can be used at high operating temperatures. This demand has led to the development of a large number of new high-temperature materials. The development of these materials has been accompanied by the need for quantitative determination of their thermophysical properties. This, in turn, has resulted in the development of a new generation of high-temperature scientific instruments.

An instrument of particular importance for measuring thermophysical properties is the pushrod dilatometer. This instrument is used to study the expansion characteristics of a wide variety of materials. For example, the effects of changes in the processing parameters, as well as the addition of fibers, fillers and catalysts, on the glass transition temperature, decomposition onset temperature, percent expansion, coefficient of expansion, etc. of polymers can be studied quantitatively using pushrod dilatometers. In addition, the effects of phase transitions on the expansion of metals and the effects of binder burnout and sintering on the expansion of ceramics can be evaluated quantitatively using these instruments.

In order to use a pushrod dilatometer for quantitative studies such as those just described, the accuracy of the instrument must first be established. This requires

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calibration of both the temperature and the length signals output by the dilatometer. The problems associated with this calibration, however, have been compounded by the continually increasing temperature range of these instruments. For example, pushrod dilatometers capable of operation up to 2000° are now commercially available. To the authors' knowledge, no temperature or length calibration studies have been published for pushrod dilatometers in this temperature range. The purpose of this paper, therefore, is to describe a method for the temperature calibration of pushrod dilatometers up to 2000°. Clearly, the calibration of the temperature is of paramount importance for pushrod dilatometers because of the physical separation of the sample and the thermocouple. The technique described in this paper may also be used for the calibration of thermomechanical analysis (TMA) systems. The length calibration of pushrod dilatometers up to 2000° will be described in a later publication.

Experimental

Approach

The temperature calibration was carried out using the melting temperatures of high-purity metals. This method has been used previously by Tant and Henderson [1] for the calibration of a low-temperature dilatometer. With this technique, a small piece of the calibration metal is placed between the pushrod and a "dummy" sample. The temperature is then programmed to a value above the melting point of the standard. When the melting transition of the standard is reached, a sharp contraction is observed in the length curve. The data obtained from a series of these measurements covering the temperature range of the dilatometer can be used for the absolute temperature calibration of the instrument.

Standards

In this work, 11 high-purity metal standards were used to cover the temperature range from approximately 30 to 1850°. This was more calibration points than actually necessary. However, an attempt was made to provide a sufficient number of intermediate melting points so that the calibration of dilatometers with other temperature ranges could be accommodated without searching for new standards. The standards used in this study were gallium, indium, tin, lead, zinc, aluminium, silver, gold, nickel, iron and zirconium. The purity of all of these standards was greater than 99.99 percent, with the exception of zirconium, which had a purity in excess of 99.9 percent.

Instrumentation

The temperature calibration study was conducted using a Netzsch model 402 ES/7 low-spring-tension, ball-bearing dilatometer. The furnace consists of a bifilar, graphite heating element mounted in a stainless-steel, water-cooled housing. The housing is protected from the heating element by graphite insulation. The pushrod and sample carrier are constructed of high-purity graphite. Both sample and furnace temperatures are monitored by a single tungsten–3 percent rhenium versus tungsten–25 percent rhenium thermocouple. The instrument is currently capable of operation up to 2000° at heating rates ranging from 0.1 to 50 deg/min. Also, because of the water-cooled housing, the cooling rate of the unit is quite high. These fast heating and cooling rates are unique for high-temperature dilatometers and are possible because of the high degree of thermal stability of the graphite components. Finally, samples can be tested in a vacuum or in a static or dynamic inert gas atmosphere. A schematic outline of the dilatometer is shown in Fig. 1.

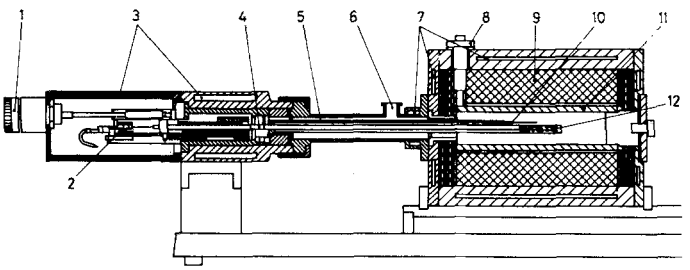

Fig. 1 Schematic of dilatometer. 1 Pushrod adjustment, 2 LVDT, 3 Temperature control water channels, 4 Pushrod, 5 Sample carrier, 6 Vacuum connection, 7 Cooling water channels, 8 Power connection, 9 Insulation, 10 Sample and control thermocouple, 11 Heating element, 12 Sample

Temperature control of the dilatometer is provided by a Netzsch model 413 programmer and model 413 controller. The analog signals representing sample temperature, length and rate of length change are conditioned by a Netzsch temperature linearization module, carrier frequency amplifier and derivative amplifier, respectively. Data acquisition and instrument control are provided by a sophisticated 16/32 bit computer system with peripheral units.

Procedure

The calibration experiments were conducted using the standard graphite pushrod and sample carrier. However, these components, as well as the "dummy" sample, were isolated from the melting standards. This was done in order to protect

these components from any reactions which might occur between the graphite and the standards. An additional problem is that many of the molten standards adhere quite readily to graphite. The protection of the pushrod and the "dummy" sample was accomplished by sandwiching the standard between thin disposable disks. Further protection of the system was provided by placing a 20.0 mm long disposable graphite liner in the sample carrier. The disks, the "dummy" sample and the end of the pushrod were all cradled in this liner. This experimental arrangement is depicted in Fig. 2.

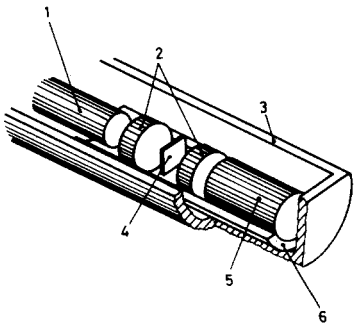

Fig. 2 Details of experimental configuration. 1 Pushrod, 2 Disks, 3 Sample carrier, 4 Metal standard, 5 "Dummy" sample, 6 Liner

All of the standards were tested in the form of thin strips approximately 3.0 mm wide by 4.0 mm long by 0.20 mm thick. For the metals gallium through gold, as well as zirconium, the standard was sandwiched directly between 6.0 mm diameter by 2.0 mm thick disposable graphite disks. The "dummy" sample was constructed of graphite and, for the standards just given, was 6.0 mm in diameter by 10.5 mm long. This sample length resulted in the standards being located directly below the monitoring thermocouple, which also corresponds to the center of a standard 25.0 mm long sample.

It should be mentioned here that the use of the disposable graphite disks and the sample carrier liner was not actually required for the eight low-temperature standards, i.e. gallium through gold. They were used in this case in order to prevent any possible contamination of the dilatometer components and to maintain consistency throughout the calibration procedure. The disposable parts were however, necessary for zirconium, since the zirconium melt reacts with and adheres strongly to the graphite.

The standards nickel and iron both react with graphite prior to melting. Therefore, it was necessary to isolate these two materials from the graphite disks. This was accomplished by sandwiching the standard between 6.0 mm diameter by 2.0 mm thick disposable alumina disks. These disks were, in turn, sandwiched

between the graphite disks. This arrangement was necessary to protect the dilatometer components from the reactions which occur between graphite and alumina at elevated temperatures. The dimensions of the "dummy" sample for the experiments conducted with nickel and iron were 6.0 mm diameter by 8.5 mm long.

The calibration experiments were conducted at a linear heating rate of 20 deg/min in a high-purity argon atmosphere with a purge rate of approximately 100 ml/min. For the standards aluminum through zirconium, the dilatometer was heated at 50 deg/min up to approximately 100 degrees below the melting point of the standard being tested, and then reduced to 20 deg/min for the remainder of the experiment.

Results

Three experiments were conducted for each of the 11 standards. A representative set of these measurements has been reproduced in Fig. 3. As can be seen, the measured melting points, T_m, were taken as the onset of the sharp contraction.

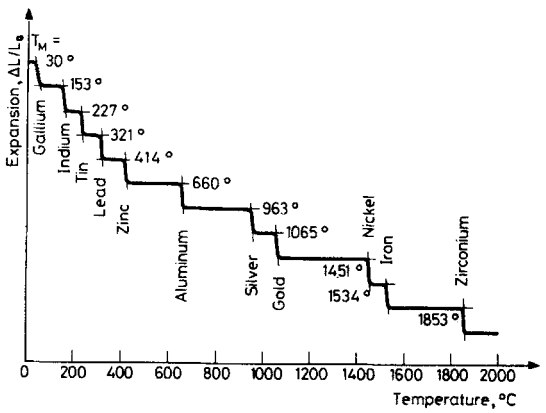

Fig. 3 Typical set of measured melting temperatures. Heating rate: 20 deg/min

These measured values were then subtracted from the published melting points. The average deviation from the published value (both in degrees Celsius and percent), as well as the standard deviation, were then computed for each of the 11 standards. In addition, the average deviation (both in degrees Celsius and percent) and the average standard deviation were computed for all 33 measurements. A summary of all of these computations is presented in Table 1. It is worth noting here that the melting temperatures could also have been determined quite easily and accurately using the length derivative.

Table 1 Summary of calibration results

Standard	Melting temperature, °C		Deviation from literature value, °C	Average deviation from literature value		Standard deviation, °C
	measured	literature		°C	percent	
Gallium	31	29.8	−1.2	−0.20	−0.67	1.00
	29		0.8			
	30		−0.2			
Indium	153	156.6	3.6	3.27	2.08	1.53
	152		4.6			
	155		1.6			
Tin	226	231.9	5.9	4.90	2.11	1.00
	228		3.9			
	227		4.9			
Lead	322	327.5	5.5	6.50	1.99	1.00
	321		6.5			
	320		7.5			
Zinc	414	419.5	5.5	5.17	1.23	0.58
	414		5.5			
	415		4.5			
Aluminum	662	660.4	−1.6	0.40	0.06	2.00
	658		2.4			
	660		0.4			
Silver	963	961.9	−1.1	−0.43	−0.05	1.15
	961		0.9			
	963		−1.1			
Gold	1063	1064.4	1.4	−0.27	−0.03	1.53
	1066		−1.6			
	1065		−0.6			
Nickel	1450	1453.0	3.0	1.67	0.12	1.53
	1451		2.0			
	1453		0.0			
Iron	1533	1535.0	2.0	1.67	0.11	0.58
	1534		1.0			
	1533		2.0			
Zirconium	1852	1852.0	0.0	0.67	0.04	2.08
	1853		−1.0			
	1849		3.0			
Average values for all experiments				2.12	0.64	1.27

The temperature calibration curve for the dilatometer is shown in Fig. 4. Plotted in this figure is the average temperature deviation for each standard (Table 1, column 5) as a function of temperature. These values, of course, represent the correction which must be applied to the measured temperature. The temperature correction between each of the data points is accomplished by linear interpolation. As shown, the maximum temperature correction required is 6.5 degrees for lead at about 327°. This represents a deviation from the published temperature of less than 2.0 percent. In fact, as shown in Table 1, the standards indium, tin and lead all have deviatoions of approximately 2.0 percent. For the standards aluminum through zirconium, this deviation is generally less than 0.1 percent, and as can be seen in Table 1, the average deviation for all experiments is 0.64 percent. This is considered to be quite low for the large temperature range covered by this calibration.

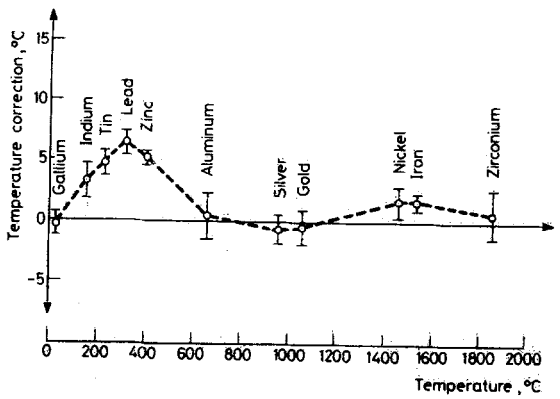

Fig. 4 Temperature calibration curve. Heating rate: 20 deg/min

The band plotted on each of the data points in Fig. 4 represents the standard deviation of the temperature for that particular standard. Clearly, the scatter in the data is quite low. With the exception of aluminium and zirconium, the standard deviation is generally less than ± 1.5 degrees and, if the average standard deviation for all experiments is considered, this value drops to less than ± 1.27 degrees. Again, these results are quite satisfactory.

Discussion

The temperature calibration of pushrod dilatometers can be accomplished satisfactorily using the technique described in this paper. The method is relatively fast and straightforward, and can be used for any dilatometer or TMA system. The

only requirement is that the components of the instrument be protected from the melting standards. This can easily be accomplished by the method used in this work.

As previously discussed, the results are clearly quite good. This speaks well for both the calibration technique and the dilatometer system. With regard to the average temperature deviation, the calibration yields a constant value of about 2.0 percent up to a temperature of approximately 327°. This deviation is believed to be due primarily to the tungsten–3 percent rhenium versus tungsten–25 percent rhenium thermocouples, which are known for their inaccuracy at low temperatures. Above 400°, this deviation drops to a value which is generally less than 0.10 percent.

Also, as previously discussed, there is little scatter in the data. The reasons for this are that the melting points of the metal standards are quite consistent and that the dilatometer system gives accurate and reproducible results over the entire range of the calibration. In addition, the melting standards generally give very clean, sharp changes in the length curve, which makes quantitative evaluation easy. The scatter which does exist in the data is thought to be due largely to the relatively fast heating rates used. Therefore, the scatter could be further reduced by lowering the heating rates to 5 or 10 deg/min. These lower rates would probably also help to reduce the average temperature deviation at the lower temperatures. This fact, however, remains to be established, and the lower heating rates certainly would require longer calibration times. In any event, the temperature calibration should be carried out at the same heating rate as is used for the length calibrations and the actual measurements.

Of the 11 melting standards used, zirconium is an exception in that it does not give the sharp changes in the length curve as discussed above. The reason for this is that zirconium melt reacts with graphite. The result of this is that the contraction curve for zirconium covers a wider temperature range. This behavior does not result in a significant evaluation problem, but probably contributes to the larger standard deviation obtained for the melting temperature.

Finally, this paper would not be complete without a short discussion of the metals which did not yield satisfactory results. Several attempts were made to use pure platinum and rhodium as standards. A number of techniques were employed to isolate the materials from the graphite, but all were unsuccessful. It is assumed that the graphite atmosphere contaminated the samples and lowered their melting temperatures. This was not important in the case of platinum, but rhodium, which has a melting temperature of approximately 1966°, would have provided a useful calibration point. An effort is presently being made to identify another standard for use above 1900°.

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References

1 M. R. Tant and J. B. Henderson, Unpublished data, Naval Surface Weapons Center, Dahlgren, VA, USA, 1979.

Zusammenfassung — Mit Hilfe von Schmelzpunkten metallischer Standards wurde eine Methode zur Temperatureichung von Schubstangendilatometern und TMA-Systemen entwickelt. Die verwendete Technik basiert darauf, daß beim Erreichen der Schmelztemperatur des hochreinen, scheibenförmigen Metallstandards, der zusammen mit einem neutralen Probekörper verwendet wird, eine deutliche, spontan einsetzende Längenänderung in der Dilatometerkurve erkennbar wird. Dieses Verfahren wurde zur absoluten Temperatureichung eines Schubstangen-Dilatometers, das bis 2000 °C arbeitet, angewandt. Die Ergebnisse dieser Kalibrierung zeigen, daß diese Technik mit einem hohen Grad an Genauigkeit und Zuverlässigkeit eingesetzt werden kann.

Резюме — Предложен метод температурной градуировки толкателей дилатометров и термомеханических систем, используя точки плавления металлов-стандартов. С помощью этого метода температуры плавления высокочистых металлов-стандартов определялись на основе резкого изменения кривизны при плавлении. Метод был использован для абсолютной температурной градуировки толкателя дилатометра, работающего до 2000 °C. Результаты такой градуировки показали, что метод является очень точным и надежным.