

AN ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL STUDY OF Ln(II) (Ln = Sm, Eu, Yb) SPECIES IN NaCl-2CsCl MELT

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In the present work cyclic voltammetry, high temperature electronic absorption spectroscopy and spectroelectrochemistry were employed for studying the behavior of Sm, Eu and Yb species in NaCl-2CsCl based melts between 823 and 1023 K.

Analysis of cyclic voltammograms showed that Ln(III)/Ln(II) reduction/oxidation is an one-electron diffusion controlled reversible process. Diffusion coefficients of LnCl_6^{3-} species were determined in the studied temperature range and are described by the following equations:

$$\lg D = -3.42 - 1417/T (\pm 0.02) \text{ for Sm} \quad (1)$$

$$\lg D = -2.68 - 2057/T (\pm 0.01) \text{ for Eu} \quad (2)$$

$$\lg D = -1.95 - 2397/T (\pm 0.02) \text{ for Yb} \quad (3)$$

Formal standard red-ox potentials of Ln(III)/Ln(II) couples in NaCl-2CsCl based melts were determined in the studied temperature range using cyclic voltammetry:

$$E^* \text{ Sm(III)/Sm(II)} = -2.899 + 8.01 \cdot 10^{-4} T (\pm 0.04) \text{ V} \quad (4)$$

$$E^* \text{ Eu(III)/Eu(II)} = -1.191 + 3.5 \cdot 10^{-5} T (\pm 0.03) \text{ V} \quad (5)$$

$$E^* \text{ Yb(III)/Yb(II)} = -2.592 + 8.48 \cdot 10^{-4} T (\pm 0.02) \text{ V} \quad (6)$$

Gibbs free energy change of the formation of LnCl_3 from LnCl_2 in NaCl-2CsCl based melts is described by the following equations:

$$\Delta G^* = -278.17 - 0.0759 \cdot T, \text{ kJ/mol for Sm} \quad (7)$$

$$\Delta G^* = -126.83 - 0.0318/T, \text{ kJ/mol for Eu} \quad (8)$$

$$\Delta G^* = -250.07 - 0.0818 \cdot T, \text{ kJ/mol for Yb} \quad (9)$$

For the reaction



the equilibrium constants can be expressed by the following equations:

$$\lg K^* = -4.057 + 14616/T \text{ (for Sm)} \quad (11)$$

$$\lg K^* = -1.663 + 6625/T \text{ (for Eu)} \quad (12)$$

$$\lg K^* = -4.297 + 13084/T \text{ (for Yb)} \quad (13)$$

A series of spectroelectrochemical experiments was performed to study potentiostatic reduction of Ln(III) ions. The concentration changes of LnCl_6^{3-} species in the melt were followed by recording the absorption spectra. Changes of the absorption of Yb(III) ions showed essentially linear dependence on the amount of electricity passed during the electrolysis, Fig. 1. Analysis of the melt after the electrolysis showed that Yb concentration in the melt remained essentially unchanged and the mean oxidation state of ytterbium decreased to 2.83.

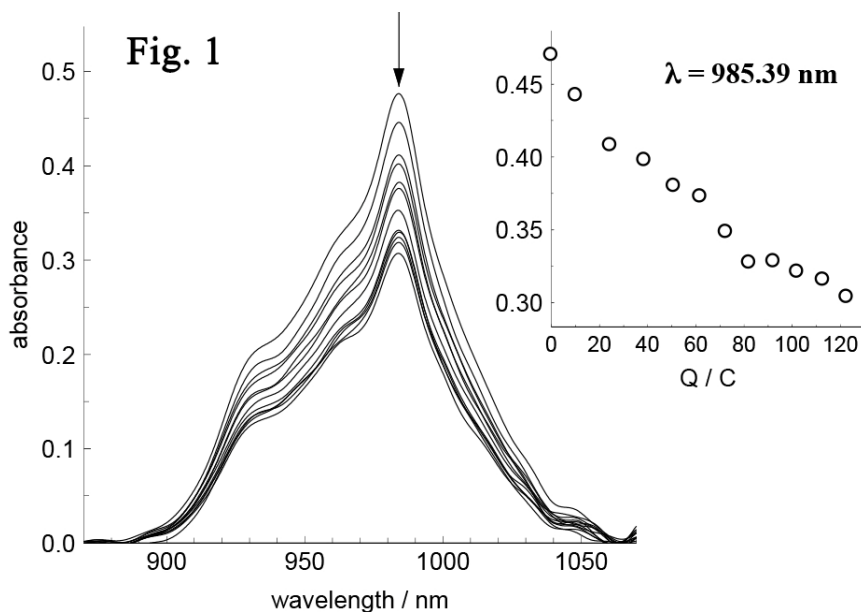


Fig. 1. Changes of the absorption of YbCl_6^{3-} ions in NaCl-2CsCl based melt during potentiostatic reduction

КОРРОЗИЯ СТАЛЕЙ И СПЛАВОВ В ХЛОРАЛЮМИНАТНЫХ ХЛОРИДНЫХ РАСПЛАВАХ

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Энергетические реакторы на быстрых нейтронах с активной зоной и теплоносителем в виде солевого расплава относятся к совершенно новому поколению безопасных ядерных реакторов, в которых может быть использовано как урановое, так и ториевое ядерное топливо. Однако внедрение ядерно-энергетических установок на основе расплавленных солей сдерживается рядом проблем, одной из которых является необходимость подбора конструкционных материалов, сохраняющих стойкость в крайне агрессивных условиях.

В настоящей работе осуществлено комплексное исследование процессов взаимодействия жаропрочных сплавов ХН60ВТ, Haynes 230 и коррозионно-