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COOPERATIVE DETERMINATION OF THE MELTING POINT OF ALUMINA

A Report prepared by

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ABSTRACT

A task force on secondary temperature standards, sponsored by the Commission on High Temperatures and Refractories, International Union of Pure and Applied Chemistry, has undertaken a programme to investigate various inorganic non-metallic substances for use as high temperature reference materials. As part of this programme a cooperative determination of the melting point of Al_2O_3 (alumina) was conducted by the task force. In all, nine scientific groups representing seven countries contributed experimental data. All work was performed utilizing a common supply of Al_2O_3 of nominal 99·9 per cent purity. Experimental techniques varied depending upon the individual investigator. The value for the alumina point as recommended by the task force is 2054 $\pm$ 6°C (IPTS 1968).

1. INTRODUCTION

In July 1965, a colloquium on the Physicochemical and Mechanical Properties of Refractories at High Temperatures[1] was held in Paris, France under the auspices of the Centre National de la Recherche Scientifique. A number of papers presented at the conference dealt with the problem of property measurement at high temperatures and the corresponding lack of suitable secondary temperature standards. Immediately following the primary sessions, an informal meeting was arranged for scientists from various nations to discuss these problems in more detail. The meeting resulted in the formation of an *ad hoc* committee on secondary temperature standards. Subsequently, the committee was formalized as a task force sponsored by the Commission on High Temperatures and Refractories, International Union of Pure and Applied Chemistry (IUPAC). As of January 1969, fourteen scientific groups, representing nine countries, comprise the membership of the task force. These include†

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† For various reasons, all task force members were not able to contribute to the present report. An asterisk (*) denotes those presenting data.

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The original assignment undertaken by the task force was to investigate the possibility of employing various inorganic non-metallic materials, particularly the metal oxides, as secondary temperature standards. The overall objective of the programme would be to promote the inclusion of additional secondary reference points on the International Practical Temperature Scale[2]. Secondary temperature standards as well as all matters pertaining to internationally recognized temperature scales are regulated through treaty by the Advisory Committee on Thermometry of the International Committee on Weights and Measures and the International Bureau of Weights and Measures. In this context the task force can, therefore, only recommend to appropriate groups that certain additional secondary temperature standards be adopted. Irrespective of this, however, it is hoped that efforts of the task force will at least result in a consensus among many scientists as to what values (transformation points) should be assigned to commonly utilized pseudo-standards.

Many materials warrant consideration as secondary temperature standards and among the metal oxides, alumina (Al_2O_3) appears to be one of the more promising substances. Prior to the adoption of the International Temperature Scale (1927) the melting point of Al_2O_3 was included as a reference point on practical scales employed the world over. Even today Al_2O_3 is used extensively for temperature calibration purposes. For these reasons the determination of the melting point of Al_2O_3 was selected as the initial endeavour of the task force. In order to obtain maximum participation only a minimum number of controls were established for individual melting point experiments. The broad guidelines were limited to:

1. Utilization of a common sample
2. Tungsten containers†
3. No restriction on equipment or technique.

This report summarizes the cooperative experimental determination of the melting point of Al_2O_3 by the task force on secondary temperature standards (IUPAC).

2. MATERIAL

The central source of Al_2O_3 was prepared from stock alumina by fusion in a solar furnace, thus, minimizing the possibility of contamination from extraneous sources‡. Full details of solar furnace techniques are reported

† Unfortunately, circumstances did not permit utilization of tungsten by all groups.
‡ The primary supply of Al_2O_3 was prepared and distributed by Dr M. Foex, France.

elsewhere[3, 4]. Individual lots distributed to task force members consisted of 400–500 grams of large conglomerates of polycrystalline Al_2O_3. X-ray patterns of the material showed only reflections identifiable with α-Al_2O_3 (corundum type). All grinding or other processing was left to the discretion of the individual task force member. As indicated by spectrochemical analyses, the alumina samples had a nominal purity of at least 99·9 per cent.

3. RESULTS AND DISCUSSION

Table 1 summarizes the essential features of the melting point determinations conducted by the various task force members. For greater detailed explanation or description of specific investigations, reference should be made to published reports[5–13].

As expected, the experimental techniques and equipment employed by the different investigators varied in several respects, with no two groups exactly duplicating one another. With one exception, all utilized optical pyrometry for temperature measurement. Furnace types included resistance, induction, and solar. Environmental conditions ranged between high vacuum and air or argon at various pressures. Both static and dynamic methods were used and included the traditional thermal analysis technique, modified quench method and the less conventional direct observation procedure.

The thermal analysis method (heating and cooling curves) has been widely accepted as one of the more desirable techniques for establishing the melting or freezing temperature of a material, especially pure metals. Five groups presenting data for this report utilized this technique. The method depends upon the absorption or liberation of heat which occurs during the melting or freezing of a material. For the simplified case, a blackbody cavity (or thermocouple) is centrally located in a crucible containing the material, allowing temperatures to be monitored while the sample is heated or cooled through the transformation point. In ideal situations the temperature of the material will remain constant during melting or freezing and a time–temperature curve will reflect the transformation point as that temperature at which the curve is flat and parallel to the time axis.

The quench technique, employed in one investigation reported here, has been found useful for melting point determinations, especially in those situations in which ill-defined thermal curves may be obtained. The method simply consists of heating a specimen to a given temperature with subsequent rapid cooling to freeze or quench in properties characteristic of that temperature. After each heating the specimen is classified as melted or not melted according to previously specified criteria. In this manner the melting point can be established as that temperature midway between the maximum temperature at which no melting occurred and the minimum temperature where fusion was complete.

The remaining three groups reporting results on Al_2O_3 all employed the direct observation procedure. In this method the material is observed during heating to detect fusion. The temperature at which the specimen slumps or flows is taken as the melting point.

Each method, of course, has attendant problems peculiar to the specific procedure. Perhaps the greatest difficulty inherent with any method is the measurement of temperature. In most instances, the entire temperature

Table 1. Summary of Al_2O_3

Investigator	*Purity*		*Furnace*		*Method*	*Temperature*
	As received	*After test*	*Type*	*Container*		*Instrument*
B. Riley, Great Britain	N.D.†	Ca = 0·01% Si = 0·02%	Resistance, Graphite tube	Tungsten, Iridium or Tantalum	Observation of specimen during heating	Optical pyrometer sighted on blackbody
T. Sata, Japan	N.D.	N.D.	Resistance, Tungsten tube	Tungsten	Observation of specimen during heating	Thermo-couple, W 5% Re–W 26% Re, located adjacent specimen
V. Ya. Chekhovskoi and V. A. Kuzichkin, USSR	N.D.	N.D.	Resistance, Tungsten	Molyb-denum	Thermal analysis, (I) Heating curves, (II) Cooling curves	Optical pyrometer sighted on blackbody
E. N. Fomichev, P. B. Kantor and V. V. Kandyba, USSR	99·994%	Mo = 0·005% (five tests) = 0·006% (ten tests) = 0·01% (fifteen tests)	Resistance, Graphite	Molyb-denum	Thermal analysis, heating curves	Optical pyrometer sighted on blackbody
A. Dietzel and W. Gorski, Germany	Fe_2O_3, TiO_2 Cr_2O_3, and N_2 not detected	Fe_2O_3 = 0·01% $N_2 = 2 \times 10^{-5}$%	Resistance, Stabilized ZrO_2 tube	Iridium	Observation of specimen during heating	Optical pyrometer, sighted on blackbody
G. Urbain, France	Alkali = <0·001% Ca, Mg = <0·0002%	Alkali = <0·005% Ca, Mg = <0·0002% W = <0·01%	Resistance, Tungsten tube	Tungsten or Molyb-denum	Thermal analysis, cooling curves	Optical pyrometer, sighted on blackbody
T. P. Jones, Australia	N.D.	N.D.	Resistance, Tantalum tube	Tungsten	Thermal analysis, heating curves	Optical pyrometer, sighted on blackbody
S. J. Schneider and C. McDaniel, U.S.A.	Si = 0·01–0·1% Cr, Fe, and Mg each = 0·001–0·01% Ag, Ca, Cu, Mn, and Ni, each = <0·001%	N.D.	Induction, Tungsten susceptor	Tungsten	Modified quench; examination of specimen after heating	Automatic photoelectric pyrometer, sighted on blackbody
T. Noguchi, Japan	Fe = 0·001% B = 0·003% Si = 0·0001% Mg = 0·0001% Cu = 0·001%	Fe = 0·001% Si = 0·0001%	Solar	None	Thermal analysis, cooling curves	Optical pyrometer, sighted on specimen. Emissivity correction made

† N.D. = Not determined
‡ N.A. = Not applicable

melting point determinations

measurement		*Environment*			*Melting point* (°C)						
System calibration		*Vacuum pressure* (mm Hg)	*Gas*	*Pressure* (mm Hg)	*No. of test*	*Accuracy*	*Precision*	*Minimum value*	*Maximum value*	*Average value*	
Material	*Temp.* (°C)										
	IPTS, 1948							IPTS, 1948	IPTS, 1948	IPTS, 1948	IPTS, 1968
Cu Au Pt Pt–Rh thermocouple	1083 1063 1769 1700		Argon	~760	10	±2	±2	2037	2043	2040	2043
Au Pd Pt Rh	1063 1552 1769 1960	2×10^{-4}	Argon	100	4	±6	±3	2040	2044	2042	2045
Au	1063	(I) 2×10^{-5}	I and II Argon	10–20	(I) 11 (II) 10	±4·5 ±3·7	±1·2 ±0·3	2049·9 2050·1	2054·4 2051·2	2051·4 2050·8	2054
Au	1063		Argon	20	14	±3·6	±0·8	2049·5	2052·1	2050·6	2054
Pt Rh	1769 1960		Air	~760	10	±7	±3	2042	2056	2051	2054
Au Pd Pt	1063 1552 1769		Argon	~760	24	±6	±2	2047	2056	2051	2054
Au	1063	$10^{-5} - 10^{-4}$			8	±6	±2·5	2050	2055	2052	2055
Au Rh	1063 1960	10^{-5}			N.A.‡	±6	±1·5	N.A.	N.A.	2052	2055
N.D.			Air	~760	30	±15	±9	2043	2086	2070	2073

measurement system (pyrometer, prisms, blackbody, etc.) was calibrated prior to actual Al_2O_3 point determination using two or more known reference points, either Au 1063°C, Pd 1552°C, Pt 1769°C, or Rh 1960 C (IPTS 1948). In addition, all pyrometers and thermocouples were separately calibrated by approved techniques.

The melting points of Al_2O_3 as determined by the individual task force members are tabulated in *Table 1.* Each melting point is an average of several separate determinations. Included also are the maximum and minimum values obtained in any one investigation. The listed precision and accuracy are based solely on the specific investigator's personal estimate.

The overall average of the nine separate reported average melting points is 2054°C (IPTS 1968) with a standard deviation calculated to be 8·4°C†. The values ranged between a minimum of 2043°C and a maximum of 2073°C with a median of 2054°C. Since six of the nine determinations were either 2054°C or 2055°C with an estimated accuracy of about ±6°C, it would appear that the median value of 2054°C is an acceptable figure for the alumina point.

4. RECOMMENDATION

The cooperative effort reported here has demonstrated that it is technically feasible to determine the melting point of Al_2O_3 with sufficient precision to warrant its use as a temperature standard. Therefore, the task force recommends to the Commission on High Temperatures and Refractories (IUPAC) that it strive through appropriate channels to promote the inclusion of the alumina point as a secondary reference point on the International Practical Temperature Scale. Furthermore, it is proposed that a melting point for Al_2O_3 of 2054 ± 6°C (IPTS 1968) be utilized for calibration purposes until such time as a specific value is officially designated.

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† For comparison it should be noted that the average melting point for all determinations (17) published since 1948 [11] is 2047°C (IPTS 1968) with a standard deviation of 11·4°C.