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THE ENTHALPY OF α-Al_2O_3 UP TO 1900 K

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The enthalpy of α-Al_2O_3 (pure synthetic sapphire) was measured by means of a high-temperature drop calorimeter in the temperature range from 900 to 1900 K. The results may be interpolated by the polynomial with the estimated multiple correlation coefficient squared 0.99953:

$$H_T - H_{298} = -2.72079 \cdot 10^4 + 8.94978\, T \cdot 10^1 + 1.56711\, T^2 \cdot 10^{-2} \quad [J \cdot mole^{-1}];$$

(accuracy $\pm$ 0.4%),
This sample is used as the reference standard for calorimetry.

The advantages of very pure α-Al_2O_3 (sapphire, corundum, ruby) as the reference standard for calorimetry are well known:

i) High and reproducible purity.
ii) Phase (crystalline) stability from very low temperatures up to the melting point (2345 K).
iii) Compact and powder states are readily available (to make holes, grooves, etc. by an ultrasonic technique is not complicated).
iv) Good electric insulator (in contrast to alumina at high temperatures).

Gomel'skii [1] compared the results of enthalpy measurements of this substance in the temperature range from 373 to 1200 K obtained in the Mendeleev All-Union Scientific Research Institute for Metrology (USSR) and in the NBS (USA) and found them to be excellent agreement (within 0.1% deviation). We are able to interpolate these data, with practically perfect correlation, with the third order polynomial

$$H_T - H_{298} = -2.08894 \cdot 10^4 + 5.01083\, T \cdot 10^1 + 7.14162\, T^2 \cdot 10^{-2} - 2.24692\, T^3 \cdot 10^{-5}\ [J \cdot mole^{-1}];\ (\text{accuracy} \pm 0.3\%). \quad (1)$$

The specific heat as a function of temperature may then be obtained by differentiation of Eq. (1), i.e. $C_p = d(H_T - H_{298})/dT$. However, the agreement of the published data for the ranges of higher temperatures reported in the comprehensive compilation by the Thermophysical Properties Research Center, Purdue University (USA) [2] is not as good as in the former case. The purpose of the present work was to contribute to this metrology problem by enthalpy measurement in the higher temperature range with respect to the coherency with the above-mentioned, recommended data.

Experimental

A high-purity monocrystal of synthetic sapphire, used as a specimen, (dimensions: cylinder with $\varnothing$ 9 mm and length 30 mm) was prepared in the Research Institute for Monocrystals, Turnov. The drop copper block high-temperature vacuum calorimeter of our own construction was used. It was described in [3].

The specific advantages of our device are:

i. The molybdenum block in the tungsten furnace (high-temperature part) for homogenisation of the temperature field around the specimen. It also allows a good calibration of thermometers.

ii. The special bridge network of copper and manganin resistances on the copper calorimeter block, with sensitivity of 10^{-6} K.

iii. In order to achieve a minimum parasitic heat flow, glass tubes were used as connection between the furnace part and the isothermal enclosure of the copper block, as well as for all leads from outside the water thermostat.

In the calibration period the enthalpy was measured over the temperature interval 900 to 1200 K and the results were evaluated according to Eq. (1), thus allowing the calorimeter constant to be established. In this manner the mentioned coherency of the data was ensured.

The accuracy of the calibration was proved by measurement of the enthalpy of the melting of aluminium. The established value $H_m = 10740 \pm 80$ J · mole^{-1} is in excellent agreement with that given by Hultgren et al. in [4] (10760 J mole^{-1}).

For measurement up to 1900 K the thermocouples (Pt6%Rh-Pt 30%Rh) were calibrated at the site of the specimen in the furnace, using gold, cobalt, nickel and palladium fixed points.

Results

The obtained enthalpy values, corrected by computer program for parasitic heat transfer, may be interpolated by the second order polynomial (a higher-order interpolation has no physical reason):

$$H_T - H_{298} = -2.72079 \cdot 10^4 + 8.94978\, T \cdot 10^1 + 1.56711\, T^2 \cdot 10^{-2} \text{ [J · mole}^{-1}\text{]}$$

for the temperature interval 900 – 1900 K, with the estimated multiple correlation coefficient squared 0.99953.

The accuracy of the measurement is $\pm 0.4\%$.

References

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3. V. LANDA and M. ROUBAL, Strojírenství (ČSSR) 25 (1975) 559.
4. R. HULTGREN, R. L. ORR, P. D. ANDERSON and K. K. KELLEY, Selected Values of Thermodynamic Properties of Metals and Alloys, Wiley, New York 1963, p. 34.

RÉSUMÉ — L'enthalpie de α-Al_2O_3 (saphir synthétique pur) a été mesurée entre 900 et 1900K à l'aide d'un calorimètre à chute pour hautes températures. Les résultats ont pu être interpolés à l'aide du polynôme suivant, avec un coefficient de corrélation estimé de 0.99953: $H_T - H_{298} = -2.72079 \cdot 10^4 + 8.94978\,T \cdot 10^1 + 1.56711\,T^2 \cdot 10^{-2}$ (J mol^{-1}); (exactitude $\pm$ 0.4%)

Cet échantillon est utilisé comme étalon de référence en calorimétrie.

ZUSAMMENFASSUNG — Die Enthalpie von α-Al_2O_3 (reiner synthetischer Saphir) wurde mittels eines Kalorimeters mit hohem Temperaturgefälle im Temperaturbereich von 900 bis 1900 K gemessen. Die Ergebnisse können an Hand eines Polynoms mit dem geschätzten multiplen quadratischen Korrelationskoeffizienten 0.99953 interpoliert werden:
$H_T - H_{298} = -2.72079 \cdot 10^4 + 8.94978T \cdot 10^1 + 1.56711\ T^2 \cdot 10^{-2}$ [J mol^{-1}]; (Genauigkeit: $\pm$ 4%)

Diese Probe wird als Referenz-Standard zur Kalorimetrie verwendet.

Резюме — С помощью высокотемпературного капельного калориметра была измерена энтальпия α—Al_2O_3 (чистый синтетический сапфир) в области температур от 900 до 1900 К. Результаты могут быть интерполированы с помощью полинома с установленным многократным корреляционным квадратичным коэффициентом 0,99953: $H_T - H_{298} = -2{,}72079 \cdot 10^4 + 8{,}94978\ T \cdot 10^1 \cdot 1{,}56711\ T^2 \cdot 10^{-2}$ (дж. моль$^{-1}$) и точность $\pm$0,4%. Этот образец используется в калориметрии как эталонный стандарт.