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Short communication

Enthalpies of formation of Ni–Sn compounds

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Abstract

Enthalpies of formation ($\Delta_f H$) of nickel–tin compounds have been measured by direct reaction calorimetry: $\Delta_f H^{\mathrm{Ni_3Sn_2\_LT}} = -29.0 \pm 0.9$ kJ mol^{-1} (approximate value); $\Delta_f H^{\mathrm{Ni_3Sn_2\_HT}} = -35.0 \pm 0.2$ kJ mol^{-1}; $\Delta_f H^{\mathrm{Ni_3Sn_2\_HT}} = -34.3 \pm 1.7$ kJ mol^{-1}; $\Delta_f H^{\mathrm{Ni_3Sn\_HT}} = -21.0 \pm 2.4$ kJ mol^{-1}; $\Delta_f H^{\mathrm{Ni_3Sn\_LT}} = -24.4 \pm 1.2$ kJ mol^{-1} and $\Delta_f H^{\mathrm{Ni_3Sn_4}} = -29.8 \pm 1$ kJ mol^{-1}.

Standard states are solid Ni and liquid Sn at the respective working temperatures: 728, 1288, 1389, 1332, 943 and 846 K.

The enthalpy of formation of the Ni_3Sn high-temperature form is measured for the first time, while that of Ni_3Sn_2_LT must be considered as approximate because the corresponding calorimetric reaction was incomplete.

The chemical and phase compositions of the specimens have been verified by electron probe microanalyses and by high- and room-temperature X-ray diffraction analyses. Unidentified thermal effects have been observed in the Ni_3Sn_2 phases region.

Keywords: Direct reaction calorimetry; Nickel–tin compounds; Enthalpies of formation

1. Introduction

Calorimetric studies of the Ni–Sn system are performed in the frame of a general examination of Sn–Bi–X and Sn–Zn–X systems (X = Cu, Ni, Ag, Ti) in relation to the development of lead-free solders. The Ni–Sn system has been subject to a number of studies summarized in various compilations [1–5]. Some thermodynamic assessments of this system have been performed as well [6–8]. Calorimetric studies of nickel–tin compounds have been done by a number of authors [9–16]. Nevertheless, the direct calorimetry method has not been applied previously to this system. There are no data about the enthalpy of formation of the high-temperature modification of Ni_3Sn, while other experimental results show some scatter. Thus, the purpose of this work is to verify previous measurements and to obtain new data for the enthalpies of formation of Ni–Sn compounds.

2. Experimental

Enthalpies of formation of Ni_3Sn_2_HT and Ni_3Sn_HT have been obtained by direct reaction calorimetry using (for experiments above 800 °C) a calorimeter designed and built [17] in a Setaram furnace (i.e. the Gachon calorimeter). Calorimetric measurements at temperatures below 800 °C (i.e. on Ni_3Sn_2_LT, Ni_3Sn_LT and Ni_3Sn_4) have been done by means of a Setaram–Calvet 800C apparatus. α-Al_2O_3 has been used for calorimeter calibrations with enthalpy increments taken from literature [18]. The standard deviation of the calorimetric constant measurements is 1 and 2%, respectively, for the Calvet and Gachon calorimeters. The enthalpy increments of pure metals are those assessed by Barin [19].

The reaction temperatures have been maintained within an interval of ±1 K (Calvet calorimeter) and ±2 K (Gachon calorimeter). Thus, the corresponding uncertainties of the final enthalpy values are estimated to be 2–3%, if the pertinent chemical reaction occurs completely.

Pellets (5 mm of diameter and 1.5 mm thick) of powdered materials (Ni (4 N) and Sn (5 N)) have been prepared with a manual press. Initially, calibrated powders (325 mesh) have been homogenized in a mortar for 40 min. Such a mixture is used for all experiments concerning a certain compound.

All manipulations have been done in a glove box under argon atmosphere (99.9995% Ar). The compositions of the initial mixtures are shown in Table 1. As no weight losses occur, these

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Table 1
Details about the working conditions and the experimental results: m—mass of the specimens (g); ΔH_f—enthalpy of formation (kJ mol^{-1}) per mol of atoms; T—working temperature (°C); time—reaction time (min); X_{Sn}—composition of the specimen (mole fraction Sn); phase—identification of the compound synthesized during the experiment

No.	X_{Sn}	Phase	T (°C)	Time (min)	m (g)	$\Delta_f H$ (kJ mol^{-1})
1	0.400	Ni_3Sn_2_HT	1015	15	0.1558	−35.07
2					0.2178	−34.89
3	0.406		1116	12	0.1221	−32.67
4					0.1005	−34.22
5					0.1266	−35.10
6	0.406	Ni_3Sn_2_LT	455	360	0.1487	−29.95
7					0.1221	−27.64
8					0.1239	−28.83
9					0.0988	−29.28
10					0.0879	−29.04
11	0.250	Ni_3Sn_HT	1059	15	0.1210	−22.74
12					0.1132	−19.89
13					0.1078	−18.39
14					0.1561	−23.41
15	0.250	Ni_3Sn_LT	670	360	0.1114	−23.83
16					0.0841	−25.16
17					0.0946	−25.01
18					0.0748	−22.47
19					0.0964	−25.40
20	0.571	Ni_3Sn_4	573	420	0.0981	−29.52
21					0.1102	−31.37
22					0.1047	−29.39
23					0.0856	−29.02
24					0.1243	−29.84

The unsuccessful experiments are marked by asterisk. Standard states are face-centered cubic nickel (f.c.c. Ni) and liquid Sn, at the respective working temperature.

compositions are related directly to the synthesized Ni–Sn compounds.

The pellets are weighed and sealed hermetically under argon in a device (distributor) to be transported and dropped into the calorimeter. The experimental conditions are shown in Table 1.

The standard states are face-centered cubic nickel (f.c.c. Ni) and liquid tin, at the respective working temperatures. Actually, when the specimen is introduced to the calorimeter, both constituents (nickel and tin) are in solid states, but the enthalpy changes needed to raise their temperature are taken into account.

3. Results

Two series of calorimetric experiments (at 1015 and 1116 °C) have been performed on the Ni_3Sn_2_HT phase (Table 1). The average enthalpy of formation of Ni_3Sn_2_HT at 1015 °C is -35.0 ± 1.3 kJ mol^{-1} and at 1116 °C is -34.3 ± 1.7 kJ mol^{-1}.

According to the phase diagram [1–8] two Ni_3Sn_2 forms (low- and high-temperature) exist. The transition between both forms of Ni_3Sn_2 is supposed to be second-order [6]. Differential thermal analyses (two runs in the interval 302–1080 K) were performed to acquire further information about the phase equilibria (Fig. 1). The expected transition temperature is between 750 and 850 K [5,12]. The peak P1, at around 785 K, is in general agreement with the expected transition temperature between low- and high-temperature Ni_3Sn_2 forms. The peak is well shaped, consequently, the respective transition is of first order. Moreover, the peak P2 around 800 K could not be identified. These observations show that the phase equilibria in this region must be subject of further studies.

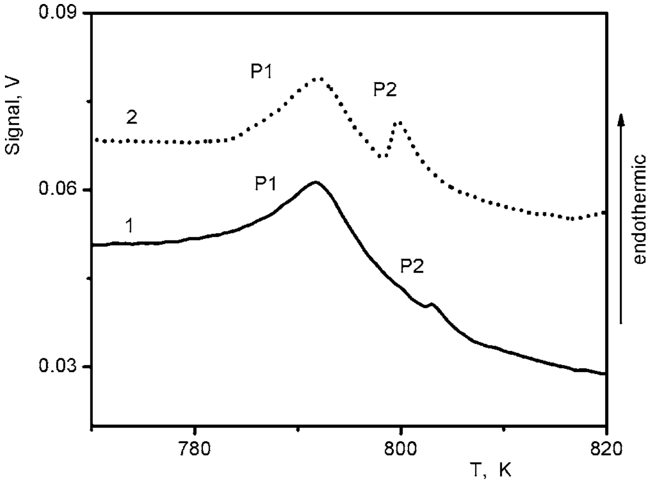

Fig. 1. DSC curves of specimen no. 4 at heating (first run—curve 1 and second run—curve 2). The working interval is 302–1080 K and the heating rate is 10 K min^{-1}. The peaks P1, at around 785 K, are in general agreement with the expected transition temperature between low- and high-temperature Ni_3Sn_2 forms. The peaks P2 at around 800 K could not be identified. The signal (V) of the differential scanning calorimeter is plotted along the ordinate and temperature (K)—along the abscissa.

Studies of the low-temperature form of Ni_3Sn_2 (Ni_3Sn_2_LT) performed at 455 °C in the Calvet calorimeter had reaction times of about 6 h. The average Ni_3Sn_2_LT enthalpy of formation is $-29.0 \pm 8.5\,\text{kJ mol}^{-1}$. Similar results (i.e. inconsistent enthalpy of formation values of the low-temperature form) are obtained by other authors [8–11]. We suppose that incomplete reactions are the causes for such discrepancies. They might be related with the complexity of this phase diagram region as stated above.

The Ni_3Sn_HT enthalpy of formation has been determined at 1059 °C (Table 1, specimens nos. 11–14). Its average value is $-21.0 \pm 2.4\,\text{kJ mol}^{-1}$.

The direct reaction determination of Ni_3Sn_LT enthalpy of formation (Table 1, nos. 15–19) are performed at 670 °C by means of Calvet calorimeter thus finding $-24.4 \pm 1.2\,\text{kJ mol}^{-1}$.

The measurements of Ni_3Sn_4 enthalpy of formation are performed at 573 °C by Calvet calorimeter (Table 1, nos. 20–24) and an average value of $-29.8 \pm 1.0\,\text{kJ mol}^{-1}$ has been found.

X-ray diffraction, electron microprobe analyses and optical microscopy have been used in order to verify the phase compositions of the specimens. A partial reaction between Ni and Sn to produce Ni_3Sn_2_LT has been observed (i.e. except Ni_3Sn_2, are observed Ni_3Sn_4 (26%), Ni_3Sn (3%) and almost pure Ni (12%)). In all other calorimetric experiments no free nickel has been found in the specimens.

4. Discussion

The measured enthalpies of formation of Ni–Sn compounds are comparable to the pertinent literature data [9–12,14–16] taking into account the experimental errors. The formation enthalpy of Ni_3Sn_LT reported by Predel and Ruge [11] ($-38.5 \pm 0.8\,\text{kJ mol}^{-1}$) differs markedly from experimental or calculated quantities of other authors (including the values obtained in this work). Such a discrepancy might be due to differences of the methods applied.

Another important observation is that the phase region of Ni_3Sn_2 is more complicated than presently assumed (i.e. more than two phases with approximate formulae Ni_3Sn_2 exist).

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