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Thermal analysis of levitation-heated samples: Application to the niobium-germanium system

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We present a new method of thermal analysis based on the position change during melting of samples heated in an electromagnetic levitation coil. The temperature is measured with a two-colour pyrometer, subject to appropriate corrections. This method appears to be a useful complement to other investigations such as differential thermal analysis (DTA) or "simultaneous stepwise heating". The technique has been applied to the determination of the melting temperatures of alloys in the Nb-rich part of the Nb–Ge system.

1. Introduction

Since the first experiments of Okress [1], electromagnetic levitation has been used as a powerful technique for metallurgical studies at high temperatures and has lead to a number of publications. Weissberg [2] melted very pure metals (Ga, In, Au, Sb), Bartholin *et al.* [3] prepared Co alloys containing rare earth components, Chekhovskoi *et al.* [4] studied the temperature distribution on levitating Ru samples, before and during melting, and Bansal *et al.* [5] found levitation melting to be the best method for preparing dilute alloys of Ce in Al. Other applications followed later, making it possible to study chemical reactions on pure metals and compounds, such as the action of oxygen in metal sulphides [6]. Thermal diffusion and equilibrium techniques using levitation-heating were reported by Sunderland *et al.* [7]. A levitation-evaporation apparatus used to obtain ultrapure metallic layers was described by Van Audenhove [8]. Optical properties such as the emissivity of liquid metals at their melting point under levitation conditions were observed by Bonnel *et al.* [9]. Electromagnetic levitation-heating is often advantageous for rapid quenching experiments with a two-piston method [10, 11], or with a rotary splat-quenching apparatus [12]. Themodynamic properties can also be measured by levitation calorimetry [13]. Electromagnetic levitation is particularly useful for studying the properties of reactive materials at high temperatures.

In spite of the number of investigations, very little is known about the determination of melting points of compounds in the levitating state. Usually, differential thermal analysis (DTA) allows one to measure correctly solid–solid transitions up to 2200° C; solidus lines can also be checked very precisely by another method, called "simultaneous stepwise heating", as described in a recent paper by the authors [14]. However, in the vicinity of the melting point, crucible contamination may lead to erroneous determination of this temperature. We encountered such a situation in determining the Nb-rich part of the binary Nb–Ge phase diagram [15]. In this case, we found that thermal analysis on levitating samples by means of pyrometry is an elegant way to measure precisely the solidus temperature of this system, avoiding all contamination problems. In this paper we give a short description of the method.

2. Equipment

Samples with a non-regular, angular shape, weighing approximately 1 g, were placed in the copper levitation coil shown in Fig. 1. The power was provided by a Huttinger 30 kW h.f. generator (300 kHz), the maximum temperature reached under

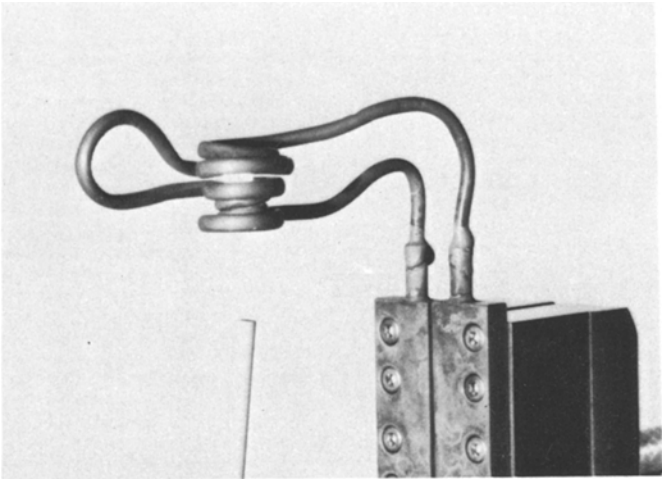

Figure 1 Water-cooled levitation coil made of copper (o.d. = 4 mm, i.d. = 3 mm). The reverse turns stabilize the sample during levitation.

the described working conditions being 3000° C.

The temperature of the sample was varied using a synchronous motor (3 r.p.m) acting on the generator power. This provided a nearly linear increase in temperature at rates up to 50° C min^{-1}, depending on the nature, the weight and the shape of the sample. The experiments were carried out in a double-walled, water-cooled furnace, permitting work under an argon pressure up to 4 atm., which was applied in order to reduce the evaporation rate of the alloys.

At the top of the furnace, on the coil axis, a crown glass prism reflects the light emitted from the sample into a two-colour Leybold pyrometer. Adjusting the relative position of the pyrometer and the prism along three directions, it is possible to observe different parts of the levitating sample in order to get some information about the temperature distribution within it. For the upper surface of all the materials investigated we found that the temperature was homogeneous within less than 10° C at 2000° C. The general assembly is shown in Fig. 2.

3. Pyrometer calibration

The main problem arising in measuring temperatures by means of a pyrometer is the unknown behaviour of the spectral emissivity of the studied materials as a function of the temperature. A two-colour pyrometer which compares the brightness at two different wavelengths reduces this problem to the study of the emissivity ratio $\epsilon_r = \epsilon(\lambda_1)/\epsilon(\lambda_2)$, which is assumed to be independent of temperature. In addition to the fact that not every material can be considered *a priori* to be a "grey body", errors due to selective absorption of the optical components are not excluded. Thus, great care has to be devoted to the calibration of the pyrometer. The influence of the selective absorption at the two considered wavelengths, $\lambda_1 = 0.45\,\mu m$ and $\lambda_2 = 0.65\,\mu m$, of the optical components (the glass window, the crown glass prism and the filter)

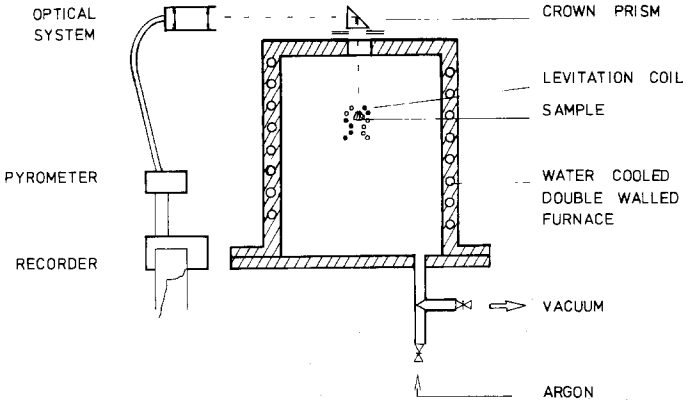

Figure 2 General assembly.

was studied by comparing the temperature of a massive W sample as determined by the pyrometer and a W–3% Re/W–25% Re thermocouple. The sample was placed inside a tantalum susceptor provided with a re-entrant bottom to accommodate the junction of the thermocouple. The latter supported the susceptor–sample assembly which was heated in a cylindrical induction coil. This set-up reached temperatures up to 2400° C. A more detailed description of this arrangement was given in a previous paper [11]. For the calibration experiment, tungsten was chosen because its emissivity at different wavelengths is very well known. From the work of Latyev *et al.* [16], we deduce that W can be considered as a good approximation to an ideal "grey body". In fact its relative emissivity ϵ_r for the two considered wavelengths (0.45 μm and 0.65 μm) varies between the values 1.068 and 1.083 at 1530° C and 2130° C respectively. This variation of ϵ_r with the temperature leads to an uncertainty $\Delta T = \pm 8°$ C at 2130° C. We found that the glass window (Maxos glass, 12 mm thickness) had a selective absorption, thereby lowering the registered temperature by an amount depending on the temperature and on the pyrometer scale. In the range above 2000° C it was necessary to interpose a filter whose absorption was taken into account. We found that the apparent measured temperature was lowered by 30° C up to 2200° C. It was impossible to detect any error caused by the crown prism.

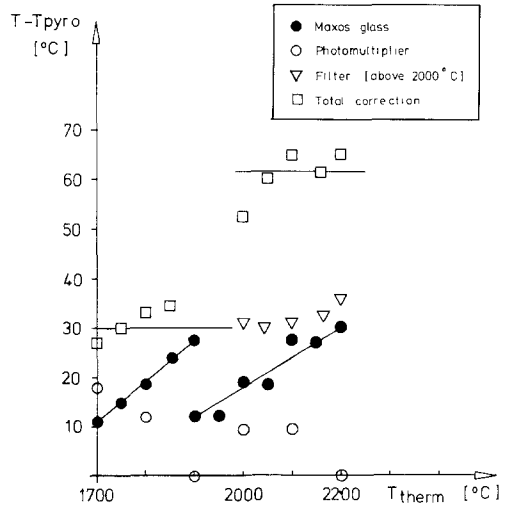

Figure 3 Corrections due to the optical components.

In addtion to the selective absorption phenomena, one has to take into account the non-linear effects introduced by the sensitivity of the photomultipliers with intensity. The results of the present investigation are represented in Fig. 3 which shows the corrections due to the glass window, the filter and the photomulitipliers. The total correction reported in Fig. 3 is only applicable to "grey bodies". Concerning the Nb–Ge system to be described below, it is important to ascertain that the variation of $\epsilon_r = \epsilon(\lambda_1)/\epsilon(\lambda_2)$ with temperature is small enough to yield an accuracy comparable to the case of tungsten. Bearing in mind that the temperature given by the thermocouple is the true temperature T, and that the temperature given by measurement with the pyrometer is T_r of the Nb–Ge alloy, it is possible to deduce the value of ϵ_r, using the relation [17]:

$$\left(\frac{hc}{k}\right)^{-1}\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)^{-1}\log \epsilon_r = \frac{1}{T}-\frac{1}{T_r}$$

The values of ϵ_r for four alloys of different compositions, i.e. $Nb_{95}Ge_5$, $Nb_{90}Ge_{10}$, $Nb_{80}Ge_{20}$ and

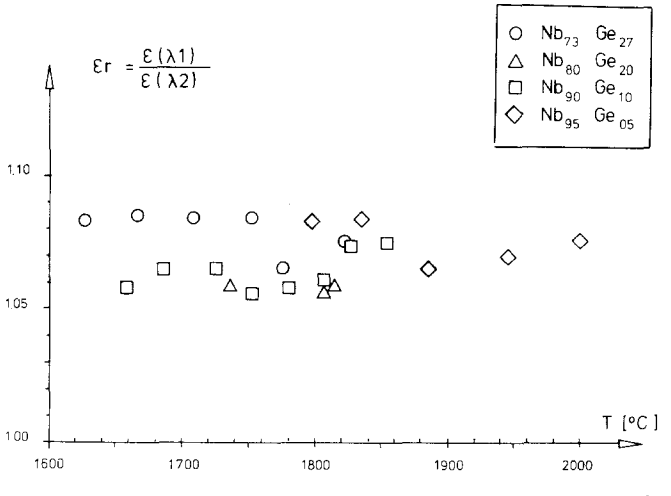

Figure 4 Emissivity ratio $\epsilon_r = \epsilon(\lambda_1)/\epsilon(\lambda_2)$ for four Nb–Ge samples. Values obtained from

$$\log \epsilon_r = \left[\frac{1}{T}-\frac{1}{T_r}\right]\cdot\frac{hc}{k}\cdot\left[\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right],$$

where T is the "true" temperature measured with the thermocouple and T_r the temperature measured with the pyrometer. $\lambda_1 = 0.45\ \mu$m and $\lambda_2 = 0.65\ \mu$m.

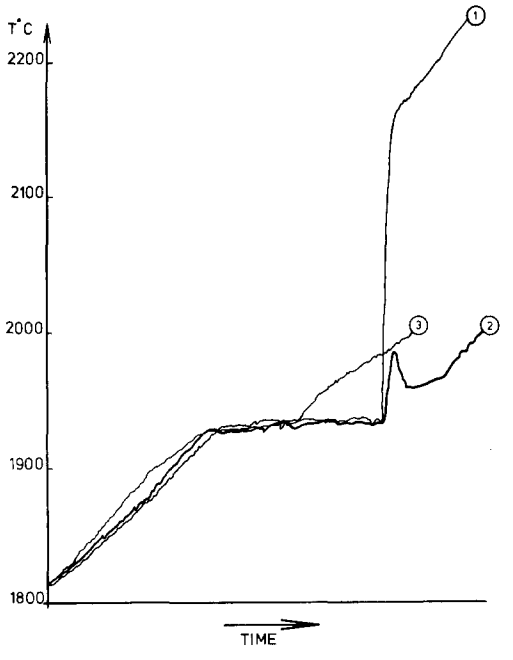

Figure 5 Fusion of levitating rhodium sample. (1) Initial sample of cubic shape. A large jump in the temperature is observed when fusion begins. (2) The same sample after the first melting. Its shape is approximately the shape of the levitating liquid. The jump in temperature is reduced with respect to that of the first run. (3) Third run for the same sample. Here the shape is exactly the same as that of the liquid in levitation. The jump in temperature disappears.

$Nb_{73}Ge_{27}$ are given in Fig. 4. It can be seen that the variation of $\epsilon_r(T)$ is small for all compositions, the average being $\epsilon_r = 1.070 \pm 0.015$ from 1600 to 2000° C. We thus conclude that the corrections given by the previous experiments on tungsten are appropriate for the Nb–Ge system, the error in ϵ_r leading to an error in the temperature of 8° C at 2000° C.

The calibration was also checked by measuring the melting temperature of pure, levitating metals, namely Nb(99.99%), Rh(99.99%) and Pt(99.999%) provided by Johnson–Matthey and Pd(99.99%) from Heräus. In these experiments the samples were placed in the levitation coil and the temperature was increased linearly as described in the preceding section. In general a plateau due to the latent heat appears when fusion begins. The fusion process is characterized by a sudden change of the sample position relative to the induction coil, its new shape being determined by the magnetic field gradient. The coupling between the melting sample in its new position and the levitation coil being now optimal, the temperature of the sample increases suddenly, as shown in Fig. 5 for the rhodium test and for three successive runs. We note that the jump in temperature disappears when the shape of the solid sample is such that the equilibrium position in the coil no longer varies upon melting (the third run in the present case). The stability of the fusion plateau is remarkable, the temperature fluctuation being less than 5° C. Here we have to note that the liquidus lines are not available by this technique because the sample does not change its shape when crossing the liquidus. The measured melting temperatures of Nb, Rh, Pt and Pd reported in Table I are in good agreement with those found in the literature [18].

4. Solidus lines in the Nb-rich part of the Nb–Ge system

In the DTA study of the binary system Nb–Ge [11, 15], we encountered some difficulty in measuring the solidus temperature of samples containing less than 22 at% Ge, the apparent peritectic formation temperature being lower than the eutectic temperature. Such behaviour would have been in contradiction with the previous work of Pan *et al.* [19], and Müller [20]. We found that the reason for this is strong reactivity of the samples with the BeO crucible at temperatures higher than 1870° C. This reactivity in the mentioned Ge concentration range (less than 22 at%) is not only found for BeO, but also for other oxide ceramics, such as ZrO_2, ThO_2 or Al_2O_3. The use of W crucibles gave satisfactory results but only during the first run, a lowering of the solidus temperature on subsequent runs indicating that a reaction occurred between

TABLE I Melting temperature of pure, levitating metals. Note that the measured temperatures are always slightly lower than those found in the literature. A small deposit of vapour on the glass window is the cause of this difference.

Metal	$T_{pyr.}$(°C)	Correction ΔT(°C)	$T_{measured}$(°C)	$T_{literature}$(°C) [18]
Nb	2391	60	2451	2468
Rh	1930	30	1960	1966
Pt	1735	30	1765	1772
Pd	1510	35	1545	1552

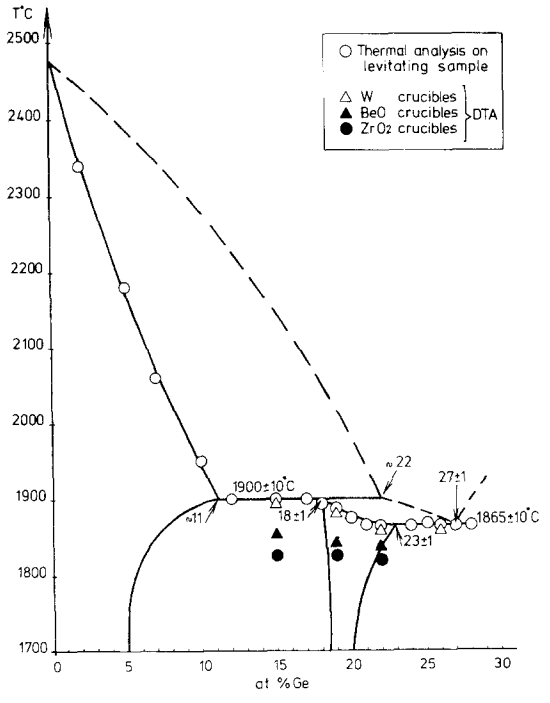

Figure 6 The high-temperature phase diagram of the Nb–Ge system.

W and the liquid compound. The only way to measure precisely the solidus line of the A15 phase in this composition range (17 to 25 at% Ge) is thus the proposed thermal analysis on levitating samples.

The melting point can be determined accurately from the starting point of the jump in temperature, when the sample changes its position in the levitation coil. In spite of the fact that the melting plateau itself is sometimes difficult to observe, we estimate the precision of this technique to be better than 10° C at 1900° C. In the case of Nb–Ge, it allowed us to distinguish clearly between the peritectic and the eutectic temperatures, which differ by only 35° C (see Fig. 6). We have summarized in Table II the melting temperatures of alloys melted by levitation and by resistive heating in refractory crucibles (DTA). We note that oxide crucibles lower the melting temperature of Nb–Ge alloys if T exceeds 1870° C. The use of DTA with BN or W crucibles avoids the lowering of the melting temperature of the Nb–Ge alloys. We conclude that the oxygen contained in the crucible reacts with the samples in the solid state, thus lowering their melting temperature.

5. Conclusions

The new method for thermal analysis we have described in this paper uses the position change of the sample in a levitation coil during the melting process as a criterion for fusion. Even restricted to systems where the spectral emissivity ratio ϵ_r does not vary too much with the temperature, it appears to be a useful technique in the study of reactive materials at high temperatures. The principal advantage is the avoidance of contamination during melting and, moreover, it is a rapid method for the determination of the solidus temperatures of alloys with a good accuracy even in the range well above 2000° C.

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References

1. E. C. OKRESS, D. M. WROUGHTON, G. GOMENETS, P. H. BRACE and J. C. R. KELLY, *J. Appl. Phys.* **23** (1952) 545.
2. R. WEISSBERG, *Rev. Sci. Instrum.* **30** (1959) 135.
3. H. BARTHOLIN, J. LAFORET, R. LEMAIRE, J. SCHWEIZER and J. SILVERA, *Acta Cryst.* **21** (1966) A94.
4. V. Ya. CHEKHOVSKOĬ, A. E. SHEINDLIN and B. Ya. BEREZIN, *High Temp. High Pressures* **2** (1970) 301.

TABLE II Comparison between the melting temperatures of Nb–Ge alloys melted by electromagnetic levitation heating and in refractory crucibles.

Alloy composition	$T^*_{pyr.}$(° C)	$T^\dagger_{DTA}$(° C)				
		BeO	ZrO_2	ThO_2	B N	W
$Nb_{85}Ge_{15}$	1900	1853	1824	–	1905	1895
$Nb_{81}Ge_{19}$	1875	1843	1825	1850	–	1885
$Nb_{79}Ge_{21}$	1865	1840	1820	–	–	1870
$Nb_{74}Ge_{26}$	1865	1860	1860	–	–	1860
$Nb_{72}Ge_{28}$	1870	1868	–	–	–	–

* The reported temperatures are those after relevant corrections.
† Results confirmed with pyrometric measurements on the same samples previously melted in refractory crucibles.

5. O. P. BANSAL and J. A. MORRISON, *Mater. Res. Bull.* **10** (1975) 1181.
6. O. C. ROBERTS, D. G. C. ROBERTSON and A. E. JENKINS, *Trans AIME* **245** (1963) 2413.
7. M. SUNDERLAND, A. E. HAMIELAC, W. K. LU and A. McLEAN, *Met. Trans.* **4** (1973) 575.
8. J. VAN AUDENHOVE, *Rev. Sci. Instrum.* **36** (1965) 383.
9. D. W. BONNEL, J. A. TREVERTON, A. J. VALERGA and J. L. MALGRAVE, "Temperature, Its Measurement and Control in Science and Industry", Vol. 4, Part 1, edited by H. Preston-Thomas, T. P. Murray and R. L. Shepard (Pittsburgh Instrument Society of America, 1972) p. 483.
10. J. M. BAKER, C. E. MIGHTON and W. R. BITLER, *Rev. Sci. Instrum.* **40** (1963) 1065.
11. R. FLÜKIGER and J. L. JORDA, "Applications of Phase Diagrams in Metallurgy and Ceramics", Vol. 1, National Bureau of Standards Special Publication 496 (1978) p. 375.
12. R. W. CAHN, K. D. KRICHNANAND, M. LARIDJANI, M. GREENHOLZ and R. HILL, *Mater. Sci. Eng.* **23** (1976) 83.
13. A. STRETZ and R. C. BAUTISTA, *High. Temp. High Pressures* 7 (1975) 197.
14. J. L. JORDA, R. FLÜKIGER and J. MULLER, *J. Less-Common Metals* **55** (1977) 249.
15. *Idem, ibid.* (to be published).
16. L. N. LATYEV, V. Ya. CHEKHOVSKOÏ and E. N. SHESTAKOV, *High Temp. High Pressures* **4** (1972) 679.
17. S. ACKERMAN, "Temperature, Its Measurement and Control in Science and Industry", Vol. 3; Part 2, edited by A. I. Dahl (Reinhold, New York, 1962) p. 849.
18. Handbook of Chemistry and Physics, 53rd edn. (CRC Press, 1972–1973) p. D142.
19. V. M. PAN, V. I. LATYESHEVA and E. A. SHISHKIN, "Metallography, Physics, Chemistry and Metals Physics of Superconductors" (Izd. Mankoa., Moscow, 1967).
20. A. MÜLLER, *Z. Naturforsch.* **25A** (1970) 1659.

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