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Původní práce

MELTING TEMPERATURES OF CaO AND MgO

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Observations of samples prepared of MgO *monocrystals and sintered* CaO *and heated jointly without coming into mutual contact have shown that* CaO *melts at lower temperature than* MgO. *In three repeated* CaO *melting temperature measurements the following values were determined: 2631, 2607, 2612 °C. Similarly for* MgO: *2803, 2826, 2841 °C. On the basis of these values and on that of an analysis of errors in their determination the final suggested values for* CaO *and* MgO *are 2617 ± 30 °C and 2823 ± 40 °C respectively.*

INTRODUCTION

The melting points of elements and compounds belong among basic thermodynamic constants. Their knowledge is necessary in a number of scientific fields. The data are indispensable for the construction and calculation of equilibrium phase diagrams, and are equally significant when assessing the suitability of application of some compound or substance when this is to be exposed to high temperatures. In spite of considerable efforts of workers mainly in the field of physics aimed at elucidating the melting process and at finding a generally valid relationship which would allow the melting temperatures to be expressed quantitatively on the basis of constants and values available at room temperature, the results obtained so far do not exhibit any satisfactory agreement with experimental data [1], [2], [3]. It seems that regardless of considerable physical knowledge on the solid state the melting of substances cannot be understood without first acquiring the same degree of knowledge on the liquid state from the point of view of quantum theory.

Experimental determination of the melting point has thus so far remained the only possible way of obtaining these values both accurately and correctly. Correctness of the measurement is ensured by suitable experimental arrangement, by the highest possible purity of the substances and by measuring the temperature according to IPTS (International Practical Temperature Scale of 1968) [4]. When these conditions are complied with the measuring accuracy is given by the standard of the instruments employed.

Table I lists experimentally established and published melting temperatures of CaO and MgO. In the case of CaO the melting temperatures appear to comprise two sets of values. The first five values oscillate around a mean value of 2600 °C, the last three being higher by about 320 °C. The highest values exceed those for the melting temperature of MgO which shows considerably lower dispersion in spite of the difficulties involved in their experimental determination as a result of significant vapourization of MgO at high temperatures.

A comparison of experiments and results obtained by Doman et al. [8], Foex [10]—[12] and Noguchi [9] who measured the melting temperature of CaO (or the liquidus curves at the CaO side) and that of Al_2O_3 shows that

Table I

Experimentally determined melting temperatures of CaO and MgO

Original value °C	IPTS-68a) °C	Medium	Year	Reference
CaO				
2572	2619	H_2	1913	Kanolt [5]
2576	2570	H_2O — 0.2 atm	1926	Schumacher [6]
2620	2625	N_2	1948	Oľšanskij [7]
2625	2630	N_2	1963	Doman [8]
2585	2590	air	1967	Noguchi [9]
2910	2916	air	1965	Foex [10]
2950	2956	air	1968	Foex [11]
2900	2906	air	1969	Traverse [12] Foex
MgO				
2800	2857	CO + N_2	1913	Kanolt [5]
2580		N_2	1916	Ruff [13]
2915			1936	Kelley [14]
2825	2830	N_2	1961	McNally [15]
2790	2795	inert	1966	Riley [16]

a) — Corrected to 4 and 19.

a) from the point of view of physics all the temperature measurement methods were correct,

b) the accuracy of temperature determination was commensurable,

c) significant contamination of the original substances can be ruled out in the experiments considered,

d) the Al_2O_3 melting temperatures were virtually identical while those of CaO showed differences of up to 380 °C. This or that temperature obviously cannot be considered correct without carrying out further experiments.

EXPERIMENTAL

The samples were prepared ouf spec-pure MgO and $CaCO_3$ reagents (Johnson Matthey Chemicals). The powders were compacted into the form of pellets (in the case of $CaCO_3$ after thermal decomposition) which were then sintered and worked into the form of parallelepipeds. The MgO samples (porosity about 5 %) were subject to such intensive vapourization at the high temperatures that the sample temperature could not be measured in spite of the exhausting of vapours employed. For this reason use was made of monocrystals selected in fused MgO; although their purity was substantially lower (determined amounts of impurities in the form of Fe_2O_3, SiO_2, Al_2O_3, Cr_2O_3 were in the range of 0.5 to 0.7 %) the vapourization was suppressed to a degree permitting the sample surface temperature to be measured.

The melting temperatures were determined in a high-frequency furnace in a non-defined atmosphere comprising CO, N_2, CO_2 and O_2. A schematic diagram of the experimental arrangement is shown in Fig. 1.

Using an optical prism and a pyrometer provided with supplementary lens permitting 33-fold magnification, the behaviour of the sample was observed in the course of heating. The correction for the optical prism employed was determined by means of a tungsten lamp in the range of 1050 to 2600 °C. The correction for the supplementary lens in terms of temperature is specified by its manufacturer. The optical pyrometer was of the disappearing-filament type made by Pyro-Werk GmbH Hannover and had been calibrated at melting points of Au, Pd, Pt, Rh and Ir while using a red filter of $\lambda = 650$ nm.

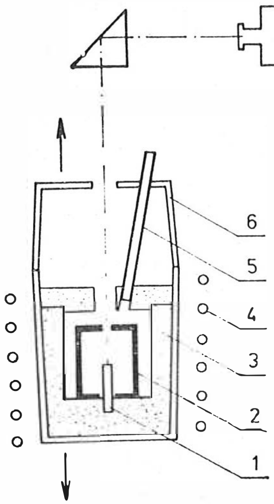

Fig. 1. Schematic diagram of the experiment;
1 — sample 2×1.5×5 mm in size, 2 — graphite susceptor, (dia. 10 mm, h = 10 mm, opening to height ratio 1 : 5), 3 — insulation of a material chemically identical with the sample, 4 — coil for HF field excitation, 5 — exhaustion of vapours, 6 — mullite casing fitted to the sliding arm of the optical microscope.

The first calibration was carried out in the device shown in the schematic diagram in Fig. 1 by measuring the temperature of the oxide base (of CaO, MgO, Al_2O_3) at which the calibration metal suported by it was in equilibrium with its melt. The ceramic bases were not in direct contact with the graphite susceptor. It has been proved that the depth of penetration of the electromagnetic HF field was greater than the wall thickness of the graphite susceptor which has brought about direct heating of the calibration metal and thus a faulty calibration as shown by testing the device at the melting point of Al_2O_3 monocrystals (99.9 %). The value of 2110 ± 20 °C was established.

For this reason the optical pyrometer was calibrated in a furnace provided with a graphite heating element in an argone medium ($p_{O_2} = 10^{-5}$ Pa). The melting temperature of Al_2O_3 monocrystals determined in this way was 2048 ± 20 °C (a mean of three measurements).

The melting points of CaO and MgO were measured in two independent stages. As indicated by Table I there are the following three possible relations between the melting temperatures (m.t.) of the two oxides: a) m.t. of MgO $\doteq$ m.t. of CaO, b) m.t. of MgO $>$ m.t. of CaO, c) m.t. of MgO $<$ m.t. of CaO. It was therefore deemed expedient to find which of the possible alternatives was correct. In the bottom of CaO insulation (3 in Fig. 1) the CaO and MgO samples were placed symmetrically, the susceptor opening was increased so as to be able to observe both samples simultaneously; the temperature was not measured, only the behaviour of the samples was followed during the heating up (heating rate of about 200 °C $\min^{-1}$ at above 1600 °C). Mutual contamination was determined by means of the X-ray microanalyzer. By observing the MgO monocrystal sample and that of sintered CaO (porosity of about 6 %) being heated simultaneously the CaO camples were found to melt at a lower temperature in each of the 10 experiments. The extent of mutual contamination was determined by point analysis at various points of sample polished sections as follows: CaO content in MgO ~ 0.2 %, MgO content in CaO max. 1.1 %.

The actual temperature measurements were carried out according to the schematic diagram in Fig. 1 with insulation 3 (Fig. 1) having been of the same oxide as the sample. The sample surface temperature was measured visually in the course of heating up (temperature increase rate was about 250 °C s^{-1} at the beginning and about 2 °C s^{-1} at the final temperatures). In the case of CaO the graphite susceptor bottom was separated from the insulation by thin MgO plates so that formation of carbides was eliminated. Substances of AR purity were used as insulation. The following melting temperatures were determined in three repeated melting temperature determinations on CaO (specpure, JMC): 2631, 2607, 2612 °C. Similarly for the MgO monocrystals: 2803, 2841, 2826 °C. On the basis of these values and on that of an analysis of the errors involved the melting temperatures of CaO and MgO are suggested as 2617 ± 30 °C and 2823 ± 40 °C respectively.

With all the melting temperatures determined the mean quadratic deviation of the entire method corrected by the Student test is specified.

DISCUSSION

Observations of the behaviour of simultaneously heated CaO and MgO samples have shown explicitly that CaO melts at a lower temperature than MgO. Contamination of calcium oxide with magnesium oxide by up to 1.1 % could not have caused any substantial decrease of the melting temperature of CaO (due to formation of a solid solution). Unfortunately, neither Foex nor Noguchi have determined the melting temperature of MgO for reasons of extensive sample vapourization. The virtually only comparable values are those reported by Doman [8] and McNally [15] or Kanolt [5]. If one would accept the CaO melting temperature values as determined by Foex and Travers [10]—[12] the MgO melting temperature could be expected to be higher than 3000 °C, so that the values specified in the present work would involve a systematic absolute error of about 300 °C. Such an error can be regarded as irrelevant for the following two reasons: a) the dispersion of values in the sets of experimental values is not extensive and corresponds to the techniques employed, b) in the course of measurement the observed part of the sample surface was well visible all the time so that no appreciable shielding of the area by cooler vapours could have taken place (the relative brightness of the pyrometer filament did not change discontinuously or in a random way with respect to the background).

The melting temperature values were established in a non-defined atmosphere comprising CO, N_2, CO_2 and O_2. It is assumed that in spite of the air recycling due to extensive exhuasting, the susceptor interior contained a reduction atmosphere. The possible dissociation of MgO or even that of CaO is not considered a source of errors as both MgO and CaO evaporate virtually instantaneously at the temperatures close to the melting of the oxides (when not taking into account structural defects). The total error due to calibration of the pyrometer and to that of the optical prism amounts to ± 20 °C; the other error of temperature scanning proper amounts to ± 10 °C in the case of CaO and to ± 20 °C in that of MgO. All the melting temperature values have been corrected for deviation from black body by the method described in [17] and [18].

CONCLUSION

Observations of simultaneously heated CaO and MgO samples have shown that the former melts at a lower temperature. The melting temperature of CaO was found to be 2617 ± 30 °C and that of MgO to be 2823 ± 40 °C.

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TEPLOTY TOPENIA CaO a MgO

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Merania sa vykonali vo vysokofrekvenčnej peci v nedefinovanej atmosfére zloženej z CO, N_2, CO_2 a O_2. Schéma experimentu je na obr. 1.

Pozorovaním vzoriek pripravených z monokryštálov MgO a spečeného CaO zahrievaných súčasne sa zistilo, že CaO sa topí pri nižšej teplote. Vzájomné znečisťovanie, stanovené bodovou analýzou pomocou rtg. mikroanalyzátoru (CaO v MgO < 0,2 % a MgO v CaO max. 1,1 %), nemohlo s ohľadom na tvorbu tuhých roztokov zapříčiniť podstatné zníženie teplôt topenia.

Stanovili sa teploty topenia CaO (s. č. JMC): 2631, 2607, 2612 °C. Pre MgO (monokryštály, obsah MgO > 99,3 %) sa získali hodnoty: 2803, 2841, 2826 °C. Na základe týchto hodnôt a chýb pri odčítaní teploty pri kalibrácii optického pyrometra s miznúcim vláknom, stanovení korekcie na optický hranol a vlastnom meraní, uvádza sa hodnota teploty topenia 2617 ± 30 ° C pro CaO a 2823 ± 40 °C pre MgO.

Obr. 1. Schéma experimentu;
1 — vzorka 2 × 1,5 × 5 mm, 2 — grafitový susceptor (∅ 10 mm, v = 10 mm, pomer otvoru k výške 1:5), 3 — izolácia z chemicky rovnakého materiálu ako vzorka, 4 — cievka na budenie VF poľa, 5 — odsávanie pár, 6 — mullitové púzdro uchytené na posuvnom ramene optického mikroskopu.

ТЕМПЕРАТУРЫ ПЛАВЛЕНИЯ CaO И MgO

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Проводились эксперименты в высокочастотной печи в среде содержащей CO, N_2, CO_2 и O_2. Схема эксперимента приводится на рисунке 1.

Исследованием одновременно нагреваемых проб: монокристалла MgO и спеченной CaO было установлено, что CaO плавится при более низкой температуре. Взаимное загрязнение, установленное точечным анализом с помощью рентгеновского микроанализатора (CaO в MgO > 0,2 % и MgO в CaO максимально 1,1 %) не могло, с точки зрения образования твердых растворов, вызывать существенное понижение температур плавления.

Были установлены температуры плавления CaO (s. č. JMC): 2631, 2607, 2612 °C. Для MgO (монокристаллы, содержание MgO > 99,3 %) получили величины: 2803, 2841, 2826 °C. На основании этих величин и учёта погрешностей при отсчете температуры, при калибрации оптического пирометра с исчезающим волокном, а также при определении коррекции на оптическую призму и при самом измерении приводится величина температуры плавления 2617 ± 30 °C для CaO и 2823 ± 40 °C для MgO.

Рис. 1. Схема эксперимента; 1 — проба 2 × 1,5 × 5 × 5 мм, 2 — графитовый сусцептор ∅ 10 мм, v = 10 мм, отношение отверстия к высоте 1 : 5), 3 — изоляция из материала химически идентичного с пробой, 4 — высокочастотный индуктор, 5 — отсасывание паров, 6 — муллитовая втулка, закрепленная на подвижном плече оптического микроскопа.