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Thermochimica Acta 345 (2000) 179–184

thermochimica
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Thermal properties of beryllium[☆]

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Received 17 June 1999; received in revised form 4 October 1999; accepted 7 October 1999

Abstract

The temperatures of transformation T_{tr} and melting T_{m} and the enthalpies of transformation $\Delta_{\mathrm{tr}}H$ and melting $\Delta_{\mathrm{m}}H$ were measured by difference thermal analysis and by anisothermal calorimetry. The results for the hcp-bcc transformation of Be are $T_{\mathrm{tr}} = (1269 \pm 1)^\circ\mathrm{C}$ and $\Delta_{\mathrm{tr}}H = (6100 \pm 500)$ J/mol and those for the melting process are $T_{\mathrm{m}} = (1283 \pm 2)^\circ\mathrm{C}$ and $\Delta_{\mathrm{m}}H = (7200 \pm 500)$ J/mol. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Beryllium; Transition temperature; Enthalpy of transition

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1. Introduction

Beryllium is used as protective coating and evaporator in the plasma torus and as neutron multiplier in the breeder blanket of future nuclear fusion reactors. For the latter application, the neutron flux is increased by the prominent inelastic nuclear reaction

$$^{9}\mathrm{Be} + n = 2n + {}^{8}\mathrm{Be} \qquad (1)$$

above the threshold energy of 2.7 MeV with the subsequent decay of ^{8}Be into two α-particles. The increased neutron flux intensifies the process of tritium breeding in the lithium containing blanket according to the (n, α)-reaction

$$^{6}\mathrm{Li} + n = \alpha + {}^{3}\mathrm{H} \qquad (2)$$

Due to the high-temperature use of beryllium and the divergent thermal properties existing in the literature a refinement of the transition temperatures and the latent heats is necessary.

2. Literature survey

Early transition temperature measurements on beryllium were made by Teitel and Cohen using the thermal analysis method. The authors had not recognised that the identified lower temperature peak is the α-β transformation of beryllium [1]. Martin and Moore succeeded in confirming unequivocally the enantiotropic transformation of beryllium by difference thermal analysis (DTA). The authors report 1269–1275°C for the transformation temperature and 1287–1292°C for the melting temperature of beryllium of different qualities [2]. Kantor et al. determined the melting temperature by enthalpy measurements with a drop calorimeter. They were not

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[☆] Presented at 13th Kalorimetrietage, Freiberg/Sa., 17–19 March 1999.

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PII: S0040-6031(99)00372-X

Table 1
Lattice parameters a and c, cell volume V, number of formula units Z per unit cell and X-ray density ρ_x of beryllium [5]

Modification	a (pm)	c (pm)	c/a	V (nm^3)	Z	ρ_x (mg/m^3)
hcp, 22°C	228.66	358.33	1.567	0.01623	2	1.844
hcp, 1250°C	234.4	365.9	1.561	0.01741	2	1.719
bcc, 1260°C	255.2	–	–	0.01662	2	1.801

aware of an α-β transformation just below the melting point of beryllium [3]. Amonenko et al. investigated the electrical resistivity as a function of temperature and found a steep increase at the transformation temperature. They observed a decrease of the cell volume at the hcp-bcc transformation [4]. The crystallographic data of beryllium are summarised in Table 1 [5]. The c/a ratio of the lattice parameters of the hcp modification is less than the ideal value $\sqrt{8/3}$. The relative cell volume contraction is $\Delta V/V = -4.5\%$. Further transition temperature measurements were performed by Francois and Contre [6] through electrical resistivity experiments as well as by Loasby and Dearden [7] and Abey [8] through DTA. The results of the transformation and melting temperatures of beryllium are compiled in Table 2.

The sum of the enthalpies of transformation and melting of beryllium was evaluated from enthalpy measurements through drop calorimetry up to 1900°C by Kantor et al. [3]. Francois and Contre calculated the enthalpies of transformation $\Delta_{tr}H$ and melting $\Delta_m H$ from the pressure dependence of the electrical resistivity in the region of the transition points with the modified Clausius–Clapeyron equations

$$\frac{dp}{dT_{tr}} = \frac{\Delta_{tr}H}{T_{tr} \cdot \Delta_{tr}V} < 0 \tag{3}$$

$$\frac{dp}{dT_m} = \frac{\Delta_m H}{T_m \cdot \Delta_m V} > 0 \tag{4}$$

using $\Delta_{tr}V = -2.2 \times 10^{-7}$ m^3/mol (see Table 1) and $\Delta_m V = +5.6 \times 10^{-7}$ m^3/mol [6]. Radenac and Berthaut measured the enthalpy of solidification of beryllium by anisothermal calorimetry in the cooling mode at a temperature starting some degrees below the melting point [9]. Loarsby and Dearden used a DTA instrument. The peak areas of the enthalpies of transition of beryllium were calibrated with those of silver and gold standards [7]. Also Abey applied the DTA for these measurements using a silver standard [8] that should be inadmissible due to different melting temperature regions of silver and beryllium. The results of the enthalpies of transformation and melting of beryllium are listed in Table 3.

The critically assessed manuals on binary alloy phase diagrams and on thermochemical properties recommend the following data for beryllium: temperature of transformation, 1254°C [10–13] and 1270°C [14]; temperature of melting, 1287°C [10–13] and 1289°C [14]; enthalpy of transformation,

Table 2
Temperatures of transformation T_{tr} and melting T_m of beryllium

T_{tr} (°C)	T_m (°C)	Method	Reference
1263	1278	Thermal analysis	[1]
1271	1290	DTA (Be by zone refining)	[2]
–	1287	Drop calorimetry	[3]
1254	–	Electrical resistivity	[4]
1260	1285	Electrical resistivity	[6]
1279	1290	DTA	[7]
1263	1285	DTA	[8]
1268 ± 1	1283 ± 2	DTA	This year
1270 ± 1	(1283 ± 2)	Anisothermal calorimetry	This year

Table 3
Enthalpies of transformation $\Delta_{tr}H$ and melting $\Delta_{m}H$ of beryllium

$\Delta_{tr}H$ (J/mol)	$\Delta_{m}H$ (J/mol)	$\Delta_{tr}H + \Delta_{m}H$	Method	Reference
–	–	14800	Drop calorimetry	[3]
7500	14600	(22100)	Clausius-Clapeyron ((T_{tr}, T_{m}) = $f(p)$)	[6]
–	-9050^{a}	–	Anisothermal calorimetry	[9]
2100	2400	(4500)	DTA (peak area integration)	[7]
7950	9200	(17150)	DTA (peak area weighing)	[8]
6100 ± 500	7200 ± 500	(13300)	Anisothermal calorimetry	This year

[a] Enthalpy of solidification

6849 J/mol [10,13] and 2552 J/mol [11]; enthalpy of melting, 7895 J/mol [10,12,13] and 12217 J/mol [11].

3. Experimental

A Netzsch 404/3 DTA unit (Selb, Germany) was used for the temperature measurements. Temperature calibrations were made with the melting points [10] of aluminium ($T_m = 660.5°C$), gold ($T_m = 1064.4°C$) and nickel ($T_m = 1455.2°C$) in the heating mode at a rate 2 K/min. The time constant τ_1 of the signal was calculated according to the tangent method [15]; it is less than 0.5 min for samples in the 50 mg range.

The transition enthalpy measurements were carried out in the heating mode using a high-temperature calorimeter HTC 1800 of SETARAM S. A. (Lyon, France). The instrument operates for this purpose anisothermally and according to the heat flux principle. The detector is made up of two alumina crucibles, one above the other, which are surrounded by two crown-shaped piles of 18 plus 18 Pt-6% Rh/Pt-30% Rh thermocouples (EL 18), each pile in one plane [16]. A platinum liner in the crucibles would result in lower standard errors of the measurements due to a more symmetric radial heat transport. However, the incompatibility of platinum with beryllium rules out the use of this liner material. Preliminary experiments have shown that a heating rate of 2 K/min is reasonable. Heating rates of 0.5 K/min and lower result in growing instabilities of the heat flux curve. The optimum mass range of the samples is 50–200 mg depending on their atomic masses. It appeared during the calorimetric calibration of the instrument that the specific latent heats of the standards and the samples should be of the same order of magnitude: decreasing masses m are to be used for decreasing atomic masses M of the specimens in order to get comparable heats Q given in μV s and, hence reliable sensitivity factors $S = (Q \cdot M)/(m \cdot \Delta H)$. The temperature and enthalpy calibrations were made with the melting points and the enthalpies of melting of aluminium, gold and nickel [10]. The time constant τ_1 of the calorimeter signal is 5 min.

It was not advisable to use the available beryllium spheres with too small diameters ≤2 mm because the surface-to-volume ratio is infavourable, the heat sinks are spatially distributed on the crucible bottom during heating and the coalescence of many small spheres to one big sphere is hindered during the melting process. It happened from calibration measurements that the material of this geometry resulted in irreproducible sensitivity factors when it was used for this purpose. Beryllium foils on the flat bottom of the crucibles were preferred which spherodise after first melting. The foil diameter was 8 mm, the mass ranged from 40 to 50 mg. The material (Heraeus, Hanau, Germany) had been extruded and hot rolled from vacuum-melted and electrolytically refined beryllium. The chemical analysis of the supplier is (in mass %): 0.03% C, 0.03% Fe, 0.02% O, 0.02% Ni, 0.01% Si, 0.01% Al, 0.006% Mg, 0.003% Mn, 0.003% Cr, < 0.04% other impurities, >99.83% Be.

4. Results and discussion

4.1. Temperatures of transformation and melting

The results of DTA reveal two peaks which are completely separated from each other by 15 degrees

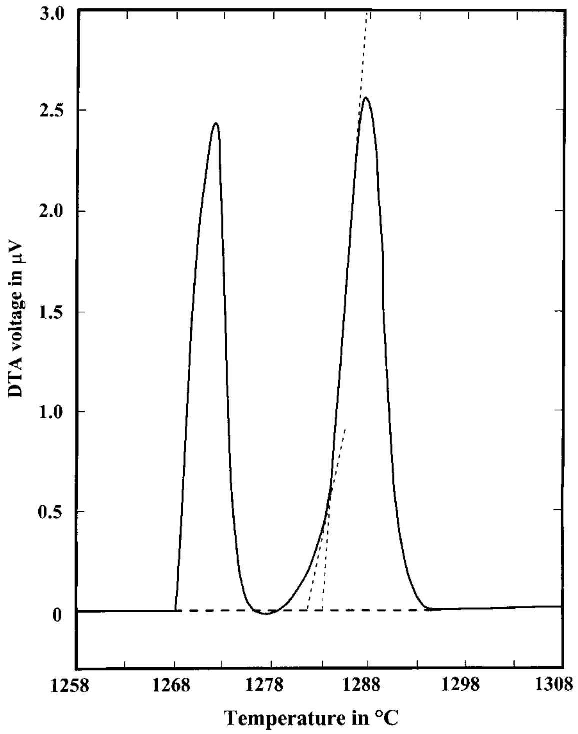

Fig. 1. Temperatures of transformation and melting of beryllium measured by DTA.

and can be related to the hcp-bcc transformation and to the melting process of beryllium. The first peak starts at (1268 ± 1)°C by a sharp increase from the base line and is attributed to the transformation temperature. The second peak leaves the base line by a bended curve with a back-extrapolated temperature of 1282°C and passes over to a linear curve. The transition in this curve is characterised by a distinct bend at 1283°C, see. Fig. 1. These temperatures cannot be attributed to the solidus and liquidus curves of the Be(O)-liquid phase field of an anomalous eutectic Be-BeO system, which would have been crossed during heating because the maximum solubility of oxygen in beryllium is reported as low as $x_O = 0.001$ at.% [17]. It is supposed that the Be-BeO system is a degenerate eutectic one. The lower observed temperature, $T = 1282$°C, can be related to a eutectic melting of impurities or beryllium-impurity compounds. The upper observed temperature is the melting temperature of pure beryllium, $T_m = (1083 \pm 2)$°C, which is only 0.03 degrees higher than the eutectic temperature of the Be-BeO system by application of the modified Clausius–Clapeyron equation. The initial slope of the liquidus curve of the Be-BeO system is about 50 K per mass % oxygen [17] which would result in a temperature increase of the liquidus temperature by 1 K for an oxygen impurity in beryllium of 0.02 mass %. Impurities of typically 0.1 mass % oxygen would result in a liquidus temperature of 1288°C, i.e. an increase of 5 K. The observed higher melting temperatures of other authors [2,7,8] could be indeed explained as liquidus temperatures induced by higher amounts of oxygen impurities.

The transformation and melting temperatures of beryllium could not be measured as precisely by calorimetry in the heating mode as by the DTA method due to the high time constant $\tau_1 = 5$ min of the signal. However, $T_{tr} = (1270 \pm 1)$°C can be given for the transformation temperature by this method.

4.2. Enthalpies of transformation and melting

The enthalpies of transformation and melting of beryllium were determined by graphical separation of both the peaks generated by anisothermal calorimetry because the tail of the transformation enthalpy peak is superimposed on the beginning of the melting enthalpy peak, see Fig. 2. The double peak was divided into two single peaks by a programmed vertical line at the position of the local maximum of the curve. As a result of five measurements the ratio of the peak areas (given in µV s) of the enthalpy of melting to the enthalpy of transformation of beryllium is 1.17 ± 0.01. However, this ratio is higher for the DTA signals because the heat transfer for liquid beryllium is obviously higher than that for solid beryllium.

The calorimeter was calibrated at a heating rate of 2 K/min with the enthalpies of melting of gold and nickel [10] using three specimens with different masses in each case. The temperature dependent sensitivity factor revealed $S = (0.535 \pm 0.016)$ µV/mW, see Table 4. The sum of the enthalpies of transformation and melting of beryllium was determined on three samples by two runs in each case. The measured peak areas Q (in µV s) were split into Q_{tr} and Q_m with the ratio $Q_m/Q_{tr} = 1.17$ obtained by computer evaluation. The results are listed in Table 5.

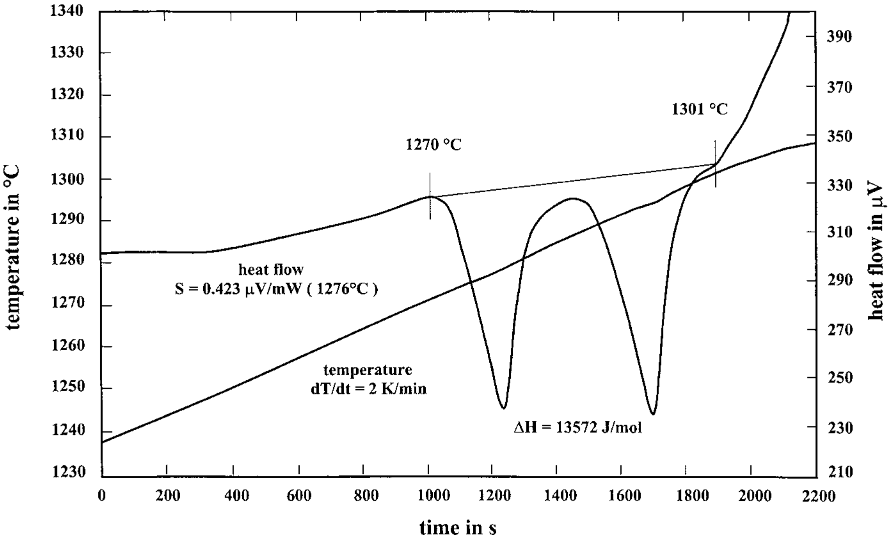

Fig. 2. Enthalpies of transformation and melting of beryllium measured by anisothermal calorimetry. Peak area ratio $\Delta_m H : \Delta_{tr} H = 1.17$.

The mean values and the 68% standard deviations of $\Delta_{tr}H$ and $\Delta_m H$ are added in the table. The corresponding standard error of the interpolated sensitivity factor S_{Be} of the calorimeter calibration is about ±5% (see Table 4) and is added to the results of the enthalpies of transformation and melting of beryllium yielding

Table 4
Calibration of the calorimeter with the enthalpies of melting of gold and nickel [10] in the heating mode at $dT/dt = 2$ K/min

Material	Enthalpies of melting $\Delta_m H$ (J/mol)	Mass m of sample (mg)	Peak area Q (µV s)	Sensitivity factor S (µV/mW)
Au	12552	244.5	8327	0.534
Au	12552	215.9	7631	0.555
Au	12552	190.2	6250	0.516
				$S_{Au} = (0.535 \pm 0.016)$ µV/mW
Ni	17472	207.1	21431	0.348
Ni	17472	137.3	12945	0.317
Ni	17472	83.9	7994	0.320
				$S_{Ni} = (0.328 \pm 0.014)$ µV/mW

Table 5
Enthalpy of transformation $\Delta_{tr}H$ and enthalpy of melting $\Delta_m H$ of beryllium in the heating mode at $dT/dt = 2$ K/min using the sensitivity factor $S = (0.423 \pm 0.021)$ µV/mW at 1276°C and $\Delta_m H/\Delta_{tr} H = 1.17$

Peak area Q (µV s)	Mass m of sample (mg)	$\Delta_{tr}H + \Delta_m H$ (J/mol)	$\Delta_{tr}H$ (J/mol)	$\Delta_m H$ (J/mol)
28331	44.8	13473	6209	7264
30327	44.8	14422	6646	7776
28141	48.7	12311	5673	6638
30592	48.7	13383	6167	7216
28810	46.8	13124	6048	7076
		13343 ± 677	6149 ± 312	7194 ± 365

$\Delta_{tr}H = (6149 \pm 312 \pm 306)$ J/mol and $\Delta_m H = (7194 \pm 365 \pm 359)$ J/mol, respectively.

5. Conclusions

The weighed mean values of the temperatures of transformation and melting of beryllium determined by DTA and calorimetry are $T_{tr} = (1269 \pm 1)°\mathrm{C}$ and $T_m = (1283 \pm 2)°\mathrm{C}$, respectively. The mean values of the enthalpies of transformation and melting applying the Gauss error propagation law are $\Delta_{tr}H = (6100 \pm 500)$ J/mol and $\Delta_m H = (7200 \pm 500)$ J/mol, respectively.

It is believed that the higher melting temperature of beryllium in earlier investigations is in reality the liquidus temperature of oxygen contaminated material in the degenerate eutectic Be-BeO system. The enthalpies of transformation and melting are indeed of the same order of magnitude which is in contrast to previous misinterpreted experimental results of critically assessed thermodynamic tables.

Acknowledgements

The author gratefully acknowledges the experimental work by Mr. W. Laumer.

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