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THERMODYNAMIC PROPERTIES OF INTERMETALLIC COMPOUNDS IN Al-Sc, Cu-Sc AND Pb-Sc SYSTEMS

WŁASNOŚCI TERMODYNAMICZNE ZWIĄZKÓW MIĘDZYMETALICZNYCH W UKŁADACH Al-Sc, Cu-Sc I Pb-Sc

The partial Gibbs free energies of formation of intermetallic compounds (IMC) in Al-Sc, Cu-Sc and Pb-Sc systems were determined by e.m.f. method. Electromotive forces of galvanic cells were measured in wide temperature range. The data obtained were used to find integral thermodynamic properties of IMC at 298.15 K.

The integral Gibbs energy of Pb_5Sc_6 formation from solid scandium and liquid lead obtained from e.m.f. measurements can be described by the equation (at 650-1040 K): $\Delta_fG\ (Pb_5Sc_6) = -\ (49.60 \pm 1.1) + (3.63 \pm 1.3) \circ 10^{-3}\ T$, kJ/mol of atoms.

The standard enthalpies of formation ($\Delta_fH^0_{298}$), of the IMC in Al-Sc system assessed using experimental data of different authors, are the following (kJ/mol of atoms): Al_3Sc: - 42.6; Al_2Sc: - 47.8; AlSc: - 51.1; $AlSc_2$ - 41.0.

The Cu-Sc intermetallides were investigated in the temperature range of 650-1050 K. Integral thermodynamic functions of IMC in Cu-Sc system can be presented as the following equations (kJ/mol of atoms): $\Delta_fG\ (Cu_4Sc) = -\ (23.1 \pm 0.8) + (9.2 \pm 1.0) \circ 10^{-3}T$; $\Delta_fG\ (Cu_2Sc) = -\ (32.8 \pm 1.0) + (14.5 \pm 1.2) \circ 10^{-3}T$; $\Delta_fG\ (CuSc) = -\ (35.5 \pm 1.3) + (13.5 \pm 1.6) \circ 10^{-3}T$.

Keywords: intermetallides, scandium, thermodynamic properties, electromotive force, molten salt

Metodą pomiaru siły elektromotorycznej ogniw galwanicznych wyznaczono cząstkowe energie swobodne tworzenia związków międzymetalicznych w układach Al-Sc, Cu-Sc I Pb-Sc w szerokim zakresie temperature. Uzyskane wyniki posłużyły do wyznaczenia własności termodynamicznych badanych związków w 298.15 K.

Energia swobodna tworzenia związku Pb5Sc6 ze stałego skandu i ciekłego ołowiu można na podstawie pomiarów SEM opisać równaniem (650-1040 K): $\Delta_fG\ (Pb_5Sc_6) = -\ (49.60 \pm 1.1) + (3.63 \pm 1.3) \circ 10^{-3}\ T$, kJ/mol.

Standardowe ciepło tworzenia ($\Delta_fH^0_{298}$), związków międzymetalicznych w układzie Al-Sc zostało oszacowane na podstawie danych doświadczalnych pochodzących z różnych źródeł, jak następuje (kJ/mol): Al_3Sc: -42.6; Al_2Sc: -47.8; AlSc: -51.1; $AlSc_2$: -41.0.

Związki międzymetaliczne z układu Cu-Sc zbadano w przedziale temperatur 650 – 1050 K; ich własności termodynamiczne opisano następującymi równaniami (kJ/mol):
$\Delta_fG\ (Cu_4Sc) = -\ (23.1\pm0.8) + (9.2\pm1.0) \circ 10^{-3}T$; $\Delta_fG\ (Cu_2Sc) = -\ (32.8\pm1.0) + (14.5\pm1.2) \circ 10^{-3}T$; $\Delta_fG\ (CuSc) = -\ (35.5\pm1.3) + (13.5\pm1.6) \circ 10^{-3}T$.

1. Introduction

The scandium alloys are of considerable interest for many years. It is well-known that dilute Al-Sc alloys have excellent mechanical properties at room and more higher temperature, due to the presence of Al_3Sc nanoparticles [1,2]. The scandium additives essentially improve also the mechanical properties of copper [3]. The Pb-Sc alloys have no significant technical applications but they are a good reference electrodes using in high-temperature electromotive forces (e.m.f.) method to investigate the potentials of other alloys containing scandium [4].

This work is a summary of the number of e.m.f. investigations which may be considered as mutually related and supplementing thermodynamic studies of scandium alloys.

Previously, the thermodynamics of Pb-Sc system has been investigated by chronopotentiometric ("dynamic") e.m.f. method. The first aim of the present paper is to show that the properties of intermetallic compounds (IMC) found by this modification of e.m.f. method are in

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reasonable agreement with those obtained by "classic" e.m.f. method.

Further, the known thermodynamic properties of liquid lead-scandium alloy were used to re-calculation of Al-Sc and Cu-Sc potentials measured to obtain their Gibbs energies of formation in relation to pure scandium. Thermodynamic properties of binary systems mentioned were studied in wide temperature range.

Besides that, we analyzed the enthalpies obtained in terms of semi-empirical models (like Miedema's approach). This consideration, in particular, allowed to assess the experimental data of different scientific groups.

Metals of the following purity were used in the investigations (wt.%): Sc (99.9), Pb (99.999), Al (99.999), Cu (99.996), Bi (99.999). Measurements were carried out in the electrochemical cell of traditional construction [5]. All the parts contacted with fused salts and metallic melts were made from sintered beryllium oxide. The current conductive parts have been mounted using molybdenum wire.

2. Lead-scandium system

The lead-scandium phase diagram have been investigated in the study [6]. Only two intermetallic compounds were determined in the composition range considered (0-70 at.% Sc in lead) – Pb_3Sc_5 and Pb_5Sc_6. These compounds are isomorphous, Mn_5Si_3 and Ti_6Ge_5 types respectively. Earlier [7] it were taken that most Pb-rich compound in Pb-Sc system matches to the composition Pb_3Sc by analogy with the other R-Pb systems (where R is rare earth metal). Taking this circumstance into account, the integral thermochemical characteristics calculated earlier using e.m.f. data, were not correct. In this study the integral thermodynamic properties were found for the intermetallic compound Pb_5Sc_6. Apparently, this composition corresponds to most lead-rich compound in the system considered. This fact was confirmed by the Miedema model calculations. The Miedema approach used in this work was specially adapted for R-Me alloys (where Me is p-metal from the group: Al, Ga, In, Tl, Sn, Pb, Sb, Bi) [8].

Using classic (equilibrium) e.m.f. method, the electromotive forces of the following galvanic cell were measured [9]

$$(-)L+BiSc \mid LiCl - KCl+0.1mol.\%ScCl_3 \mid L+Pb_5Sc_6(+). \quad (1)$$

Here L is liquid solution of scandium in Me (bismuth or lead).

Measurements have been carried out in the temperature range of 610-1140 K. The results of measurements were recalculated relative to metallic scandium using the known and recommended values of the thermodynamic properties of BiSc compound. The scandium content in the (L+intermetallic compound) alloys was from 12.3 to 24.7 at.%. These values are deliberately higher than scandium solubility in liquid lead and bismuth in the temperature interval considered. Therefore, only integral thermodynamic characteristics calculation results will depend on the intermetallic compound composition. The experimental data (and partial Gibbs energy) are not depend on the composition mentioned above.

The second experimental technique was the "dynamic" e.m.f. method [10]. The galvanic cell used was the following:

$$(-)L + Pb_5Sc_6 \mid LiCl - KCl + 5mol.\%ScCl_3 \mid Sc(c)(+). \quad (2)$$

Thin scandium layer was electrolytically deposited to the copper plate placed in the molten salt (current density 50-100 mA/cm^2, deposition time 1-3 minutes). Plate size was about 0.5 cm width and about 4 cm length with the thickness 0.15-0.20 cm. After the current interruption the time dependence of e.m.f. E (τ) have been registered for the temperature predetermined. The first region of e.m.f. stabilization on the E (τ) curves corresponds to the e.m.f. difference between the reference electrode (L + Pb_5Sc_6 alloy) and solid metallic scandium (Sc(c)). More than 100 E(τ) curves have been obtained for different temperatures in the range of 650-1040 K. Further the ordinary temperature dependencies have been calculated for the galvanic cell (2).

To compare the results of both e.m.f. method measurements modifications, we present the electromotive forces of (L + Pb_5Sc_6) melts recalculated relatively to the metallic scandium (Table 1). It can be seen that the "classic" e.m.f. values are very close to the "dynamic" values. The statistical analysis was carried out by well-known methods described in details in [11-13]. This analysis has shown that the results of the studies [9,10] are statistically compatible for the significance level q=0.05. All the data belong to the same entire assembly.

TABLE 1

Electromotive forces for the alloys (L+Pb_5Sc_6)

e.m.f., mV					ΔT, K	Ref.
650 K	750 K	850 K	950 K	1050 K		
298.6±2.0	296.5±1.4	294.3±1.1	292.2±1.3	290.1±1.8	608-1111	[9]
300.3±2.9	297.6±1.8	295.0±1.4	292.3±1.8	289.6±3.5	650-1040	[10]

The e.m.f. temperature dependencies E(T) have been described as linear functions E=a+b T. The following parameters are necessary for full statistical description of the results: linear regression coefficients a (mV) and b (mV/K); average temperature (<T>, K) and e.m.f. (<E>, mV); values of

$$B = \sum_{i=1}^{l}(T_i - <T>)^2, K^2.$$

the quantities of measuring dispersion S_0^2, mV^2 and the number of experimental points l.

The generalized linear dependence was calculated by the method described in [12]. It can be written as

$$E = (314.14 \pm 7.2) - (0.023 \pm 0.008) \circ T, mV.(3)$$

The statistical parameters for this linear equation are: b=- 22.97 $\circ$ 10^{-3} mV/K; <E> = 294.54 mV; <T> = 853.2 K; S_0^2 = 32.96 mV^2; B = 1911125 K^2; l = 136.

The equation (3) allows one to determine partial Gibbs energy of Sc in the liquid alloy (L + Pb_5Sc_6):

$$\Delta\overline{G}_{Sc} = -(90.93 \pm 2.1) + (6.7 \pm 2.3) \circ 10^{-3}T, kJ/mol, \quad (4)$$

and, further, the thermodynamic functions of Pb_5Sc_6 formation from condensed(c) scandium and liquid (L) lead:

$$\Delta_f G(Pb_5Sc_6) = -(49.60 \pm 1.2) + (3.65 \pm 1.3) \circ 10^{-3}T, kJ/mol \text{ of atoms}. \quad (5)$$

Taking into account the thermodynamics of the lead melting enables one to find the standard thermodynamic properties of Pb_5Sc_6 intermetallic compound (at 298.15 K) using the Neumann-Kopp rule:

$$\Delta_f H^0 = -47.41 \pm 1.2 (kJ/mol \text{ of atoms}), \quad (6)$$

$$\Delta_f S^0 = 0.0 \pm 1.3 (J/(mol \text{ of atoms})K). \quad (7)$$

The estimations of the standard thermodynamic functions of Pb_5Sc_6 formation obtained in the paper [14] show some differences from the values found in the present study: $\Delta_f H^0$ = -41.9 ± 1.5 (kJ/mol of atoms); $\Delta_f S^0$ = -0.8 ± 3.2 (J/(mol of atoms)$\circ K$).

The calculation of the integral enthalpy of formation using the adapted Miedema model gives the following value for Pb_5Sc_6: -43.7 kJ/mol of atoms. One can see that the experimental enthalpy value is within the confidential interval declared by authors [8].

So, the thermochemical properties of liquid two-phase Pb-Sc alloys were determined in two experiment series using different modifications of the e.m.f. method in molten salts.

The data obtained by "classic" e.m.f. method and its "dynamic" version are in good agreement. As the result, mutually consistent data allowed us to find the partial thermodynamic properties of scandium in liquid Pb-Sc alloy with more accuracy: $\Delta\overline{G}_{Sc}$ = - (90.93 ± 2.1) + (6.7 ± 2.3)$\circ 10^{-3}$ T, kJ/mol. These investigations and new data concerning the composition of the intermetallic compounds in scandium-lead system enabled us to find the integral thermodynamic characteristics for Pb_5Sc_6 compound.

3. Aluminium-scandium system

The thermodynamic properties of aluminium-scandium system were investigated by different authors [15-20]. Thermochemistry of solid Al-Sc alloys has been studied mainly in the papers [16-18]. In the number of cases different researchers present the data with significant disagreements. Liquid alloys properties systematized in [20] also show the disperancy for different measurement methods.

Here, the thermodynamic properties of aluminium-scandium intermetallic compounds were investigated by the "dynamic" e.m.f. method [10, 20]). The electromotive force of cells of the type

$$(-)L + Pb_5Sc_6 \mid LiCl - KCl(eutectic) + 5.0mol.\% \; ScCl_3 \mid Al - Sc(solid \; alloy)(+) \quad (8)$$

has been measured over the temperature range of 680-870 K. The experimental technique was the same with those described in chapter 1 (the aluminium plate of the same size was used). The measurement time for one current interruption curve was about 300-1800 s and depended on the coating parameters and the temperature.

Four intermetallic compounds were found in Al-Sc system: Al_3Sc, Al_2Sc, AlSc, $AlSc_2$ [19]. The phase diagram is shown in Fig. 1. Integral Gibbs energies of IMC formation in Al-Sc system for the middle of temperature interval investigated are presented in Fig.2. Data of this work (squares, solid line) are in reasonable agreement with the values obtained from assessed $\Delta_f G$ (T) dependences taken from paper [17].

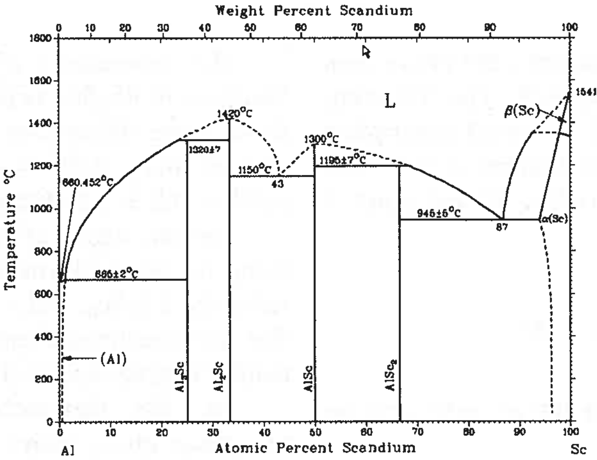

Fig. 1. Al-Sc phase diagram [19]

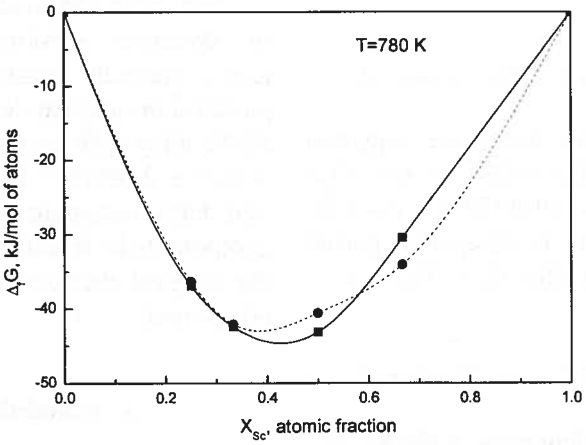

Fig. 2. Integral Gibbs energies of formation in Al-Sc system at 780 K. Our data (aquares, solid line) and assessed values (circles, dashed line) according to [17]

Integral heats of formation of the IMC in Al-Sc system taken from different experimental works and also calculated and statistically assessed values are given in Table 2. One can see that the data of the study [16] (e.m.f.) are in good agreement with the data of the work [17] (calorimetry) for IMC Al_3Sc and Al_2Sc. At the same time, the data differences for the other intermetallics are significant.

TABLE 2

Standard enthalpies of formation ($\Delta_f H^0_{298}$) of the intermetallic compounds in aluminium-scandium system

IMC	$-\Delta_f H^0 298$, kJ/mol of atoms				
	[16]	[17]	[18]	Model calculation according to [8, 20]	assessed
Al_3Sc	41.3	43.5	59.8	36	42.6
Al_2Sc	47.6	48.0	94.1	46	47.8
AlSc	67.1	46.0	62.0	51	51.1
$AlSc_2$	42.6	37.0	28.2	40	41.0

The data [18] (HCl solution calorimetry) are considerably different also for Al_3Sc and Al_2Sc compounds. Nevertheless, these data were taken into account.

Many attempts to calculate integral enthalpies and other IMC properties using semi-empirical approaches are known. One of most successful of them is the Miedema model. Using of this model for calculation of the concentration dependence of $\Delta_f H^0$ requires the knowledge of the number of adjusted parameters (electronegativity parameter etc.).

Miedema approach [21] to calculation of standard formation enthalpies was successfully applied to R-Me alloys in the studies [8, 20]. Model parameters found on the basis of the known experimental data allowed us to describe these data with the confidence interval for any point approximately about ± 13 kJ/mol of atoms. According to [8, 20] this prediction accuracy is considerably higher than the imprecision of the experimental $\Delta_f H^0$ determination. Nevertheless, taking into account great systematic differences between the results of different scientific groups, the model prediction may be very useful to estimate unknown values or to analyze strongly different experimental data.

The assessed values of enthalpies of formation of intermetallides have been calculated by the following procedure. Initially we found the squared deviations of the experimental points from the model enthalpy values calculated using adapted Miedema model [8, 20] and presented in Table 2. Further we assumed the statistical weight for each experimental value. These weights were inversely proportional to the squared deviations mentioned. Of course, the weights for each intermetallide were normalized and their sum was reducted to 1. The assessed value of the enthalpy has been calculated by averaging of the experimental values with the corresponding weights.

It can be easily seen that assessed values of the heats of formation are close to those calculated by the Miedema model adapted for given alloys group [8, 20].

4. Copper-scandium system

The phase diagram available for Cu-Sc alloys is presented in the paper [22]. It is shown in Fig.3. In this work the thermodynamic properties of copper-scandium intermetallic compounds were investigated by the chronopotentiometric ("dynamic" e.m.f. method [10, 20]). The electromotive force of cells of the type

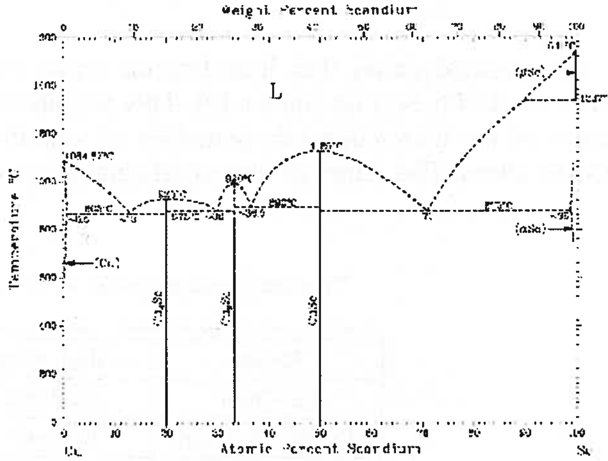

Fig. 3. Cu-Sc phase diagram [22]

$$(-)L + Pb_5 Sc_6 \; LiCl - KCl(eutectic) + 5.0 mol.\% \; ScCl_3 \; Cu - Sc(solid \; alloy)(+) \tag{9}$$

has been measured over the temperature range of 650-1040 K. The experimental technique was the same with those described in chapter 1. The typical chronopotentiogram (current interruption curve) is shown in Fig. 4. One can see that the number of regions of the e.m.f. stabilization is equal to the number of two-phase regions in the phase diagram. The authors of handbook [20] widely use this fact to analyze the thermodynamics of R-Me systems. They assumed that the diffusion of initial R coating into the plate of Me causes the sequential forming of the intermetallides from R-rich to R-poor within short time interval (about several minutes). The second assumption was that the thermodynamic properties of the IMC in two-phase regions are close to the equilibrium (due to high temperatures of experiment). Of course, this supposition is disputable. But we often can see [20] a good agreement between "classic" and "dynamic" e.m.f. data both for R-rich part of phase diagram (for instance Sc+CuSc, see Table 1) and for R-poor part. So, we used the "dynamic" method here and the question "how close the system is to the equilibrium" can have different answers for different binary alloys and different temperatures and other conditions. Nevertheless, to compare "classic" and "dynamic" data is of considerable interest in any case.

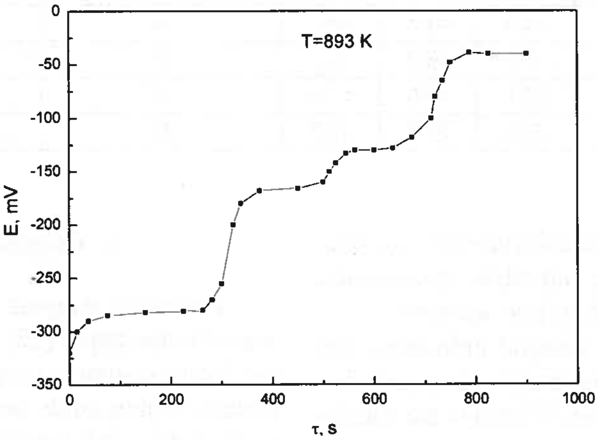

Fig. 4. Typical current interruption curve at 893 K. Here τ is the exposure time (in seconds) and E – electromotive force (mV)

The thermodynamic data including the errors estimation for (L+Pb_5Sc_6) are known [9]. This permits calculation of the thermodynamic potentials of scandium in Cu-Sc alloys. The values of the partial enthalpies and entropies of scandium in various regions of the phase diagram Cu-Sc are reported in Table 3. Also partial molar Gibbs energies at 850 K (a middle of temperature interval investigated) are presented.

TABLE 3

Thermodynamic properties of Sc in two-phase regions of Cu-Sc phase diagram

Region	$-\Delta H_{Sc}$, kJ/mol	$-\Delta S_{Sc}$, J/mol o K	$-\Delta G_{Sc}$, kJ/mol
$Cu+Cu_4Sc$	115.3±4.2	46.0±5.0	76.2±0.4
Cu_4Sc+ Cu_2Scpm	81.5±4.5	40.7±5.2	46.9±0.6
Cu_2Sc+ CuSc	43.5±4.3	10.7±5.1	34.3±0.5

The data of Table 3 were used to calculate integral Gibbs energy of formation values for the phases Cu_4Sc, Cu_2Sc and CuSc (J/mol of atoms): $\Delta_f G$ (Cu_4Sc) = -23100 + 9.2 T; $\Delta_f G$ (Cu_2Sc) = -32800 + 14.5 T; $\Delta_f G$ (CuSc) = -35500 + 13.5 T. The integral enthalpy data of our work are in good agreement with the values calculated by using the semi-empirical model of Miedema [23]. The model predictions are the following (kJ/mol of atoms): $\Delta_f H$ (Cu_4Sc) = - 22.1; $\Delta_f H$ (Cu_2Sc) = - 33.3; $\Delta - fH$ (CuSc) = - 35.6. The calorimetric data [23] show considerable differences (kJ/mol of atoms): $\Delta_f H$ (Cu_4Sc) = - 14.0; $\Delta_f H$ (Cu_2Sc) = - 17.4; $\Delta_f H$ (CuSc) = - 20.9.

5. Conclusion

Different modifications of the e.m.f. method were applied to investigate thermodynamic properties of intermetallic compounds in Pb-Sc, Al-Sc and Cu-Sc systems. The thermodynamic data for Pb-Sc liquid two-phase alloy and Pb_5Sc_6 intermetallide show good agreement between "classic" e.m.f. and "dynamic" chronopotentiometric e.m.f. method. Enthalpies of formation obtained for Al-Sc and Cu-Sc alloys demonstrate some differences with those obtained by calorimetry. It is not unusual situation, especially for rare-earth metal alloys.

Therefore the assessment procedures were performed to coordinate the data and to estimate "accepted" enthalpies of formation for Al-Sc intermetallides.

The analogous procedures have not been performed for Cu-Sc system because our values of $\Delta_f H$ almost coincide with those estimated using Miedema's model [23]. The Gibbs energies of formation studied by e.m.f. method can be, undoubtedly, considered as reasonably accurate in temperature ranges studied.

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