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Journal of Alloys and Compounds 228 (1995) 159–163

Journal of
ALLOYS
AND COMPOUNDS

Thermodynamic properties of scandium carbides

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Received 17 November 1994; in final form 25 April 1995

Abstract

The Gibbs energy, enthalpy and entropy of formation of scandium carbides have been determined by e.m.f. measurements in the temperature range 823–1033 K. The extreme values of these functions are observed in the range of homogeneity of scandium monocarbide.

Keywords: Scandium carbides; Thermodynamic properties

1. Introduction

According to the phase diagram (Fig. 1) three intermediate phases are formed in the Sc–C system. $Sc_{15}C_{19}$ is formed by peritectic reaction at 2067 ± 4 K and has a range of homogeneity from 54.5 to 56.5 at.% C. $\alpha - Sc_4C_3$ decomposes below 1223 K. The δ phase (ScC_{1-x}) has a wide range of homogeneity (about 23.5–34.5 at.% C at room temperature). The solubility of carbon in α-scandium is very small below 1473 K [1]. There is no information on the thermodynamics of formation of scandium carbides. The aim of this work was to determine the Gibbs energies, enthalpies and entropies of formation of the $Sc_{15}C_{19}$ and ScC_{1-x} phases from pure components.

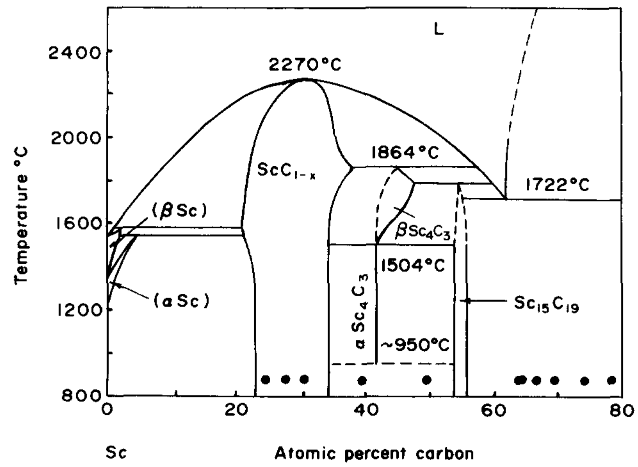

Fig. 1. Sc–C phase diagram [1]: ●, compositions of the investigated alloys.

2. Experimental details

The thermodynamic properties of the Sc–C alloy system have been studied by e.m.f. measurements of concentration galvanic cells

$$(-)[ScSi + Si] \,|Sc^{+3} \text{ ions in molten salts}|\, Sc_xC_{1-x}\ (+) \quad (1)$$

in the 823–1033 K temperature range for $x_{Sc} > 0.565$ and in the 773–1033 K temperature range for $x_{Sc} < 0.565$. A scandium–silicon alloy corresponding to the equilibrium [ScSi + Si] studied previously [2] was used as a comparison electrode in order to avoid the interaction of scandium with molten salts at high temperatures. This research method has already been described in detail [3]. The alloys for investigation were prepared from scandium (purity, at least 99.92 wt.% Sc) and carbon (ash, 0.05 wt.%; S, 0.023 wt.%; Fe, less than 0.002 wt.%) by melting the components in an arc furnace under argon. For the sake of homogeneity the ingots were annealed step by step under an argon atmosphere at 1973 K, 1873 K, 1273 K, 1173 K, 1023 K and 923 K for 208 h for the alloys in the composition range $[Sc_{15}C_{19} + C]$ and

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SSDI 0925-8388(95)01701-1

1973 K, 1873 K, 1073 K and 923 K for 216 h for the alloys in the composition range [$Sc_{15}C_{19}$ + ScC_{1-x}] in graphite crucibles with Hf shafings as a getter. For the preparation of the alloys in the homogeneity range of the δ phase (25, 28 and 32 at.% C) use was made the alloy with 33.3 at.% C. The alloys of desired compositions were obtained by melting the 33.3 at.% C alloy with appropriate amounts of scandium. The chemical analysis of all the alloys showed their compositions to be in good agreement with the nominal composition. These alloys were annealed for 3 min under an electric arc. Control runs were performed using attested samples of known phase and chemical compositions which had been obtained when investigating the phase diagram of this system [1].

Vacuum-fused (10^{-2} Pa) mixtures of dried potassium, sodium and barium chlorides with melting temperature $T_{melt} = 815$ K and potassium, lithium and barium chlorides with $T_{melt} = 593$ K [4] were used as an electrolyte. Dried $ScCl_3$ was previously fused with KCl–NaCl under helium and then the mixture obtained was introduced into the electrolyte as a small addition (about 0.3% by mass).

3. Results and discussion

The temperature dependence of the e.m.f. was approximated by the linear equation

$$E = A + BT \equiv \bar{E} + B(T - \bar{T}) \qquad (2)$$

where $\bar{E}$ and $\bar{T}$ are the mean values of e.m.f. and temperature respectively. Parameters of Eq. (2) were calculated by the least-squares fit method and are given in Table 1 in the form recommended in Ref. [5]. The errors of determination of the thermodynamic functions were estimated at the 95% confidence level. The experimental temperature dependence of the e.m.f. for carbon-rich alloys is shown in Fig. 2. It is

Table 1
Results of e.m.f. measurements of galvanic cells (1)

x_C	Phase composition	n	$\bar{T}$ (K)	$\bar{E}$ (mV)	A (mV)	B (mV K^{-1})	$\sum_i (T_i - \bar{T})^2$ (K^2)	δ_0^2 (mV^2)
0.565–1	$Sc_{0.435}C_{0.565}$ + C	151	932	37.31	299.56	−0.281 22	343 064.18	20.39
0.643								
0.648								
0.671								
0.699								
0.750								
0.791								
0.345–0.545	$Sc_{0.655}C_{0.345}$ + $Sc_{0.455}C_{0.545}$	53	936	−157	15.80	−0.185 05	288 087.17	5.98
0.397								
0.498								
0.235–0.345	δ-phase (ScC_{1-x})							
0.320		22	896	−254.78	84.19	−0.378 51	17 281.46	33.17
0.280		31	931	−397	−297.18	−0.107 58	62 506.71	34.77
0.250		29	899	−437	−450.72	0.015 40	54 341.03	28.35

n is the number of measurements,
$B = \sum_i (E_i - \bar{E})(T_i - \bar{T}) / \sum_i (T_i - \bar{T})^2$
where E_i and T_i are values of individual measurement, and
$\delta_0^2 = \sum (E_i - E)^2/(n-2) = \sum \Delta E/(n-2)$
where E is value calculated from Eq. (2).

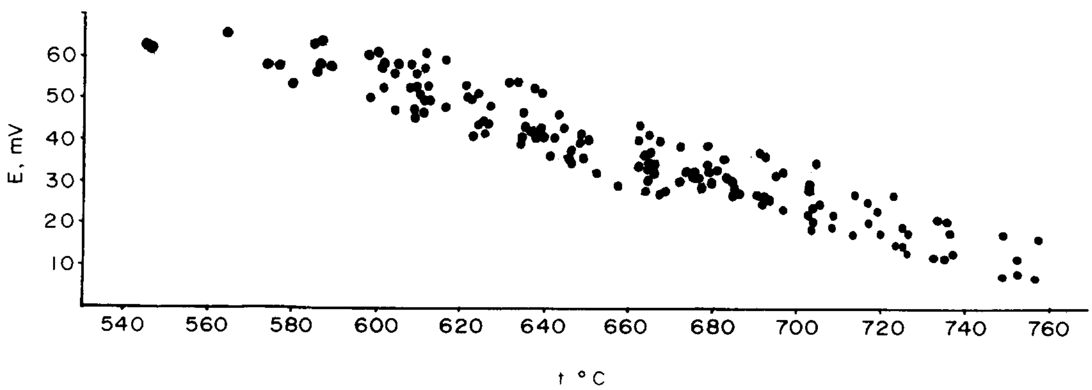

Fig. 2. Temperature dependence of the e.m.f. of galvanic cells for Sc–C alloys in the [$Sc_{15}C_{19}$ + C] region.

Table 2
Thermodynamic properties of the Sc–C system relative to α-Sc and C (graphite) at 923 K

x_C	$-\Delta\bar{G}_{Sc}$ (J mol^{-1})	$-\Delta\bar{G}_C$ (J mol^{-1})	$-\Delta\bar{H}_{Sc}$ (J mol^{-1})	$-\Delta\bar{H}_C$ (J mol^{-1})	$-\Delta\bar{S}_{Sc}$ (J mol^{-1} K^{-1})	$\Delta\bar{S}_C$ (kJ mol^{-1})	$-\Delta_f G°$ (kJ mol^{-1})	$-\Delta_f H°$ (J mol^{-1} K^{-1})	$-\Delta_f S°$ (J mol^{-1} K^{-1})
0.565[a]–1	164 420 (±320)	0	260 800 (±5900)	0	104.4 (±6.4)	0	$164.42(1-x_C)$	$260.8(1-x_C)$	$104.4(1-x_C)$
0.345[b]–0.545[a]	108 000 (±620)	45 270	178 700 (±7400)	65 900	76.6 (±8.0)	−22.4	$108.0-62.75x_C$	$177.8-111.2x_C$	$75.6-52.5x_C$
0.320	76 100 (±1000)	109 430	198 500 (±23 100)	26 100	132.6 (±25.8)	90.3	86.77	143.3_3	61.2
0.280	38 100 (±1080)	198 670	88 100 (±13 400)	285 300	54.2 (±14.4)	−93.9	83.06	143.3_2	65.3
0.250	26 510 (±890)	230 960	43 700 (±12 600)	409 100	18.6 (±14.0)	−193.0	77.62	135.1	62.3
0–0.235[b]	0	314 000	0	545 600	0	−250.9	$314.0x_C$	$545.6x_C$	$250.9x_C$

[a]Borders of the homogeneity range of the $Sc_{15}C_{19}$ phase.
[b]Borders of the homogeneity range of the ScC_{1-x} phase.

characterized by a large negative slope. This dependence is confirmed by both the reversibility and the consistency of the results obtained with six different alloys of mass compositions 64.3, 64.8, 67.1, 69.9, 75 and 79.1 at.% C in the rather wide (823–1033 K) temperature range, the total number of measurements being 151. Using the $E = f(T)$ dependence obtained earlier for the Sc–Si comparison electrode by reference to solid pure α-scandium (E(mV) = 601.53 − 0.079 55 T [2]) and the rule of addition of e.m.f. values, the equations for the e.m.f. dependence on temperature of the Sc–C alloys, with reference to pure α-scandium, were obtained. These equations were used for the determination of the partial Gibbs energies, enthalpies and entropies for scandium using the usual equations of the e.m.f. method:

$$\Delta \bar{G}_{Sc} = \Delta \bar{H}_{Sc} - T\,\Delta \bar{S}_{Sc} = -zFA - zFBT \quad (3)$$

where F is the Faraday constant and z is the charge of the scandium ion (+3 according to Ref. [6]). The partial thermodynamic functions of carbon were determined by the Gibbs–Duhem integration:

$$\Delta \bar{I}_C = \int_0^{x_{Sc}} [x_{Sc}/(1 - x_{Sc})]\, d(\Delta \bar{I}_{Sc}) \quad (4)$$

Integral thermodynamic functions of formation of scandium carbides from pure components were calculated from the Euler equation:

$$\Delta I = x_{Sc}\,\Delta \bar{I}_{Sc} + x_C\,\Delta \bar{I}_C \quad (5)$$

Calculation of the thermodynamic properties of the scandium carbide $Sc_{15}C_{19}$ was made by taking into account the composition of the carbon-rich border in its one-phase region. The small range of homogeneity (less than about 2 at.%) was neglected. Values of the partial and integral thermodynamic properties of two phases formed in the Sc–C system are given in Table 2 and Figs. 3 and 4. The results obtained show that the extreme values of the Gibbs energy, enthalpy and entropy of formation of Sc–C alloys under the conditions of the present investigation are observed in the range of homogeneity of the scandium monocarbide.

It is interesting to compare the enthalpies of formation of the MeC_{1-x} carbides for compositions with the maximum contents of carbon in sequence from scandium to chromium, considering the Cr_3C_2 carbide to be the most carbon-rich compound in the Cr–C binary

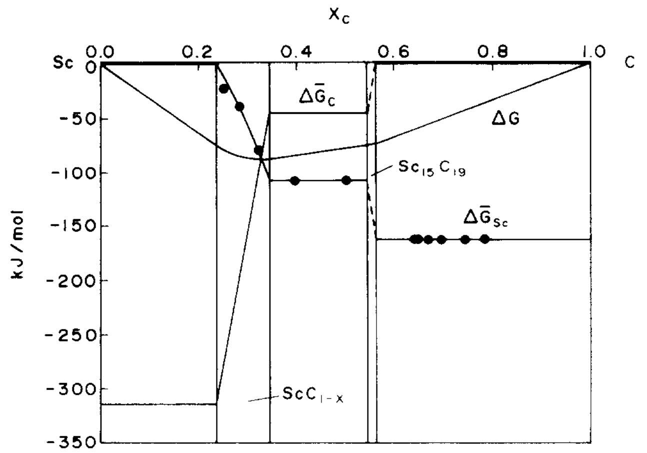

Fig. 3. The Gibbs energies of formation of Sc–C alloys at 923 K.

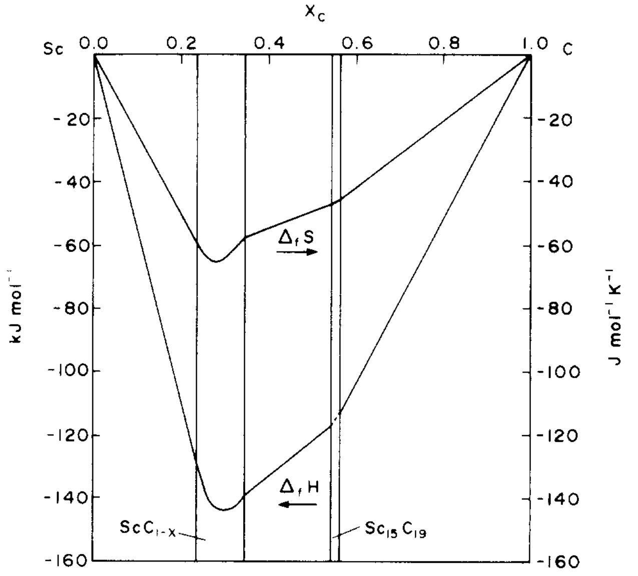

Fig. 4. The enthalpies and entropies of formation of Sc–C alloys at 923 K.

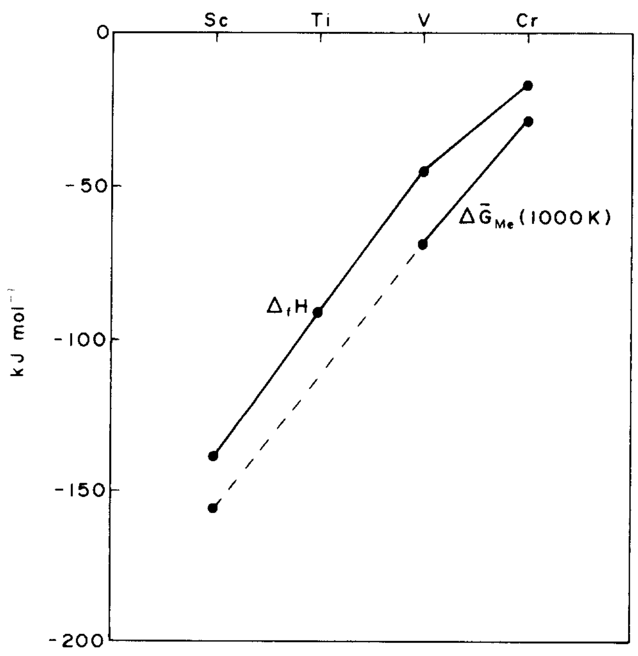

Fig. 5. The enthalpies of formation of the carbides MeC_{1-x} (Me = Sc, Ti, V), Cr_3C_2 and the $\Delta \bar{G}_{Me}$ values in the (MeC_{1-x} + C) biphase domain.

system. Taking into account that such a comparison of the $\Delta_f H$ values for compounds with somewhat different stoichiometries is to some extent incorrect, the $\Delta\bar{G}_{Me}$ values in the (MeC_{1-x} + C) area are presented as well. The $\Delta_f H$ value for TiC_{1-x} was taken from Ref. [7]. The $\Delta_f H$ and $\Delta\bar{G}_{Me}$ values for the Cr–C [8] and V–C systems were obtained in our laboratory by the method of e.m.f. measurements ($\Delta\bar{G}_V$ ($J\ mol^{-1}$) = $-84946 + 15.96T$ at 1000–1130 K; for $V_{0.533}C_{0.467}$ (V_8C_7) $\Delta_f H = -45.3$ kJ mol^{-1} [9]). The dependence observed (Fig. 5) with a minimum for chromium is typical for most compounds of 3d metals, for example silicides, germanides, antimonides, tellurides, stannides [3].

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