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Journal of Alloys and Compounds 239 (1996) 107–110

Journal of
ALLOYS
AND COMPOUNDS

High-temperature electrochemical synthesis and properties of intermetallic compounds in the Ni–Sc system
Part 2. Thermodynamic and mechanical properties

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Received 3 March 1995; in final form 24 April 1995

Abstract

The Gibbs's energy of the formation at 988 K of intermetallic compounds in the Ni–Sc system from solid components was calculated using chronopotentiometric data. The ScNi compound was shown to be the most stable in the system under investigation. This conclusion is in accordance with the published data. The $ScNi_2$ compound has the maximum microhardness both in the series of the isostructural $REMNi_2$ compounds and in the searched system.

Keywords. Nickel; Scandium; Intermetallic compounds; Molten salts; Thermodynamic properties; Chronopotentiometry; Microhardness

1. Introduction

Data about the electrochemical behaviour of Sc(III) in a $NaCl–KCl–ScF_3$ melt have been presented earlier [1]. Scandium cation reduction on the nickel electrode was shown to proceed with significant depolarisation due to intermetallic compound formation on the electrode surface. However, the method of cyclic voltammetry used in Ref. [1] does not allow for a more detailed research of the compounds to be produced. Discharge chronopotentiometry offers better possibilities. Using data obtained by this method the thermodynamic properties of the Ni–Sc intermetallic compounds can be calculated. Information on the system under investigation can be found in Ref. [2], in which the enthalpy of formation of Ni–Sc intermetallic compounds (IMC) was calculated using the electronegativity and electron density parameters of the elements and information on the Ni–Sc phase diagram. Microhardness of the intermetallic compounds was measured as one of the mechanical properties. The preparation and details of the experiments were described in Ref. [1].

2. Results and discussion

A Ni electrode immersed into a $NaCl–KCl–ScF_3$ melt was polarised under galvanostatic conditions at a current density of 30 mA cm^{-2} for 40 min. The application of less current density does not result in the formation of scandium metal for a long time, but application of more current density can lead to non-equilibrium conditions under which intermetallic compounds may form. In the discharge chronopotentiogram presented in Fig. 1, six plateaux with constant or slowly varying potentials can be seen. The existence of plateaux with constant potentials in time corresponds to the occurrence of two-phase regions with constant activity of the components on the electrode surface. The number of two-phase regions in the Ni–Sc phase diagram shown in Fig. 2 of Ref. [1] is in accordance

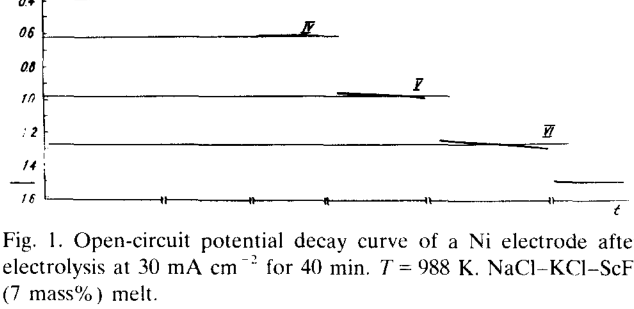

Fig. 1. Open-circuit potential decay curve of a Ni electrode after electrolysis at 30 mA cm^{-2} for 40 min. $T = 988$ K. $NaCl–KCl–ScF_3$ (7 mass%) melt.

0925-8388/96/$15.00
SSDI 0925-8388(95)01696-1

with the number of plateaux in the chronopotentiogram shown in Fig. 1.

The difference in the nickel and scandium potentials was determined by immersing these metals into molten salt. It should be noted that the use of scandium metal as a reference electrode introduces a certain error into the measurement of potentials due to existence of the reaction [1]:

$$Sc(0) + 3K(I)(Na(I)) \rightleftarrows Sc(III) + 3K(0)(Na(0)) \qquad (1)$$

and due to a constant but slow change of the reference electrode potential. Numerous experiments have shown that the difference in Ni and Sc potentials is 1.52 V under the following conditions: $T = 988$ K, $C_{Sc(III)} = 0.5$ mass%. By comparison, in Ref. [3] the difference in the nickel and scandium formal standard potentials in LiCl–KCl at 450°C is given as 1.432 V. According to calculations from thermodynamic data for the individual chlorides, the difference in Ni and Sc standard potentials at 450°C is 1.517 V, at 700°C it is 1.506 V, at 800°C it is 1.500 V and at 1000°C it is 1.501 V.

The investigation of the component distribution over a cross-sectional area of a nickel sample, onto which scandium was deposited for 5 h at a current density of 30 mA cm^{-2}, revealed the existence of five intermetallic compounds as well as nickel and scandium metal (Fig. 2). Microprobe analysis made at each plateau of the component distribution curve has identified all five compounds existing in the Ni–Sc system (Table 1). A micrograph of the Ni–Sc sample cross-section is shown in Fig. 3, on which layers of the intermetallic compounds with different composition can be seen distinctly. Comparison of the data in Figs. 1 and 2 and Fig. 2 of Ref. [1] makes it possible to identify the phase composition of all the plateaux on the chronopotentiogram. The results are given in Table 2.

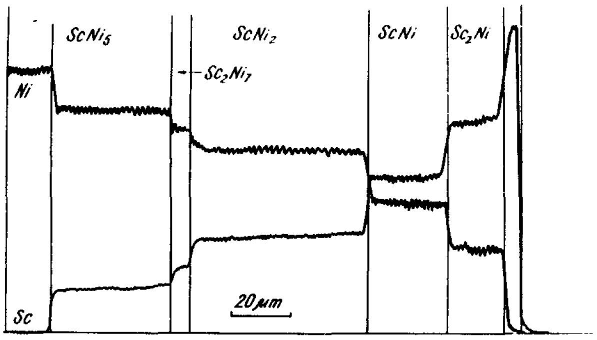

Fig. 2. Component distribution over a cross-sectional area of a nickel sample. Preparing conditions: duration, 5 h at a current density of 30 mA cm^{-2}. $T = 988$ K. NaCl–KCl–ScF$_3$ (7 mass%) melt.

Table 1
Results of microprobe analysis over the cross-sectional area of the nickel–scandium sample obtained under the following conditions: $j = 30$ mA cm^{-2}, $T = 988$ K, NaCl–KCl–ScF$_3$ (7 mass%) melt

Ni (mass%)	Sc (mass%)	Compound
99.83 ± 0.001	00.14 ± 0.01	Ni
86.31 ± 0.01	13.71 ± 0.01	$ScNi_5$
81.51 ± 0.01	18.48 ± 0.01	Sc_2Ni_7
72.26 ± 0.01	27.88 ± 0.01	$ScNi_2$
55.33 ± 0.01	44.74 ± 0.01	ScNi
39.20 ± 0.01	61.01 ± 0.01	Sc_2Ni
00.09 ± 0.01	100.01 ± 0.001	Sc

MS-46 "Cameca", a beam diameter 1 μm, depth 1–1.5 μm.

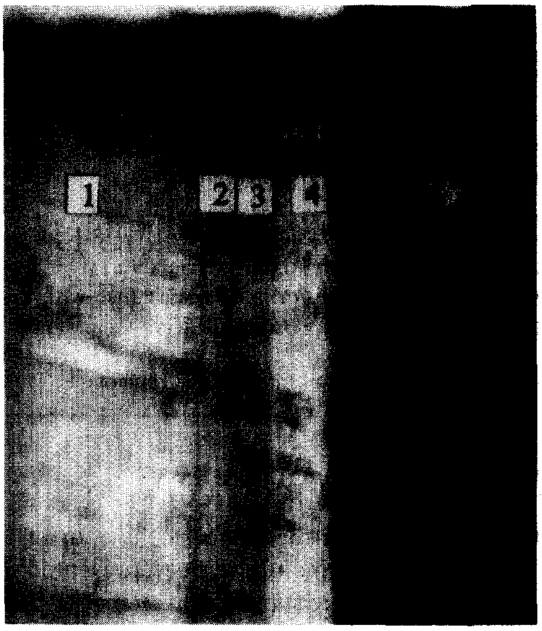

Fig. 3. Micrograph of cross-sectional area of the Ni–Sc sample (× 200). Preparation conditions are the same as in Fig. 2. 1, Ni; 2, $ScNi_5$; 3, Sc_2Ni_7; 4, $ScNi_2$; 5, ScNi; 6, Sc_2Ni; 7, Sc.

Table 2
The plateau potentials on the chronopotentiogram and the two-phase compositions at $T = 988$ K. The potentials are given with respect to metallic scandium

Phase	E(V)	Two-phase composition
I	0.00 ± 0.01	$Sc + Sc_2Ni$
II	+0.15 ± 0.01	$Sc_2Ni + ScNi$
III	+0.39 ± 0.001	$ScNi + ScNi_2$
IV	+0.62 ± 0.01	$ScNi_2 + Sc_2Ni_7$
V	+0.98 ± 0.01	$Sc_2Ni_7 + ScNi_5$
VI	+1.28 ± 0.01	$ScNi_5 + Ni(Sc)_{ss}$

The difference in the potentials of the scandium reduction (see Fig. 1(a) of Ref. [1]) and Sc_xNi_y IMC formation (see Fig. 1(b) of Ref. [1]) is 0.60 V. This is in satisfactory accordance with the potential of plateau IV (Fig. 1, Table 2). The maximum prolongation of this plateau on the chronopotentiogram and the maximum thickness of the $ScNi_2$ layer (Figs. 2 and 3) very likely resulted in more beneficial kinetic conditions of its formation in comparison with the other IMC. This allows one to refer the cathodic (− 1.65 V) and anodic (− 1.20 V) peaks in Fig. 1(b) [1] predominantly to the formation and dissolution of the $ScNi_2$ compound.

Typical of molten salts, the alloy-formation process occurs at the equilibrium potentials at high temperature [4]. Therefore, the chronopotentiometry data may be used to determine the thermodynamic properties of the intermetallic compounds of the Ni–Sc system. Data on the chemical potential of scandium ($\Delta\bar{G}_{Sc}$) in the two-phase regions are presented in Table 3. Further calculations allowed determination of the Gibbs's energy change during the IMC formation from the solid components. Results are given in Table 4 and presented in Fig. 4. The large values of the Gibbs's energy change during the formation of one mole of Sc_xNi_{1-x} alloy indicates the bonds in the IMC of Ni–Sc system are of considerable strength. Similar observations were made in the Ge–Sc [5] and Si–Sc [6] systems. The ScNi compound apparently has the highest stability of the five compounds of nickel and scandium, though it is not the most refractory in this system. The data regarding IMC formation enthalpies of the Ni–Sc system calculated from the parameters of the electronegativity and of the electron density of the elements and based on phase-diagram information, have been presented in Ref. [2]. The following values of ΔH_f were calculated (kJ (mol of alloy)$^{-1}$): −29 for $ScNi_5$; −53 for $ScNi_2$; −56 for ScNi; −41 for Sc_2Ni. On the basis of Ref. [2] and according to our results it may be concluded that ScNi compound is the most stable of all the compounds in this system.

To determine the nature of the bonds in the compounds, the electronegativity difference (Δæ) parameter was used. According to Pauling $\text{æ}_{Ni} - \text{æ}_{Sc} = 0.5$ and according to Olred-Rochow $\text{æ}_{Ni} - \text{æ}_{Sc} = 0.55$ [7]. The ionic character degree of the bond is about 6% [4] which corresponds predominantly to a covalent type of bond.

We also determined the microhardness of the intermetallic compounds and of nickel. The data obtained are given in Table 5. The microhardness was measured using the indentation of a diamond pyramid (Vickers' method) at a load of 10 g. According to Ref. [8] the hardness of nickel is $HB = 60$–80 kg mm^{-2}, and that of scandium is reported as $HB = 75$–130 kg mm^{-2} [9], 143 kg mm^{-2} [10], 220 kg mm^{-2} [11]. Both impurities and metal deformations in the cold state (cold-working) influence the microhardness value. For instance, cold-working increases the microhardness of rare-earth metals by a factor of 1.5–2 [9]. The large value of HV for nickel we obtained may originate from the influence of these factors. The data on microhardness are limited for intermetallic compounds of rare earth metals and nickel. For $GdNi_2$ $HV = 600$ kg mm^{-2} [12], for $CeNi_2$ $HV = 550$ kg mm^{-2} [13], for $PrNi_2$ $HV = 470$ kg mm^{-2} [14], for YNi_2 $HV = 765$ kg mm^{-2} [15].

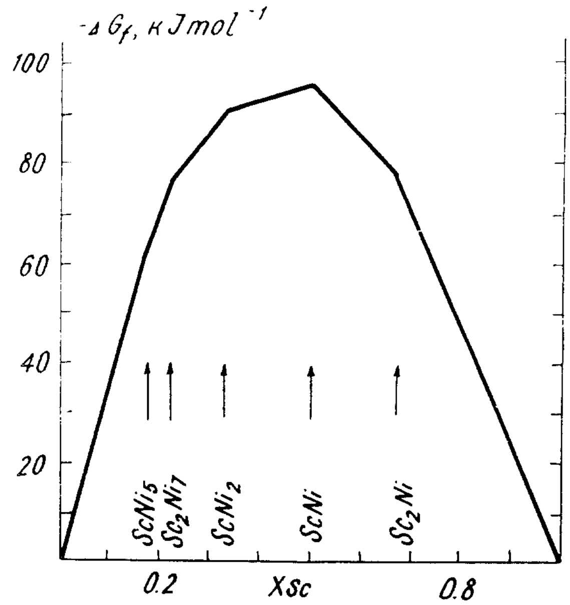

Fig. 4. Gibbs's energy change during formation of Sc_xNi_{1-x} compounds from the solid components at $T = 988$ K.

Table 3
Potentials of the solid alloys of the Ni–Sc system at 988 K and chemical potentials of scandium ($\Delta\bar{G}_{Sc}$)

Phase	Two-phase region composition	E(V)	$\Delta\bar{G}_{Sc}$ (kJ mol^{-1})
I	$Sc + Sc_2Ni$	0.00 ± 0.01	0.0 ± 2.9
II	$Sc_2Ni + ScNi$	+0.15 ± 0.01	−42.0 ± 2.9
III	$ScNi + ScNi_2$	+0.39 ± 0.01	−112.9 ± 2.9
IV	$ScNi_2 + Sc_2Ni_7$	+0.62 ± 0.01	−179.5 ± 2.9
V	$Sc_2Ni_7 + ScNi_5$	+0.98 ± 0.01	−283.7 ± 2.9
VI	$ScNi_5 + Ni(Sc)_{ss}$	+1.28 ± 0.01	−370.5 ± 2.9

Table 4
Gibbs's energy change at $T = 988$ K during intermetallic-compound formation in the Ni–Sc system from the solid components

	$-\Delta G_f^{988}$ (kJ(mol of comp)$^{-1}$)	$-\Delta G_f^{988}$ (kJ(mol of alloy)$^{-1}$)
$2Sc + Ni = Sc_2Ni$	235.2 ± 2.5	78.4 ± 0.8
$Sc + Ni = ScNi$	193.2 ± 1.9	96.6 ± 0.9
$Sc + 2Ni = ScNi_2$	273.6 ± 1.4	91.2 ± 0.5
$2Sc + 7Ni = Sc_2Ni_7$	688.5 ± 0.9	76.5 ± 0.1
$Sc + 5Ni = ScNi_5$	371.4 ± 0.5	61.9 ± 0.1

Table 5
Microhardness of nickel and intermetallic compounds of the Ni–Sc system

Phase	HV (kg mm^{-2})
Ni	120–140
$ScNi_5$	640–720
Sc_2Ni_7	580–620
$ScNi_2$	850–930
ScNi	230–250
Sc_2Ni	240–260

The microhardness of $ScNi_2$ is higher than the data reported for the $REMNi_2$ compounds. This compound is the hardest of the all the intermetallic compounds in the Ni–Sc system.

In conclusion, using the chronopotentiometry data we have calculated the Gibbs's energy of formation of the intermetallic compounds in the Ni–Sc system from the solid components. The large values of the formation energies correspond to a large bond energy for all compounds. The ScNi compound is shown to be the most stable compound in the Ni–Sc system.

On the basis of cyclic voltammetry and chronopotentiometry data the supposition was made about the more preferable kinetic conditions of $ScNi_2$ formation when scandium is electrodeposited onto nickel.

The $ScNi_2$ compound has the largest microhardness value both in the series of isostructural $REMNi_2$ compounds (according to data published) and in the Ni–Sc system.

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