Journal of Thermal Analysis, Vol. 53 (1998) 151-160

RAPID HEATING IN HIGH-TEMPERATURE THERMO-MICROSCOPIC ANALYSIS

Ya. I. Gibner and I. G. Vasilyeva

Institute of Inorganic Chemistry, Siberian Division of Russian Academy of Sciences
Pr. Lavrentyeva, 3, Novosibirsk, 630090 Russia

(Received November 29, 1997)

Abstract

A new technique of rapid heating in high-temperature thermomicroscopic analysis is suggested. The apparatus is described, the metrological features of the method and its advantages and limitations are discussed. Application of the technique to studying the behaviour of refractory Nd_3S_4, GaP and MoS_2 compounds in the temperature range from 25 to 2500°C shown.

Keywords: high-temperature, rapid heating, thermomicroscopic analysis

Introduction

There is a large number of refractory compounds for which reliable measurement of the melting point (*m.p.*) is difficult due to the change of their initial composition during heating. Two factors are responsible for the change in composition: the incongruent sublimation and the interaction of the melt with the crucible material. This is especially true in the case of oxides, borides, sulphides and pnictides of transition metals. The information on their *m.p.* is for this reason rather poor and contradictory. To measure the *m.p.* of these compounds in commercial high-temperature DTA apparatus, usually sealed crucibles made of Mo, Ta or W are used [1, 2]. However, these metals are ideally suited only for a limited number of refractory compounds and, besides, the practical use of such crucibles is limited by the failure of sealing at high temperatures due to the high porosity [3]. When open crucibles are employed, the conservation of the initial composition of compounds decomposing before melting is achieved by applying high pressures of an inert gas, under a suitable flux where possible, or by using specially designed crucibles inserted into each other [4].

The technique of rapid heating seems to be more promising, in which the time of melt-crucible contact is shorter and the decomposition is suppressed owing to kinetic factors and/or the changes in the sublimation mechanism. Such tech

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

niques, where the onset of melting is detected visually, have already been used to determine the *m.p.* of different compounds [5–8]. However, the visual indication makes the measurement of *m.p.* dependent on the observer's response and, besides, it is incapable to detect other transitions in the test substance except melting.

For lack of commercial apparatus with heating rates higher than $2°C\ s^{-1}$, different laboratory instruments have been designed for rapid heating [4–6, 9–11]. The present work is devoted to a new rapid heating technique for measurements of the temperature of different transitions in solids in the range of 26 to 2500°C. According to the theoretical concepts presented in [8–10], such type of technique, unlike the classical slow-heating one, requires general miniaturization and a sharp decrease in the weight of sample. To meet these requirements, the idea of recording the emitted radiation rather than the thermal effect from a heated solid was implemented. It is based on the known facts that any physical and/or chemical transitions in a solid being heated are accompanied by variations in the radiation coefficient [8, 9, 11]. If these variations are recorded as a function of the temperature using, for example, a suitable IR photodiode, the heating curves obtained can give information on the high-temperature behaviour of the solid. This concerns both the non-diffusion processes like congruent melting running fast enough to be independent of the heating rate and the sluggish diffusion-controlled processes such as incongruent melting, sublimation, and the like. However, since the mechanism of diffusion is known to vary with the heating rate, it is essential for an experimental apparatus to operate in a wide range of heating rates. This feature was taken into account in the design of the apparatus and the development of the experimental procedure. In doing so we were governed by the ICTA requirements.

Experimental

General arrangement

The schematic diagram of the apparatus described in [12] is shown in Fig. 1. A water-cooled working chamber (1) operates under static (0.1–500 kPa) pressure of pure helium supplied by a gas unit (2). The chamber has a demountable window (3) made of optical quartz, two current leads (4) to a heater (5) and a 5/20 W-Re thermocouple (6) as a temperature sensor. The thermocouple serves also as a support for a Mo crucible (7) 6 mm long and 3 mm in diameter with two axial borings. With its lower boring 3 mm deep and 1.2 mm in diameter the crucible is fitted over the thermocouple junction providing the minimum sample/thermocouple separation. The sample is placed in the upper boring 2 mm deep and 2 mm in diameter. The position of the crucible relative to the heater and thermocouple is rigidly fixed. The e.m.f. of the thermocouple with the cold junc-

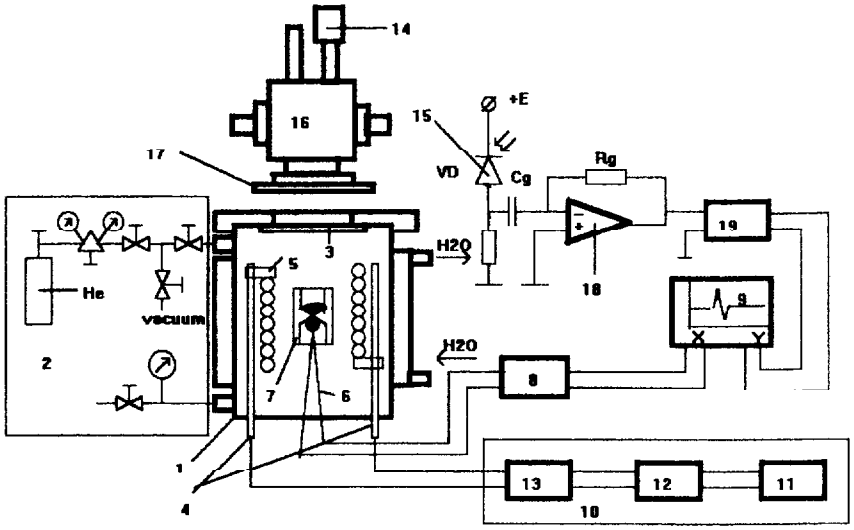

Fig. 1 Schematic diagram of the apparatus for thermomicroscopic analysis in the range from 25 to 2500°C

tion compensator (8) is fed to the 'X' input of a H306 plotter (9) with a time constant of no more than 0.05 s at the maximum recording speed of 75 cm s^{-1}. Heating from 25 to 2500°C is performed linearly at any digital rate in the 1–50°C s^{-1} interval. The temperature control unit (10) includes a regulator (11), a thyristor power amplifier (12), and a current transformer (13). When the furnace was switched off, the sample could be quenched at the rate of 200°C s^{-1}. Owing to the predominantly radiation heating, the small mass, and low thermal inertia of the measuring head, the quenching could be performed in about 3°C steps. The step width was primarily limited by the speed of the recorder used.

Heater and temperature pattern (TP)

For an apparatus ensuring rapid heating it is extremely important to generate a uniform, symmetric, extended, and time-stable temperature field because these parameters determine the accuracy of *m.p.* measurements. Besides the heater itself, also the crucible/heater distance and the gas pressure affect the *TP* owing to a combined action of radiation heating and convective flows in the furnace. The effect of varying heater geometry on *TP* for a given heating rate and fixed position of the crucible was studied experimentally. As is seen from Fig. 2a, the temperature gradient of *TP* produced by the cylindrical heater (ø=10, *h*=15 mm) at 1 atm pressure amounted to 120°C. Only the heater with the geometry presented in Fig. 2b was found to give a gradient of 5°C over a 15 mm length, which was

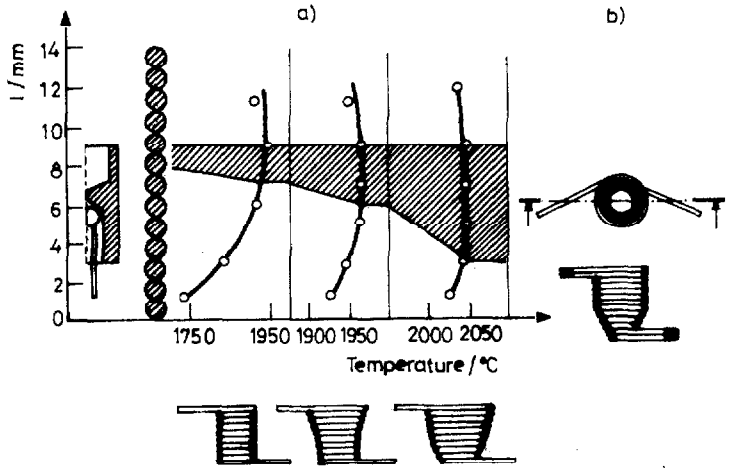

Fig. 2 Effect of heater geometry on the temperature pattern (a) and the optimum heater geometry (b)

more than enough for the 6 mm crucible. Note that high thermal conductivity of the crucible is also favourable to the shaping of the desired *TP*. The shape of *TP* is maintained at any pressure within the 0.1–3 atm interval.

The long-term stability of *TP* was found to depend on the design of the heater. The spiral spring heater was unsuitable for prolonged work due to the plastic deformation of tungsten at high temperature, resulting inter-coil shorting. Only the heater shown in Fig. 2b gave *TP* with reproducible characteristics for 200 and more heating-cooling cycles up to 2500°C. In this design two parallel tungsten wires 1.2 mm in diameter were closely wound on the required form.

Detection of radiation

Built into a special extension (14), a photodiode (15) was mounted in the ocular focal plane of a microscope (16). The microscope was fitted with two diaphragms. The first, iris diaphragm (17), limited the radiation intensity to prevent saturation of the photodiode. The second, unadjustable one, limited the field of view by the surface of the sample in the inner part of the crucible, protecting the photodiode from any parasitic illumination, thereby increasing its sensitivity. After a differential amplifier (18), the photodiode signal passed through a low-pass filter (19) tuned to 100 Hz and entered the Y-input of the plotter. With the thermocouple e.m.f. on the X-input, any phase transition in the solid under study manifested itself as a peak in the heating curve. During program-controlled heating the heating curves were recorded in $dE/d\tau$–T coordinates, where $dE/d\tau$ is the time derivative of the sample radiation.

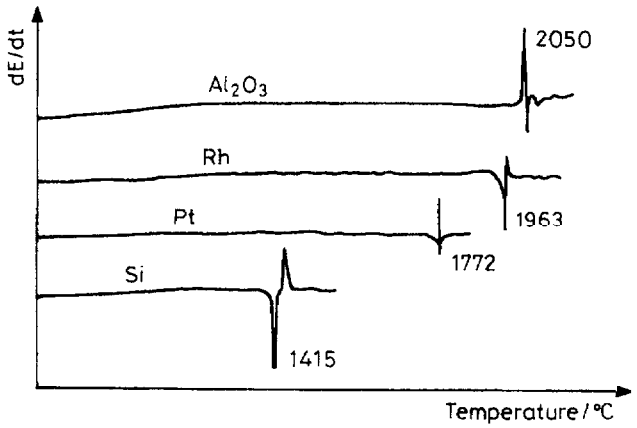

Fig. 3 Heating curves and melting points (°C) of the reference substances. Experimental conditions: weight 2.4 mg (below maximum mass), heating rate 17°C s^{-1} and gas pressure 1 atm

Reference substances

The experimental procedure was performed with different heating rates and gas pressures in the apparatus as the only parameters influencing the form of the heating curves. As reference substances with different thermal properties and *m.p.*, Rh, Pt, Si, Al_2O_3 were taken which undergo no transition other than congruent melting.

Their heating curves presented in Fig. 3 consist of a baseline changing monotonously with the temperature and corresponding to the absence of any change in the state of the substances, and the peaks due to melting. The peak positions on the temperature axis were well reproducible and their shapes were specific for each of the substances. In almost all cases the melting signals had some characteristic points, contrary to what might be expected for a peak of congruent melting. Only the first peak was taken to be correlated with melting, and its extremum point was taken as the melting point. Indeed, according to Fig. 4, the radiation coefficient is a linear function of the temperature before and after melting, and its slope only changes at the melting point giving a peak after differentiation. If the melting rate is higher than the heating rate, the peak width is determined by the time constant of the differentiating circuit $\tau=R$ C. The time constant was calculated from the requirement that the error in temperature determination at the given heating rate did not exceed 2°C judging by the circuit response to a square input pulse. This value was correlated with the frequency characteristics of the plotter. To clarify the origin of the secondary peaks, quenching was performed at each characteristic point of these peaks, followed by the inspection of the sample shape, color, and where possible, transparency. The secondary effects were

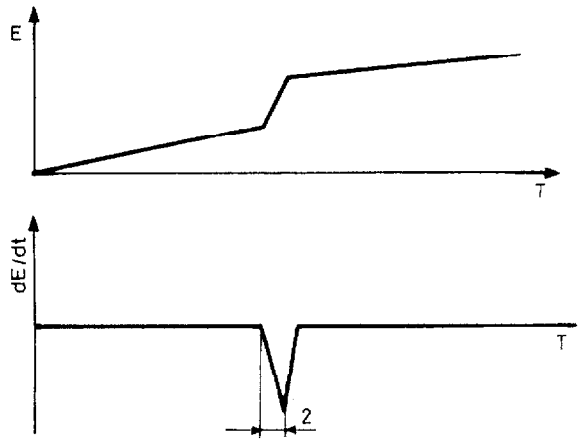

Fig. 4 Typical heating curve with characteristic point of melting in E–T and $dE/d\tau$–T coordinates for substances melting congruently

found to be connected with the wetting of the crucible by the melt and, in the case of Al_2O_3, with the loss of oxygen from the melt. Platinum showed no separate peak corresponding to the known pre-melting anomaly in brightness [13]. It should be noted that the position of the peak above the baseline is not determined by exo/endothermic effects as in DTA, but by the total change in the radiation from the sample and the inner walls of the crucible. This radiation was also dependent on the character of the sample/crucible interaction and, hence, carried no direct information on the origin of the transition. Since the height and width of the peaks were dependent on the amount of sample, temperature range and, in the case of diffusion-controlled transitions, on the reaction kinetics, these characteristics were used so far only for qualitative identification of the processes.

Effect of sample parameters on m.p. values

Large temperature gradients can arise across a sample of nonzero thickness as a result of rapid heating. The maximum thickness (R) was estimated for a permissible value of ΔT=5°C and heating rate, b=50°C s^{-1}, from the known equation [8]: $\Delta T\lambda/c_p d=bR^2/2$, where d is the density, c_p is the specific heat, and λ is the heat conductivity coefficient. The values calculated were equal to 0.85, 0.05, 0.7 and 1.5 cm for Si, Al_2O_3, Rh and Pt, respectively. Since these estimates are somewhat uncertain for lack of the high-temperature values of C_p and λ, the effect of mass, grain size and packing on the *m.p.* was also checked experimentally. The results obtained at 17°C s^{-1} rate and 1 atm pressure are listed in Table 1.

As can be seen, even though the sample mass taken was much less than the maximum allowed, *m.p.* could be determined without a loss in accuracy. This

Table 1 Effect of sample parameters on the measured *m.p.*

Sample		Maximum mass/ mg	Mass/ mg/e.m.f/mV			
Si	crystal	2.3	1.0/22.3	0.8/22.2	0.6/22.3	0.35/22.2
	powder		2.5/22.3	1.1/22.2	0.7/22.3	0.40/22.3
Al_2O_3	crystal	2.2	2.9/29.8	2.7/29.8	2.2/29.9	1.80/29.8
	powder		2.9/29.9	2.7/29.8	2.4/29.9	1.4/29.8
Pt,	plate	22	3.8/27.0	2.2/27.0	1.3/27.1	0.8/27.1
Rh,	plate	12	3.4/28.0	1.2/28.0	0.9/28.0	0.4/28.0
m.p./°C		Si 1415±5	Al_2O_3 2050±5	Pt 1773±6		Rh 1960±4

was possible due to the high sensitivity of the apparatus to transitions signals. The effect of grain-size and packing is shown to be within the experimental error determined mainly by the response time of the plotter. Thus, this sensitive and rapid method can supply accurate quantitative information on *m.p.* values even when using small amounts of substance.

Calibration of the apparatus

The apparatus was calibrated by measuring the *m.p.* of the reference substances recommended by ICTA [8, 11] and of other standards having only one characteristic temperature: Au(1063), Cu(1084), Si(1415), Pd(1554), Pt(1772), Rh(1963), Al_2O_3(2050), Y_2O_3(2439) and Ir(2444), for which the values are shown in parentheses are the *m.p.* in °C. These substances were 99.99% pure, in the form of bulk crystals for Au, Cu, Si, Y_2O_3 and Al_2O_3 or plates for Pd, Pt, Rh, Ir and Pt. E.m.f. values were measured for each sample (n=5–7) and a multivariate regression method was employed to build a mathematical model for the calibration of *m.p.* as a function of the measured e.m.f. A mathematical equation with parameters determined during the calibration process was found for each rate, for example T=91.72+54.36x+0.00043x^4 for a rate of 17°C s^{-1}. This allows to determine the *m.p.* of the samples not included in the calibration set with an accuracy of 1%. In view of possible deviations of instrument responses over a period of time, the calibration is checked before each experimental run.

Application of the method

The above mentioned reference substances exhibit only a melting effect and, in the case of Al_2O_3, evaporation. However, the unique possibilities of the technique can also be applied to studying the high-temperature behaviour of some decomposing materials. Some of their heating curves are shown in Fig. 5.

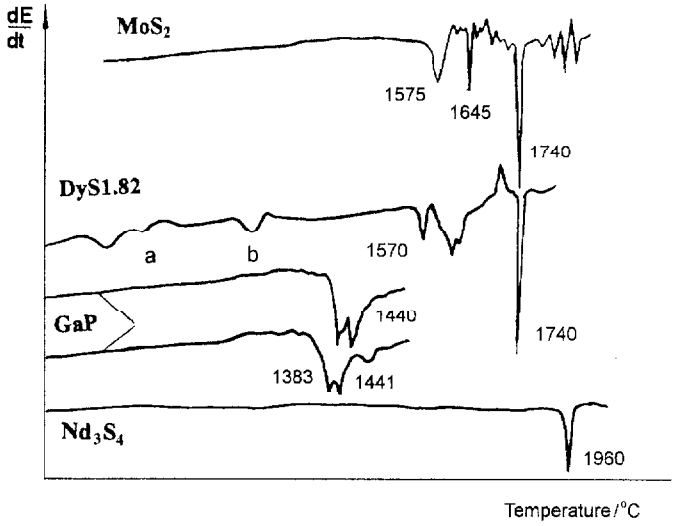

Fig. 5 Heating curves and transition temperatures (°C) for some refractory compounds. Conditions – weight (mg), heating rate (°C s^{-1}) and gas pressure (atm) respectively: Nd_3S_4–2.2, 17 and 1; GaP (lower curve) – 1.2, 17 and 1, (upper curve) – 1.8, 17 and 3; MoS_2 – 2.0, 17 and 1

Table 2 Melting point of Nd_3S_4 obtained by different techniques

Method	Sample holder	Amount/mg	T/°C
DTA	Closed Mo	100–200	1950±10
DCK	The same	100–200	1965±5
Calorimetry	The same	1000	1945±5
This method	Open Mo crucible	1–3	1960±10

The curve of Nd_3S_4 has only the melting peak with a characteristic temperature of 1960°C. This value was found to agree with those obtained by us using other techniques [14] as is listed in Table 2.

Table 2 shows that the technique proposed here gives the same accuracy with the advantage of easy preparation of the crucible and small amount of the substance needed.

Two peaks appeared in the heating curves of GaP decomposing before melting. The first peak was dependent on the pressure only, the second one shifted with changing pressure and heating rate. The first peak corresponds to the 'boiling' of the solid (intensive sublimation) and the second one to the melting of the altered composition due to some loss of phosphorus. Therefore, the information on P_{diss} of GaP and temperature of the liquidus line can be obtained in a single ex-

periment. As one could expect, the vapour pressure data obtained fall on the straight line of the known $\lg P-1/T$ dependence for solid GaP. This fact confirms the reliability of the proposed technique. The obtained *m.p.* values were found to decrease with decreasing heating rate. They differ from the known *m.p.* of GaP (1467±3°C) due to the corresponding variations of the initial stoichiometric GaP along the liquidus line.

The heating curve of the polysulphide $DyS_{1.85}$ has a more complicated form. To identify the nature of the observed transitions, heating at different rates and some quenching experiments were performed. It was found that the group of peaks marked 'a' and 'b' corresponded to the loss of sulphur and structural transitions of the sulphide according to the $DyS_{1.85}\rightarrow DyS_{1.5}$ reaction. The last peak belongs to the melting of $DyS_{1.5}$. All intermediate peaks may be connected with solid–solid transitions in the $DyS_{1.5}$ structure confirmed by the local Raman spectroscopy.

In MoS_2 the loss of sulphur was found to run according to the reaction $MoS_2\rightarrow MoS_{1.5}\rightarrow Mo$ and its heating curve reflected the boiling and melting of the reactants and their mixtures. The first peak corresponded to the boiling of solid MoS_2 occurring when its vapour pressure became equal to the gas pressure. The P_{MoS_2} values obtained in this way for a number of temperatures coincided with those calculated from the known $P_{MoS_2}=f(T)$ equation. The second peak was related to the melting of the $MoS_{1.5}$+Mo eutectic. This temperature was lower than the melting point of $MoS_{1.5}$ itself which was determined to be 1740°C. The same values of *m.p.* of $MoS_{1.5}$ were also reported by other authors. Above the *m.p.* of $MoS_{1.5}$ the intensive evaporation of sulphur from the liquid was manifested as a group of peaks. This evaporation ended by the formation of Mo which remained in the solid state up to 2610°C.

The above examples show that even with relatively small samples a diversity of information on the high temperature behaviour of samples can be extracted from a single experimental run. For processes running rapidly in solids, the transition temperatures measured are sufficiently reliable for the interpretation of the equilibrium state in spite of the use of rapid heating. This is not necessarily so for processes running slowly. Here we will not discuss the whole problem of obtaining reliable data for diffusion-controlled transitions because of the wide diversity of compounds. It will be considered in the study of each concrete type of the compounds. The first to be investigated were A^2B^6 compounds reported in this issue of the journal.

Conclusions

A new technique is proposed for measuring the temperatures of the solid–liquid, solid–vapour, liquid–vapour transitions in refractory compounds in the range of 25 to 2500°C and 10^{-5}–3 atm. It features a new thermomicroscopic ap-

paratus with rapid heating with the original heating and recording systems. An experimental procedure based on rapid heating was developed to determine melting points of congruently sublimating and decomposing compounds in an open crucible. Additionally, a possibility is shown to obtain information on the vapour pressures of these compounds, on the kinetics of their decomposition, and melting points of the components formed or their mixtures in a single run.

References

1 H. Spychiger and E. Kaldis, Helv. Phys. Acta., 55 (1982) 351.
2 E. Kaldis, J. Less. Comm. Met., 76 (1980) 163.
3 R. Steiger, High Temper. Sci., 7 (1975) 204.
4 G. H. Moh, Topic in Current Chemistry, 76 (1978) 108.
5 M. Addamiano, J. Phys. Chem., 61 (1957) 1253.
6 I. Vasilyeva, Ya. Gibner and L. Kurochkina, Neorg. Mat., 18 (1982) 360.
7 S. Sennikov, G. Revsin and M. Chistiakova, Zh. Neorg. Khim., 27 (1982) 1797.
8 O. P. Shlenskii and G. E. Vishnevskii, Dokl. Acad. Nauk, 246 (1979) 151.
9 W. Wendlandt, Thermal Methods of Analysis, World, Moscow 1978, 240 p.
10 Cheng Du, Doct. Dissertation, Ruhr-Universität Bochum, 1987.
11 J. Šesták, 'Thermophysical properties of solids', World, Moscow 1987.
12 Ya. I. Gibner and I. G. Vasilyeva, Patent USSR, SU 1806358 A3 1992.
13 V. Fridman, Inzh.-Fiz. Zv., 44 (1983) 986.
14 B. Ja. Tchechovskoi, B. D. Tarasov and I. A. Zhukova, Technika visokich temperature, 12 (1974) 1239.