

Inverse drop-calorimetry. A study of metastable and nonequilibrium phases

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ABSTRACT

The method of inverse drop-calorimetry was extended for studying the thermodynamic properties of metastable and nonequilibrium phases over a wide temperature range and in the phase transition regions.

KEYWORDS: drop-calorimetry, heat content, transformation enthalpy, metastable and nonequilibrium phases

INTRODUCTION

One of the primary trends in chemical thermodynamics is thermodynamics of metastable and nonequilibrium states, but the absence of adequate calorimetric methods hinders the development of experimental studies in the field. This paper presents a method of inverse drop-calorimetry that allows one to measure the heat content values of solids in a temperature range of 400 to 1700 K with an error that is less than 1.5 per cent.

EXPERIMENTAL

The measurements were performed using a HT 1500 SETARAM high-temperature heat flux calorimeter illustrated in Figure 1. Briefly, the experimental procedure consists of dropping sample (5–50 mg) which has been thermostated at 298.15 K into the upper cell of calorimetric detector. The detector is located in the isothermal zone of a high-temperature furnace. The operating principles and specifications are described in detail by Arpshofen et al., 1979 and Naumann and Petzold, 1981.

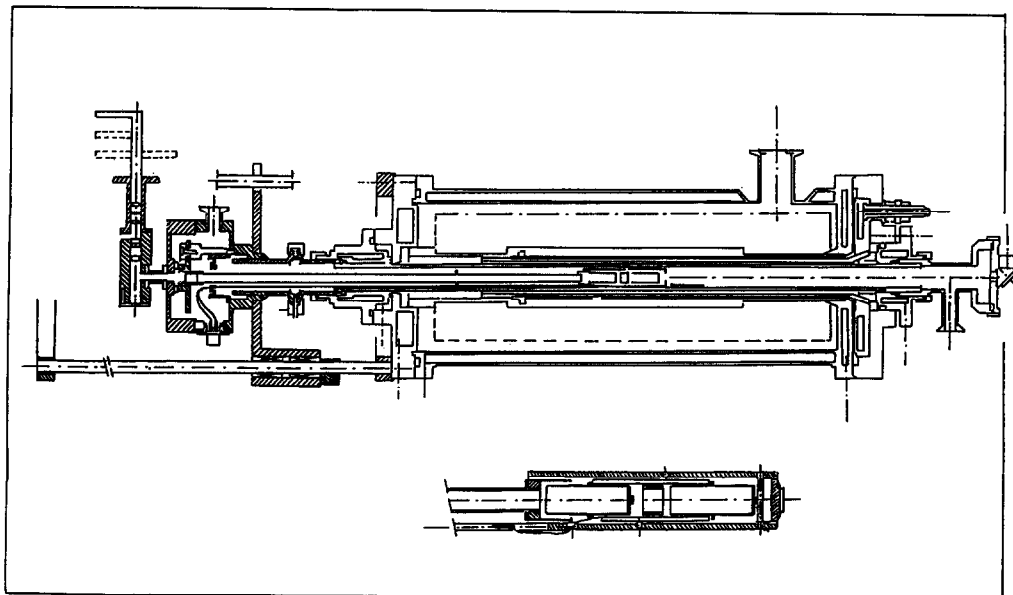


Figure 1 SETARAM HT 1500 high temperature calorimeter.

The computational equation for the heat content value is as follows:

$$[H^0(T) - H^0(298.15K)]_s = \frac{k(T)}{m_s} \int \Delta T dt \quad (1)$$

where $k(T)$ is the calibration coefficient at the experimental temperature calculated from the equation:

$$k(t) = \frac{H^0(T) - H^0(298.15K)]_r m_r}{\int \Delta T dt} \quad (2)$$

In equation (2) m_s and m_r are the masses of the sample studied and the standard, ΔT is the temperature difference between the upper (operating) and lower (reference) calorimeter cells and t is the time. The area under the ΔT vs t curve was determined using an ITC SETARAM electronic integrator. The calorimetric detector is calibrated directly in the course of the experiment by samples of material under study and the standard (monocrystalline α -Al₂O₃ and high-purity (99.999 %) molybdenum) being dropped one after another. Values of the calibration coefficient $k(T)$ are calculated for each sample using an equation approximating the dependence of $k(T)$ on the degree of filling the calorimetric cell at an experimental temperature (Figure 2), which allows one to raise considerably the accuracy of the method used.

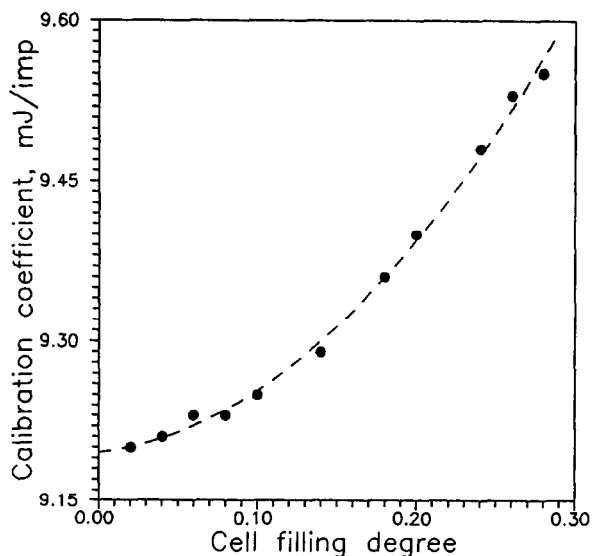


Figure 2 The dependence of calibration coefficient on the cell filling degree at $T = 896$ K.

The calorimetric cell temperature was taken using a Pt(10%Rh)/Pt thermocouple and F-283 digital voltmeter. The thermocouple was calibrated according to the Barrall's (1973) method: the melting temperatures of high purity Zn, Al and Cu were used as reference points. The error in temperature measurements in the experiment did not exceed ± 1 K over the temperature range under study.

To improve the stability of the calorimeter signal, a voltage stabilizer was used and the temperature of the furnace shell was kept constant by controlling the water flow rate in the cooling system. The deviations of calorimetric detector temperature in the isothermal experiment did not exceed ± 0.5 K.

The calorimeter design makes it possible to carry out experiments both in vacuum and in different gases (air, O_2 , CO_2 , N_2 , Ar) which considerably expands the range of materials that can be studied.

RESULTS AND DISCUSSION

The main advantage of the method presented is the rapid establishment of thermal equilibrium in the calorimetric cell after sample dropping. This allows one to apply the method, in contrast to traditional ones, for studying metastable and nonequilibrium phases. It should also be mentioned that, contrary to conventional drop-calorimetry, the experimental technique described here allows to eliminate the possibility of metastable and/or nonequilibrium states formation during calorimetric experiment, as well as to avoid a systematic error due to heat loss of the dropping specimen under study.

In order to illustrate the potential of the method proposed, the measurements of wurtzite boron nitride (wBN) enthalpy within the temperature range of 400 to 1300 K have been carried out. wBN was chosen to be studied due to the fact that it shows no thermodynamic stability region in the boron nitride phase p, T -diagram (Solozhenko, 1988) and at atmospheric pressure undergoes a polymorphic transformation into a graphite-like form (gBN) even at 700 K, which makes it impossible to study its thermodynamic properties at higher temperatures by traditional calorimetric methods such as drop-calorimetry or DSC.

The measurements were carried out on the wBN micropowder produced by shock compression of high-ordered gBN. Using a differential scanning calorimetry (DSC 7 PERKIN-ELMER) and a thermomechanical analysis (DL-1500 H SINKU-RIKO) it was shown that the start temperature of wBN \rightarrow gBN polymorphic transformation (T_0) for a wBN sample studied at the pressure of 0.1 MPa in inert atmosphere is 685 ± 5 K. The purity of the wBN sample under study was determined by mass-spectrometry, spectral analysis and chemical analysis. Impurities did not exceed 0.3% by mass and included C - 0.1%, O - 0.1%, Cr - 0.04%, Si - 0.03%, Al - 0.02%, and Fe - 0.01%. X-ray diffractometry (STADI P STOE) and IR-spectroscopy (PERKIN-ELMER 1600 FTIR) have not revealed any impurities of other boron nitride forms in the wBN under study.

The measurements were taken in a high purity argon atmosphere with oxygen content less than 0.0007 % by volume at a pressure of 0.105 MPa. A calorimetric detector with a Pt(10%Rh)/Pt thermopile and crucibles of melt alumina were used. Figure 3 shows a typical $T(t)$ curve after a wBN sample is dropped. The a-b branch of the curve corresponds to heat absorbed by the sample during its heating up to the calorimeter temperature, and the b-c branch corresponds to the endothermic process of wBN \rightarrow gBN transformation in the calorimetric cell. If the sample mass did not exceed 5 mg these thermal effects can be resolved in the 700-1300 K range. Thus one can determine a $\int \Delta T dt$ value for each of the effects and calculate the corresponding enthalpy values.

The heat content values for wBN obtained in the experiment are shown in Figure 4. This figure also shows the data of Solozhenko and Holodov (1990) for heat content of thermostabilized wBN with $T = 1315 \pm 5$ K obtained by Solozhenko (1989). A good correlation between the two series of experiments was observed as is shown in Figure 5 and this allows one to conclude that the heat content of phases undergoing transformations can be measured by the above method with sufficient accuracy.

On the other hand, the method permits one to determine the transition enthalpies of metastable and nonequilibrium phases at high temperatures. Thus, the $\int \Delta T dt$ values in the b-c branches of calorimetric curves were determined in the series of experiments at 1280 K and the $+13 \pm 5$ kJ/mole value for the wBN \rightarrow gBN transformation enthalpy was calculated taking into account 0.35 \pm 0.05 transition degree. The obtained H value is in a good agreement with $\Delta H_r(1280 \text{ K}) = +14 \pm 3$ kJ/mole, calculated using standard value of wBN \rightarrow gBN transformation enthalpy (Leonidov et al., 1988), as well as heat content temperature dependences both for wBN (the present work) and gBN (McDonald and Stull, 1961) at high temperatures.

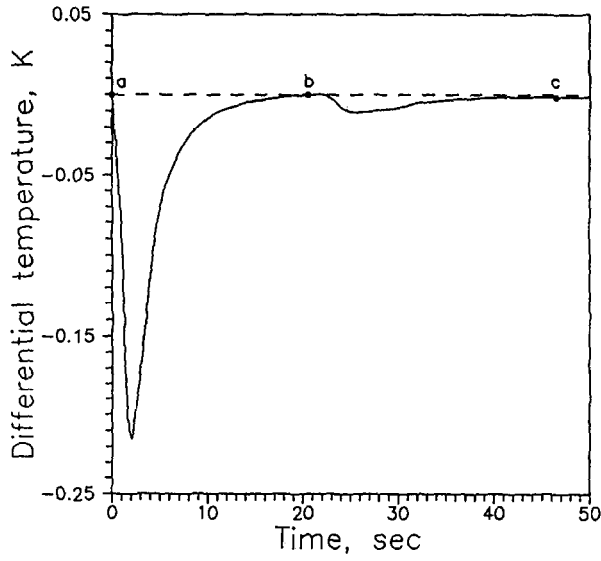


Figure 3. Registered signal curve after a wBN sample was dropped (calorimeter temperature is 1280 K)

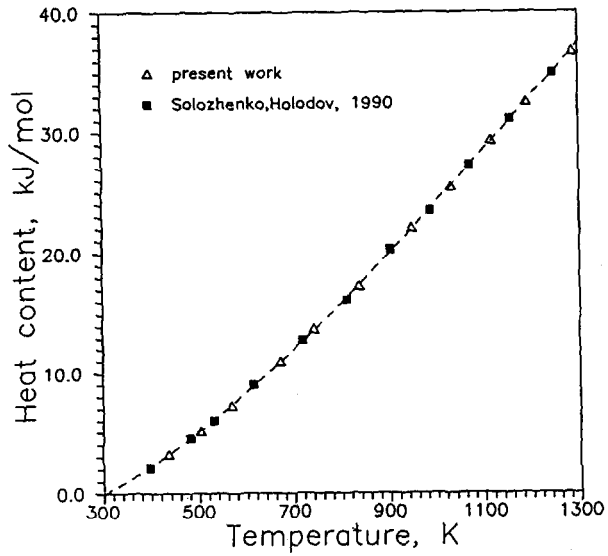


Figure 4. Experimental heat content values for wBN (dashed curve approximates the results obtained by Solozhenko and Holodov (1990)).

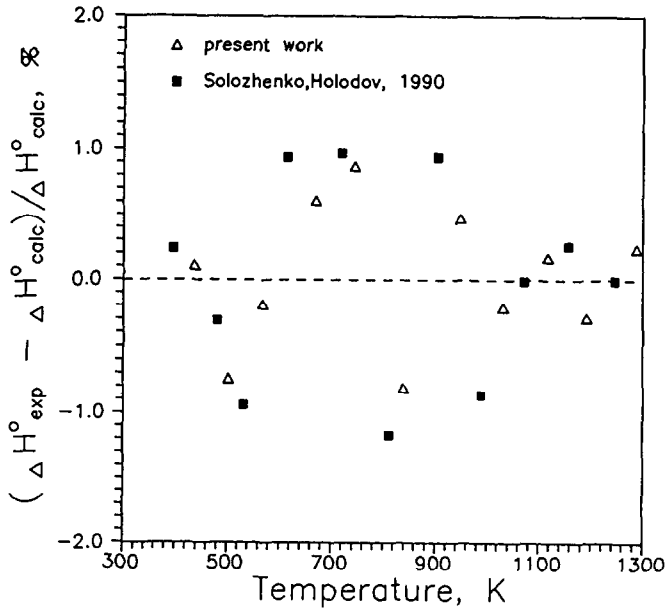


Figure 5. Deviations of wBN heat content values from the curve approximating Solozhenko and Holodov (1990) results.

CONCLUSION

The inverse drop-calorimetry can be recommended for studying the thermodynamic properties of metastable and nonequilibrium phases over a wide temperature range and in the region of their transformations, in particular.

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