

Corrosion of Nickel-Chromium Alloy in the Molten Mixture LiF-NaF-KF

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Abstract

Corrosion of nickel-chromium alloy in molten mixture LiF-NaF-KF was investigated at the temperature of 680 °C. Two methods were used: chronopotentiometry for determination of concentration of corrosion products and the measurement of the polarization resistance. Both methods were compared by digital simulation of the corrosion process. The agreement between these two methods is very good.

Keywords: corrosion of alloys, polarization resistance, corrosion in molten salts

Introduction

Molten salts are promising medium for a new generation of nuclear reactors and/or for the treatment of spent nuclear fuel. One of the most important problems related to the industrial application of this idea is a development and testing of suitable materials which can resist corrosion attack of molten salts. This work is an introduction to this topic. We have chosen the eutectic mixture of alkali metal fluorides as a model medium for corrosion studies. Two methods were used. The first one is based on the determination of concentration of corrosion products by chronopotentiometry. The second method is based on the measurement of the polarization resistance. The results of both these methods are compared.

Experimental

The corrosion measurements were carried out in a resistor heated vertical furnace in argon atmosphere (Fig. 1). Composition of nickel-chromium alloy used for the study was determined by the X-ray microanalysis (JEOL JXA-840A, Japan): The composition is presented in Table 1.

Table 1. Composition of the alloy

Element	x / (at. %)	w / (wt. %)	Error (±)
Si	0.49	0.24	0.02
Ti	0.63	0.52	0.06
Cr	28.30	25.25	0.20
Fe	0.67	0.64	0.11
Ni	65.28	65.75	0.54
Mo	4.62	7.61	0.14
total	100.00	100.00	

Measurement of polarization resistance is widely used technique in corrosion monitoring (Joska and Novák 2001). The polarization resistance R_p of a material is defined as the slope of the potential-current density curve at the free corrosion potential. It holds:

$$j_{kor} = \frac{B}{R_p} \quad (1)$$

$$B = \frac{b_a \cdot b_c}{2,303(b_a + b_c)} \quad (2)$$

$$R_p = \frac{\Delta E}{\Delta j} \quad (3)$$

where:

j_{kor} denotes corrosion current density; R_p is polarization resistance calculated near the corrosion potential ($\Delta E \rightarrow 0$); b_a slope of the Tafel dependence $\log j = f(\Delta E)$ in anodic area; b_c slope of the Tafel dependence $\log j = f(\Delta E)$ in cathodic area; ΔE is overvoltage related to corrosion potential and Δj denotes current density at ΔE .

Rate of corrosion can be calculated according to Faraday laws.

Chronopotentiometry (Bard and Faulkner 2001) is the electrochemical technique based on the measurement of potential of the working electrode (in our case the Ni-Cr alloy) as function of time when constant current passes through the system. The electrode potential changes as a result of the electrochemical consumption of electroactive species at the surface of the electrode. When the surface concentration of the electroactive substance decreases to zero, potential of the electrode changes rapidly. Time from the beginning of the electrolysis to the abrupt change of potential is called the transition time, τ . When the rate of the electrochemical process is controlled only by diffusion of the electroactive species the process is described by Sand equation (Sand 1901):

$$\tau^{1/2} = \frac{nFc^0 \pi^{1/2} D^{1/2}}{2|j|} \quad (4)$$

where:

τ denotes transition time; n is number of exchanged electrons; F is Faraday constant ($F = 96485,3 \text{ C mol}^{-1}$); D diffusion coefficient; j denotes current density.

It follows that the equation relates the transition time with current density, concentration of the electroactive species, and the diffusion coefficient of the electroactive species. The diffusion coefficient can be determined independently for known concentration of the electroactive species. Than the chronopotentiometry can be used as an electroanalytical method.

Chemicals.

The following chemicals were used: LiF (Suprapur, Merck), NaF (p.a. Merck), Kf (pure, Lachema). LiF and NaF were heated at 600 °C for 2 h. KF is hygroscopic. Therefore it was dried in vacuum dryer in the presence of P_2O_5 for 7 days.

Working Procedure

135 of the eutectic mixture 46.5 mole % LiF + 11.5 mole % NaF + 42.0 mole % KF was weighed –in a graphite crucible. The mixture was heated in argon (99.99 %, Linde). Argon was bubbled through concentrated sulphuric acid. Traces of oxygen were removed by copper shaving at 350 °C prior to inlet to the furnace. When the desired temperature 680 °C was achieved the electrodes were immersed to the melt. The working electrode (Ni-Cr alloy) had following dimensions: width 5 mm, thickness 2 mm, immersion in the melt 8 mm. Prior

to use, the working electrode was polished with diamond paste (15 μm). Aluminium electrode (see Fig. 1) was used as a reference electrode.

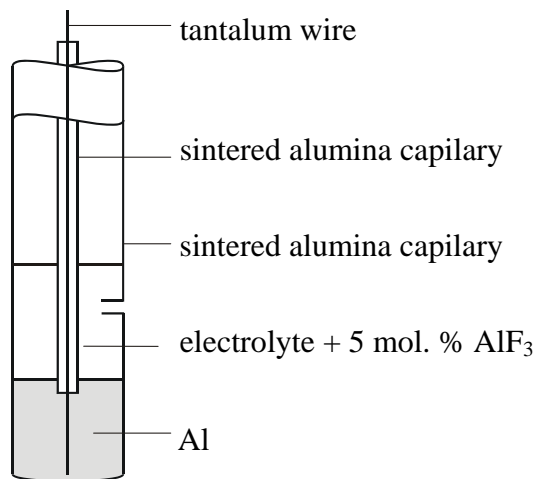


Fig.1. Aluminium reference electrode.

Measurement of the polarization resistivity

The dependence $I = f(E)$ was measured in the potential range ± 200 mV from the corrosion potential E_{cor} with sweep rate 1 mV /s. Electrochemical analyser AUTOLAB (ECO Chemie, Netherland) was used. The measurement was repeated several times in 1 h intervals.

Chronopotentiometry

This measurement was done in a similar experimental arrangement as mentioned above using the same electrochemical analyser. Current was changed in the interval from -0.050 A to -0.450 A with step 0.025 A. Surface of the working electrode was 1.09 cm². Also these measurements were repeated in 1 h intervals.

Analysis of surface of samples

Surface of samples was analysed by X-ray microanalysis (EDX, probe EPMA JEOL JXA-840 A, Japan), by electron scanning microscope Zeiss EVO 40, REM TESLA-BS 300. Corrosion products were identified also by powder X-ray diffraction (STOE stadi P, Bruker)

Results and Discussion

Then polarization resistance and the corrosion current density were determined on two identical samples. For illustration, the experimental dependence of current vs. potential both in linear and logarithmic scales are shown in Fig. 2. The results are summarized in Table 2.

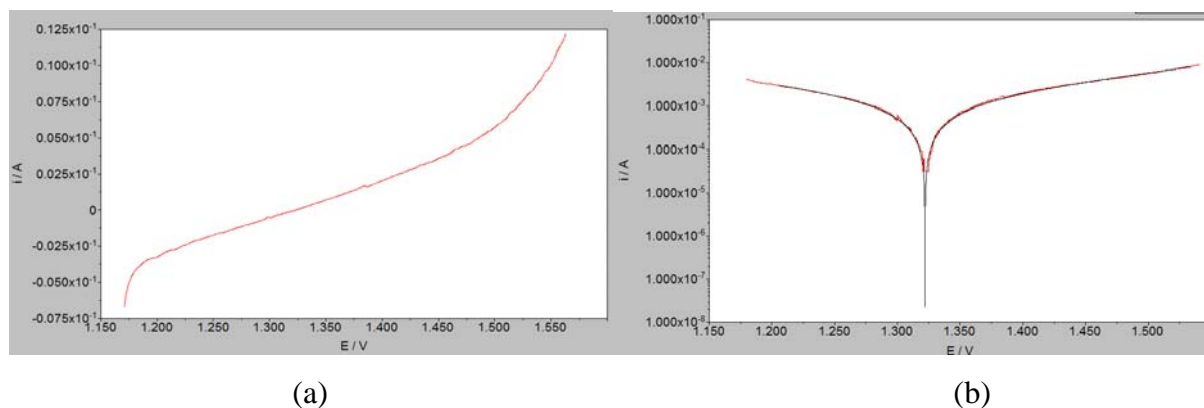


Fig. 2. Polarization resistance curve; (a) – Measured curve (sample 1 in 1 hour); (b) – Measured curve recalculated into logarithmic scale.

It follows that reproducibility of the measurement, especially for the first two hours, is good. After 4 h of exposition of the sample in the melt, the polarization resistance could not be determined. We assume that this is caused by the formation of corrosion products on the surface of the working electrode. SEM showed changes in structure of the surface. It was found that molybdenum and chromium dissolved preferentially. X-ray micro analysis of surface of the samples and the X-ray analysis of corrosion product proved that the surface of the electrode was covered crystals containing 36.3 mole % Cr and 33.6 mole % Ni. When the corrosion product was removed the surface of the electrode contained only 2.5 mole % Cr and 78.8 mole % Ni. It seems that also crystals of Li_2NiF_4 were formed on the surface. This data were used for estimation of the number of electrons exchanged at the oxidation of metal substrate. It follows that $n = 2.6$. This number was used for calculation of the rate of corrosion (Table 2).

Table 2. Measurement of polarization resistance and corrosion current density

t / h	E_{kor} / V	$R_p / (\Omega \text{ cm}^2)$	$b_c / (\text{V A}^{-2})$	$b_a / (\text{V A}^{-2})$	$10^4 \times j_{kor} / (\text{A cm}^{-2})$	$10^{11} \times \Delta m / (\text{g cm}^{-2} \text{ s}^{-1})^*$	$10^{11} \times \Delta d / (\text{mm s}^{-1})^*$
sample 1							
0	1.351	192.64	0.642	0.391	5.48	3.72	4.50
1	1.322	71.67	0.313	0.293	9.17	6.23	7.54
2	1.353	106.49	0.196	0.167	3.68	2.50	3.02
3	1.345	229.24	0.195	0.205	1.89	1.29	1.56
4	cannot be evaluated						
sample 2							
0	1.348	208.13	0.843	0.435	5.99	4.07	4.92
1	1.319	79.56	0.518	0.219	8.40	5.71	6.91
2	1.353	114.51	0.297	0.278	5.44	3.70	4.48
3	1.349	236.92	0.178	0.229	1.84	1.25	1.51
4	cannot be evaluated						

* Immediate change in mass and thickness calculated under assumption that average number of electrons exchanged at electrochemical process is 2.6 (see text below).

Time dependence of the concentration of electroactive species in the course of corrosion measured by chronopotentiometry is plotted in Fig. 3. (Diffusion coefficient was estimated to be $D = 5 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.) This plot clearly shows that the rate of corrosion decreases with time, which is in agreement with the measurement of the polarization resistance.

In Fig. 3 comparison between data obtained by polarization resistance measurements and by chronopotentiometry is shown as well. Data obtained by polarization resistance measurements were treated by digital simulation of diffusion of soluble corrosion products into bulk of the electrolyte. Digital simulation was based on the approach presented in (Feldberg 1969) and concentration of corrosion products at sample (electrode) surface was calculated. It can be seen from Fig. 3 that both measurements are in good agreement.

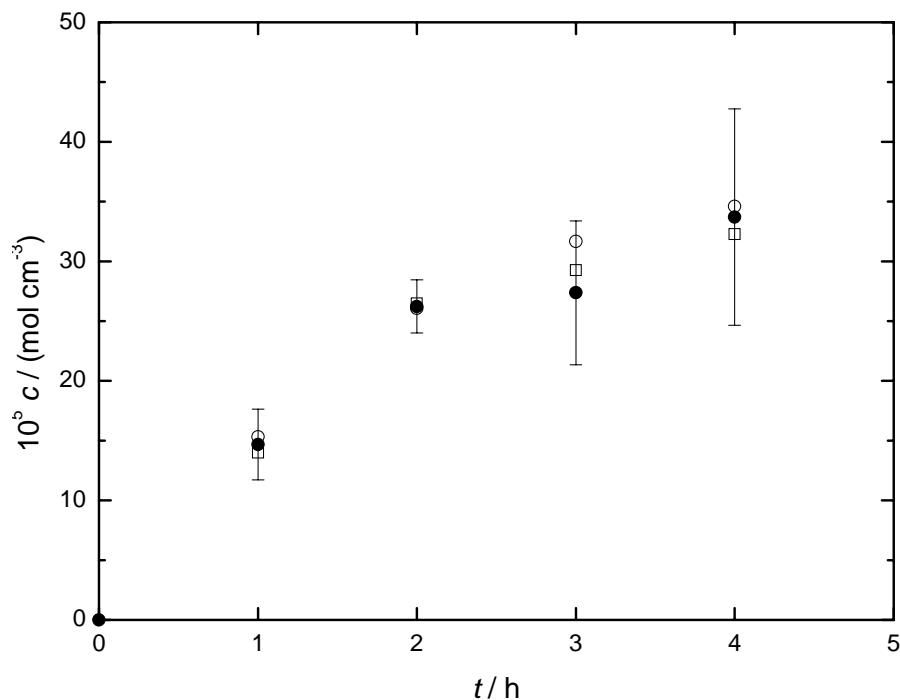


Fig. 3. Comparison of surface concentration of corrosion products obtained by chronopotentiometry and by digital simulation of polarization resistance measurements. ● - data obtained by chronopotentiometry; □, ○ - data obtained by digital simulation.

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