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High-temperature electrochemical synthesis and properties of intermetallic compounds of the Ni–Sc system

Part 1. Electrochemical behaviour of Sc(III) in chloride–fluoride melts

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Abstract

The electrochemical behaviour of Sc(III) in chloride–fluoride molten salts was studied. Sc(III) reduction is observed to proceed in a three-electron stage. Scandium metal interacts with the halide electrolyte leading to the formation of the alkaline metal. Sc(III) reduction on the surface of a nickel electrode proceeds with significant depolarization due to intermetallic compound formation.

Keywords: Scandium; Molten salt; Electrochemical behaviour; Halide electrolyte

1. Introduction

The use of rare earth metals as well as scandium for micro-alloying cast iron, steel and heat-proof alloys on nickel and cobalt bases allows us to change the structure and properties of these alloys. However, the large vapour pressure of the metal introduced at operating temperatures renders precise alloying impossible. One way to solve this problem is to use alloys of the necessary rare earth elements. For instance, when scandium is added to the alloy the intermetallic compounds (IMCs) of the Ni–Sc system may be used as a convenient admixing material. This investigation is devoted to the use of high-temperature synthesis to control IMC composition and formation kinetics. The electrochemical behaviour of Sc(III) cations in chloride–fluoride melts and the interaction of the latter with metallic scandium are described in this Part 1. Part 2 will be devoted to the investigation of thermodynamic and mechanical properties of the intermetallic compounds produced. The formation of IMCs of various composition in molten electrolytes by means of currentless transfer will be discussed in Part 3, and the influence of the main electrochemical synthesis parameters on the kinetics and phase composition of the Ni–Sc compounds will be considered in the Part 4.

Sc(III) electrochemical behaviour in chloride–fluoride melts has been insufficiently studied. When scandium–aluminium alloy equilibrium potentials in chloride and chloride–fluoride melts were measured, the authors of Ref. [1] concluded that the addition of scandium fluoride to the KCl–NaCl melt results in an alloy potential shift to the negative region in comparison with KCl–NaCl–$ScCl_3$ chloride melt. In this case no significant scandium transfer into the metallic phase was observed. However, NaF addition to the chloride melt containing ScF_3 enabled an Al–Sc alloy to be produced with scandium concentration up to 14.5 wt.% [2]. Intensification of the discharge process at the halide melt–aluminium metal border became possible due to the shift of aluminium electrode potential to the negative region when the F^--ion concentration was increased. Such influence of F^--ions on the electrode potential is natural and typical for the chloride and chloride–fluoride melts containing rare-metal ions [3,4].

Having determined the scandium cation oxidation state in chloride melts based on KCl–LiCl [5] and KCl–NaCl [6], the authors concluded that Sc(III) cations exist in equilibrium with metallic scandium. Musaev et al. [7] are also of the opinion that only the highest oxidation state is typical for scandium in

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chloride melts since it is the only wave that is recorded on both cathodic and anodic voltammograms. F^--ion addition with molar ratio $[F]/[Sc] = 4.0$ results in cathodic wave disappearence and bifurcation of the anodic wave when the voltammogram is recorded with a scandium electrode as working electrode. This fact, as well as marked scandium corrosion in the chloride–fluoride melt, suggests the existence of Sc(II) cations [7] which, in our opinion, is erroneous. Firstly, it is a regular feature for halide melts containing rare metal ions to stabilize the highest oxidation state of the latter at the transition from chloride to chloride–fluoride melts [3,4,8,9]. In contrast, the cathodic wave disappearance on the voltammogram is explained by a decrease of the difference in reduction potentials of alkaline metal ions and scandium [10]. Therefore, in this case the rate of scandium metal interaction with the background electrolyte cations becomes higher, which explains the significant scandium corrosion in the chloride–fluoride melt. The bifurcation of the scandium dissolution anodic wave after F^--ion addition is perhaps the result of Sc(III) complex formation with different ligand composition (see for instance Ref. [11]). The proof of the supposition is the existence of only one anodic wave as the [F]/[Sc] ratio is increased up to 12.5 mol per mol. Only fluoride Sc(III) complexes are formed in the near-electrode space under these conditions.

In addition to the paper cited above the use of KCl–NaCl–NaF(6 wt.%)–ScF_3(18 wt.%) electrolyte for Sc–Zn alloy production was described in Ref. [12]. No other publications on this problem have been found.

It is apparent that Sc electrochemical behaviour in chloride–fluoride melts has been insufficiently studied and a more detailed investigation is necessary.

2. Experimental

Sodium and potassium chlorides ("Chemical pure"), necessary for the electrolyte preparation, were first recrystallized and dried at 120–150°C. Placed into a molybdenum crucible, they were installed into a hermetic vessel made of stainless steel which was evacuated under a stepwise heat. The salts were then melted under cleaned and dried argon. Scandium fluoride was prepared by Sc_2O_3 fluorination. Electrolytical scandium metal (99.95%) was used. Molybdenum and nickel wires 1 mm in diameter were used as working electrodes. The reference electrode was a half-element Ag|KCl–NaCl + AgCl(2 wt.%)||, immersed in a sealed alundum tube. To avoid interaction of the tube material with F^--anion, the reference electrode contacted with melts only during the voltammogram recording. The rest of the time it was placed over the electrolyte. All experiments were carried out under cleaned argon atmosphere.

3. Cyclic voltammetry

Cyclic voltammetry was used to investigate the electrochemical behaviour of scandium cations in chloride–fluoride melts. A molybdenum rod was selected as a working indifferent electrode. According to Ref. [13], no intermediate compounds have been found in the eutectic type Sc–Mo system. The scandium solid solution in molybdenum contains 8 at.% of Sc at 1150°C. The addition of ScF_3 to the NaCl–KCl melt results in the appearence of a cathodic wave at − 2.05 V against a silver/silver chloride reference electrode and one anodic wave of the product oxidation reduced in the cathodic cycle (Fig. 1(a)). The anodic wave at − 0.15 V corresponds to molybdenum dissolution. The substance produced during potentiostatic electrolysis at − 2.05 V was identified by X-ray diffraction analysis as metallic scandium. Consequently, the cathodic process of Sc(III) cation reduction is realized in a three-electron stage:

$$\mathrm{Sc(III)} + 3e^- \Rightarrow \mathrm{Sc(0)} \qquad (1)$$

If the cathodic process is reversible, the increase of Sc(III) concentration must result in a wave potential shift to the positive region. However, increasing F^--ion content compensates for this effect by a potential shift to the cathodic region. As a result, additions of ScF_3 do not change the cathodic wave position (Fig. 1(a)).

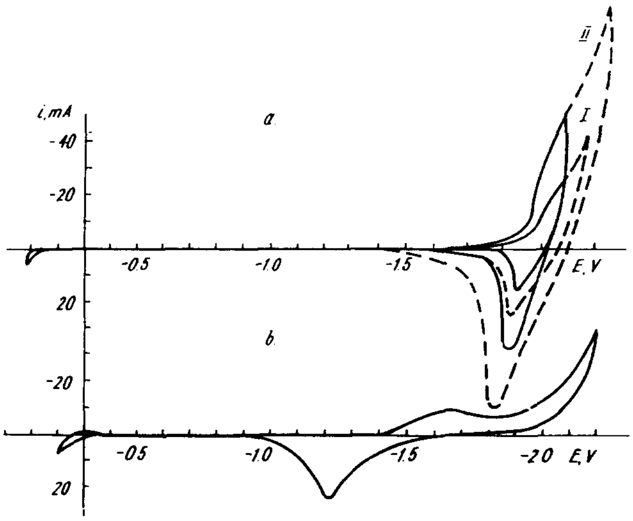

Fig. 1. Voltammograms of NaCl–KCl–ScF_3 melt, $T = 730$°C, sweep rate $V = 0.1$ V s^{-1}, working electrode surface $S = 0.165$ cm^2, silver/silver chloride reference electrode. (a) Working electrode Mo, $C_{Sc(III)} = 0.295$ mass% (I), 1.06 mass% (II); (b) working electrode Ni, $C_{Sc(III)} = 0.295$ mass%.

Metallic scandium exposure in the NaCl–KCl–ScF_3 melt has not qualitatively changed the shape of the cyclic voltammogram, but has only resulted in a cathodic wave increase due to changes of scandium ion concentration in the melt. Scandium concentration growth was confirmed by atomic absorption analysis. This proves the absence of the low oxidation state of scandium cations in chloride–fluoride melts. The cause of Sc(III) content increase is the interaction between metallic scandium and supporting electrolyte cations by the reaction

$$Sc(0) + 3Na(I)(K(I)) \Leftrightarrow Sc(III) + 3Na(0)(K(0)) \qquad (2)$$

with the formation of alkali metals dissolved in molten salts. Reaction (2) is possible due to the proximity of scandium and the base electrolyte cation reduction potentials, this is seen clearly in Fig. 1(a). Therefore, the Sc(III) reduction wave has no maximum typical of more electropositive metals, but is a shoulder on the alkaline metal reduction wave. Both sodium and potassium metals are observed to have a considerable solubility in molten salts under these experimental conditions. For instance, the solubility of sodium in NaCl at 811°C is 2.8 mol.% and that of potassium in KCl at 770°C is 10.5 mol.% [14]. As the electrolyte is saturated with the reduced alkaline metals, the colour of molten salt changes from white to dark grey. Since the temperature of the experiment is significantly higher than those of sodium (98°C) and potassium (64°C) melting, the metals volatilize and crystallize on the cool parts of the vessel. Potassium and sodium were observed to burn when the cover was opened. The condensed electrolyte solution is of an alkaline nature.

Unlike the indifferent molybdenum electrode, the nickel electrode interacts with scandium in the process of its reduction. Therefore, the shape of the cyclic voltammogram recorded with the nickel electrode (Fig. 1(b)) is distinguished from that recorded with a molybdenum one. The cathodic wave at − 2.05 V and the corresponding anodic wave disappear and are not recorded within a wide interval of polarization rates and Sc(III) cation concentrations in the melt. At the same time a cathodic wave at a more positive potential (− 1.65 V) and an anodic wave (− 1.2 V) corresponding to it are recorded. At − 0.3 V against the silver/silver chloride reference electrode dissolution of nickel begins. The value of 0.6 V depolarization occurring at Sc(III) reduction is due to the formation of intermetallic compounds on the nickel electrode surface. The absence of both cathodic and anodic waves characteristic of scandium reduction–oxidation on indifferent electrode is perhaps due to weak kinetic limitations of IMC formation in these conditions. There are five intermetallic compounds in the Ni–Sc system, $ScNi_5$, Sc_2Ni_7, $ScNi_2$, ScNi and Sc_2Ni. The Ni–Sc phase diagram constructed on the base of data [15,16] is presented in Fig. 2. Four IMCs are characterized by very narrow homogeneity regions, but the positions of ScNi and Sc_2Ni compounds on the phase diagram do not correspond to their exact stoichiometric compositions [16]. According to the data [17], the Sc_2Ni_7 intermetallic compound exists within the interval of 21–23 at.% Sc. The $ScNi_2$ compound, being the most refractory of all the compounds, has a wide homogeneity region (31–35 at.%). Its own potential conforms to each of the IMCs at which a dissolution wave of the compound is recorded in the anodic part of the voltammogram. This is not observed, perhaps because of alloy formation kinetics and because the potential of the working electrode is not changed spontaneously but according to the given program. In this case no equilibrium state is reached. More informative in this regard is the method of discharge chronopotentiometry.

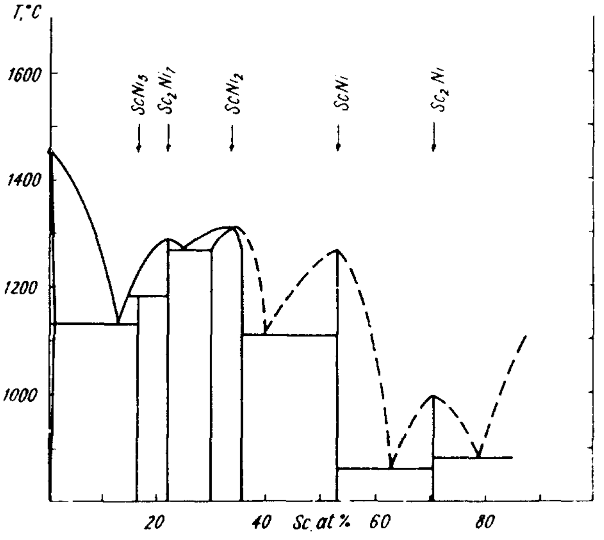

Fig. 2. Ni–Sc phase diagram [15,16].

4. Conclusions

As a result of the investigation of Sc(III) electrochemical behaviour in chloride–fluoride melts it can be inferred that:

–Sc(III) cation reduction in NaCl–KCl–ScF_3 melt on an indifferent electrode occurs in a three-electron stage at a potential of about − 2.05 V against a silver/silver chloride reference electrode. Scandium cations of the low oxidation state were not found;

–scandium metal interacts with NaCl–KCl–ScF_3 melt with the formation of dissolved atoms of alkaline metals by reaction (2);

–Sc(III) reduction on an unindifferent nickel electrode proceeds with significant depolarization due to intermetallic compound formation on the electrode surface.

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