J Therm Anal Calorim (2011) 105:141–143
DOI 10.1007/s10973-011-1448-2

SHORT COMMUNICATION

Curie temperature of nickel

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Received: 22 October 2010 / Accepted: 7 March 2011 / Published online: 20 March 2011

Abstract Nickel presents a magnetic transition ferromagnetic/paramagnetic with a variation of temperature; this transition is classified as a second order transition using the Ehrenfest criteria. The end of this transition is characterized by a point called Curie point. This temperature is used for the calibration of thermogravimetric apparatus. As the Curie temperature is not a fixed point, no scientific authority has decided what the temperature of this point is. As different values are proposed in the literature, it appeared that it was necessary to further explore measurement of this point.

Keywords Nickel · Curie temperature · Thermogravimetry

Introduction

In 1832, Pouillet found that for some substances like nickel, iron and cobalt, a limit existed for the temperature involving the magnetism. In 1895 Curie explained this phenomenon. It is a transition from ferromagnetic to paramagnetic. A consequence of this transition is the variation of the C_p versus that of the temperature, which presents a maximum; this maximum is called the Curie point. This kind of transition has been classified by Ehrenfest as a second order transition because the second derivative of the Gibbs function $G = f(T)$ presents a discontinuity. The shape of the curve $C_p = f(T)_p$ recalls the Greek letter λ, for this reason this curve is sometimes called 'lambda curve'. The calculated curve using SGTE unary system data base is presented in Fig. 1.

This property is used in thermal analysis for the calibration in temperature of thermogravimetric analysis apparatus (TG) (T.A. Instrument. Thermal Application Note TN-24); in these conditions, it is absolutely necessary to know with absolute precision the Curie temperature of the selected elements or alloy used for the calibration (Fig. 2).

About nickel, we found in the literature that the temperature of Curie was between 353 and 360 °C. It is the reason why we decided to perform a determination of this temperature.

Historical information

Pouillet in 1832 proposed a Curie temperature for Ni of 358 °C. This value has been confirmed by Neel [1]. In 1966, Keffer [2] in his handbook of Physics proposed a temperature of 354 °C. The same year, Kubaschewski et al. [3], in 'Metallurgical thermochemistry' proposed a temperature of 357 °C. In 1973 Hultgen et al. [4], in 'Thermodynamic Selected Properties of Inorganic Substances', selected a value of 358 °C. The same year, Barin and Knacke [5] in 'Thermochemical Properties of Inorganic Substances' selected the value of 357 °C, but in the edition of 1977, Barin et al. [6] selected a value of 358 °C, agreeing with the selected value of Hultgren. In 1989, in a report for NPL (DMA (A) 195), by Dinsdale [7], the selected value is 360 °C. This value is actually the one which is selected by SGTE (Scientific Group Thermodata

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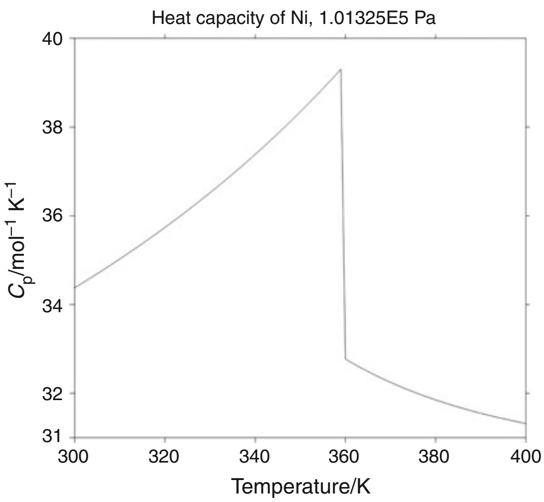

Fig. 1 $C_p = f(T)$ for Ni

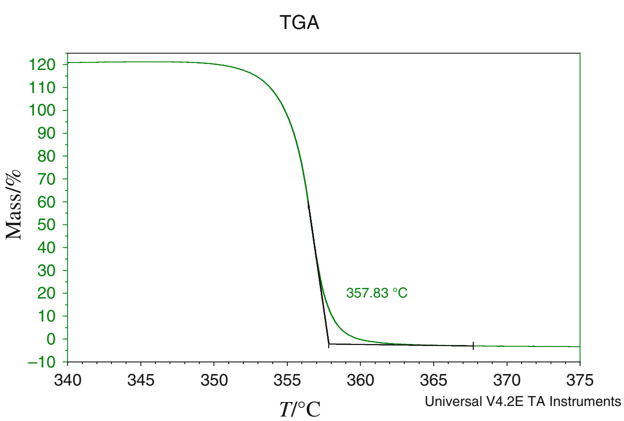

Fig. 2 TG: m = f(T) for Ni (with a magnet)

Europe). In 1992, in ASM Handbook Vol 3 Alloy Phase Diagram edited by Backer et al. [8], in the appendix 4.9 (Magnetic transition temperature of the elements) the selected temperature is 354.2 °C. In 1993, in the 6th edition of Materials Thermochemistry by Kubaschewski et al. [9] the selected value is 358 °C.

Experimental information

A sample of Ni, provided by TA Instrument, with a purity of 99.99% (mol), as been used for the experiments. The Curie transition is given by TA Instrument at 358.28 °C ± 0.35.

We performed our experiment by DSC (TA Q1000). Calibration has been performed with pure metals (5 N) In, Sn and Pb.

The results are as follows

	T_{fus}/°C measured	T_{fus}/°C recommended by [10]	$\Delta_{fus}H$/Jg^{-1} measured	$\Delta_{fus}H$/Jg^{-1} recommended by [11]
In	156.56	156.598$_5$	28.57	28.62
Sn	232.01	231.928	57.71	60.38
Pb	327.55	327.462	22.07	23.08

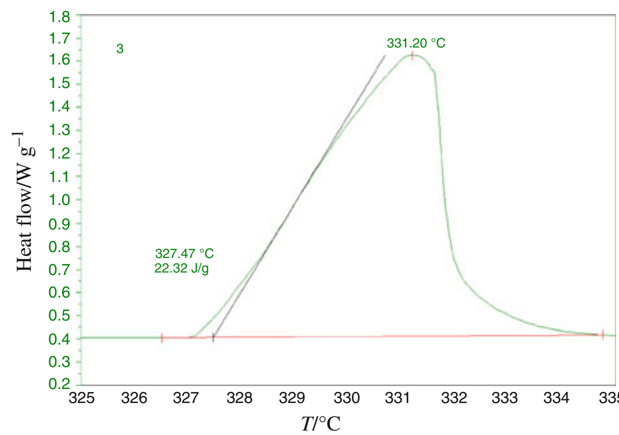

Fig. 3 DSC Hf = f(T) for Pb

A verification of the calibration of the apparatus has been performed with the melting points of pure lead (5 N), because it is the nearest point of the Curie temperature of Ni. The recommended value of the temperature of fusion of lead is extracted from a technical report of IUPAC [10], this value is $T_{fus} = 327.462$ °C.

With a view to knowing the standard deviation of the apparatus, the melting point of a sample of lead of a mass of 7.12 mg was measured ten times with a heating rate of 10 °C/min (Fig. 3). Measurements have been performed under nitrogen atmosphere (U quality) provided by Messer Company.

The containers used are in aluminium alloy (with holes).

The average value is $T_{fus} = 327.49$ °C with a standard deviation $\sigma = 0.02$, the correction ΔT is of 0.03 °C.

Curie temperature of Ni has also been measured ten times in the same experimental conditions (Fig. 4).

The average value measured is: $T_c = 358.31$ °C with a standard deviation $\sigma = 0.04$, with the correction, the Curie temperature is $T_c = 358.28$ °C and $\sigma = 0.04$. As we can see, this measured temperature is in a perfect agreement with the one given by TA Instrument (358.28 ± 0.35 °C).

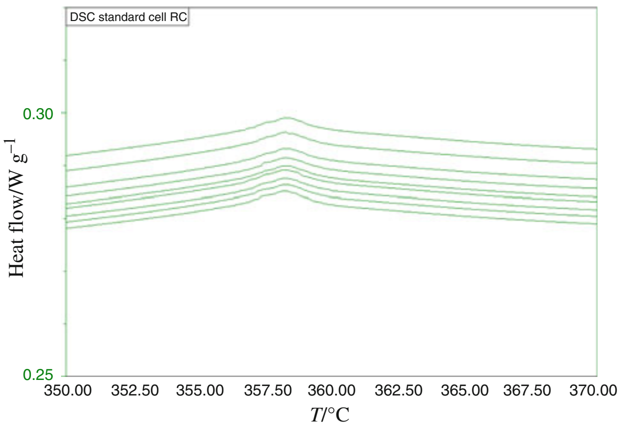

Fig. 4 DSC Hf = f(T) measurement of Ni

Discussion

The purity is an important factor for the determination of the precise Curie temperature. As this kind of transition (second order) is not associated with an enthalpy of transition, it is not possible in these conditions to use the Vant' Hoff law. A survey of the binary phase diagram shows that there is not a lot of information concerning the variation of the Curie points versus that of the composition.

We used the compilation of Massalski [11] (Binary Alloy Phase Diagrams A.S.M. 1990). As we can see, only 12 binaries present information on the Curie temperature, and the authors have not the same Curie temperature value for Ni. When in a binary, Curie temperature is represented versus that of the composition; it is possible to make an approximation. We considered that the variation is linear and it is then possible to calculate the influence of the impurities on the behaviour of the Curie temperature. For some elements this temperature increases, for other it decreases.

$T_c = aX + b$

X is the molar fraction of Ni.

The calculations have been performed for impurities of 0.01 mol% and are presented in the following table. ΔT is the variation of Curie temperature between pure Ni (used by the author of the binary phase diagram) and an alloy of Ni.

We can observe that this variation is very low, and comparable with the standard deviation of the measurement realized by DSC.

	a	b	T_c Ni/°C	T_c/°C $X_{Ni} = 0.9999$	ΔT/°C
Co	−760	1121	361	361.076	0.08
Cu	1177.41	−823.0009	354.4	354.2823	−0.12
Fe	−1128.5	1482.8	354.3	354.4129	0.11
Ge	3200	−2840	360	359.68	−0.32
Mn	214.444	138.5556	353	352.9786	−0.02
Pd	442.875	−88.575	354.3	354.2557	−0.04
Pt	357.5342	3.4657	361	360.9642	−0.04
Sb	187.5	192.5	380	379.9813	−0.02
Tl	31.3131	239.6869	361	360.9969	−0.003
V	166.6667	193.3333	360	359.9833	−0.02
W	5461.538	−5106.54	355	354.4538	−0.55
Zn	1864.211	−1510.01	354.2	354.0136	−0.19

Conclusions

A precise Curie temperature of nickel depends of the nature of impurities. With a view to using this property for the calibration of TG instruments, the purity of the standard must be at least of 99.99 mol%, and the recommended value is $T_c = 358.28$ °C ± 0.04.

Acknowledgments The authors are grateful to Alan Dinsdale of NPL for proving the calculated curve $C_p = f(T)$.

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