

Corrosion of Nickel in the Molten Mixture LiF-NaF-ZrF₄

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Abstract

Corrosion of pure nickel (Nickel 201) in molten mixture LiF-NaF-ZrF₄ was investigated at the temperature of 680 °C by measurement of polarization resistance. It seems that after 700 hours the melt was saturated with corrosion products and corrosion rate decreased rapidly.

Keywords: polarization resistance, corrosion in molten salts, materials for nuclear energy

Introduction

Molten salts are used as medium in numerous industrial applications. The most important is the exploitation of molten salts as electrolytes used for electrowinning of metals (e.g. aluminium, magnesium, titanium) and chemical deposition and electrodeposition of metals and metalloids. They can be used in high temperature fuel cells, medium for chemical reactions, etc. Tested is the application of molten salts as heat carriers. In nuclear reactors, molten salts can serve both as a solvent for nuclear fuel and heat transfer.

The idea to use molten salts in nuclear reactors is not new. In the fifties and the sixties the molten salts nuclear reactor was tested in Oak Ridge National Laboratory (ORNL) in USA. It was proved that this approach is feasible. Today, the concept of molten salt nuclear reactor (as a member of so called Generation IV reactors) is considered promising both from the point of view of economy and safety. Probably the most important is that these reactors could use spent nuclear fuel from present reactors. The following systems based on molten fluorides have been considered (Williams et al., 2006):

1. Alkali metal fluorides: LiF –KF; LiF – RbF; FLiNaK (LiF – NaF – KF); LiF – NaF – PbF.
2. Fluoride systems containing ZrF₄: LiF – NaF (KF, RbF) – ZrF₄, LiF – NaF - ZrF₄, NaF – RbF - ZrF₄.
3. Fluoride systems containing BeF₂: LiF - BeF₂, NaF - BeF₂, LiF – NaF - BeF₂.

One of crucial points is to find a suitable corrosion resistant material for construction of molten salt reactors. Currently as most promising are considered following alloys: Hastelloy N (with or without admixture of Ti), HN80MT, and nickel-chromium-molybdenum alloys (Hosnedl, Ignatiev and Matal, 2008). It is also assumed that these alloys could be modified with molybdenum.

Aim of this work is to determine the corrosion resistance of Nickel 201 that is the basic material in alloys mentioned above in the melt LiF – NaF – ZrF₄ at the temperature of 680 °C. Composition of the melt was as follows (mole %): 42.0 % LiF + 29.0 % NaF + 29 % ZrF₄. The corrosion resistance was determined on the basis of the polarization resistance measurement. The polarization resistance is evaluated from the plot of the polarization current vs. the electrode potential in the Tafel region of the polarization curve (Joska and Novák, 2001) (see Fig. 1).

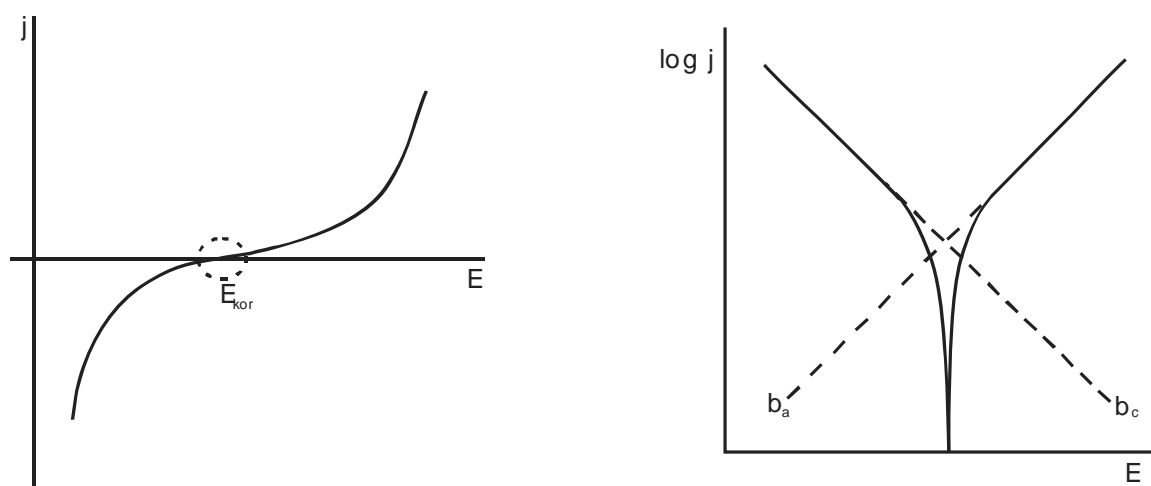


Fig. 1 Polarization resistance measurement scheme

The corrosion current density can be determined from the experimentally determined polarization curve (tested material serves as the working electrode) according to the following relationships (Joska and Novák, 2001):

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

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

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

j_{kor} is the corrosion current density, R_p is the polarization resistance obtained in the vicinity of the corrosion potential ($\Delta E \rightarrow 0$), b_c and b_a are the slopes of Tafel curve $\log j = f(\Delta E)$ in the cathodic and anodic region, respectively. ΔE is the difference between the measured potential and the corrosion potential, and Δj is the current density at ΔE . Corrosion rate is proportional to the corrosion current density and it can be evaluated using Faraday laws (Koryta, 1980, Malinovský and Roušar, 1987)

Experimental

The following chemicals were used: LiF (Suprapur, Merck), NaF(p.a., Merck), ZrF₄ (99.9 %, Sigma Aldrich). All chemical were dried for 2 h at 600 °C. All operations with chemicals were carried out in the absence of air or oxygen. 60 g of sample (LiF – NaF – ZrF₄ mixture) was weighed-in a graphite crucible and placed in a laboratory furnace with controlled atmosphere (argon 99.99 %, Messer Tatragas). Prior to furnace inlet, argon was bubbled through concentrated sulphuric acid. Traces of oxygen were removed at 350 °C by copper chips. After melting, the molten salt mixture was kept at constant temperature of (680 ± 2) °C and the electrodes were submerged into the melt. The graphite crucible served as a counter electrode, working electrode was the investigated metal sample (width 5 mm, thickness 2 mm, submersion 11 mm). Before use, the electrode was polished with diamante paste (15 μm). Potential of the working electrode was measured against the nickel reference electrode. Scheme of the nickel reference electrode is shown in Fig. 2.

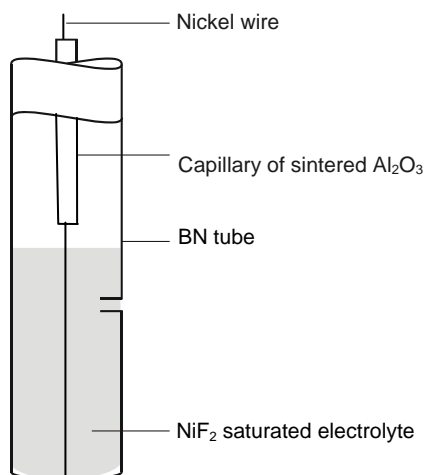


Fig. 2 The nickel reference electrode

The reference electrode consists of a BN tube closed at one end. Nickel wire was immersed in fluoride melt of the same composition as that used for corrosion studies. The melt was saturated with NiF₂. Conducting connection with the melt in the crucible was made by a small orifice in the BN tube. The reference electrode was submerged into the melt 15 min before measurement and then withdrawn. The dependence $I = f(E)$ was measured in the range ± 200 mV from the corrosion potential E_{cor} with the rate 1 mV/s. For the measurement, the potentiostat AUTOLAB (ECO Chemie, Netherlands). The corrosion experiment lasted for 78 h. During this time, the measurement of the polarization resistance was several times (typically 3 times) repeated. After the experiment, surface of the sample was analysed by X-ray microanalysis (EDX probe EPMA JEOL JXA-840A, Japan) and by AFM microscopy (AFM CP-II, VEECO, USA).

Results and Discussion

The same samples as that used for electrochemical determination of corrosion rate were exposed to the melt for 100, 300, and 1000 hours, respectively. Exact immersion of samples was checked after the corrosion experiment. Details about the tested samples are summarized in the Table 1.

Table 1 Experimental condition of the samples

Sample No.	Time/h	Immersion/mm
1	100	9
2	100	9
3	300	10
4	1000	7

The results are presented in Figs. 3 – 5

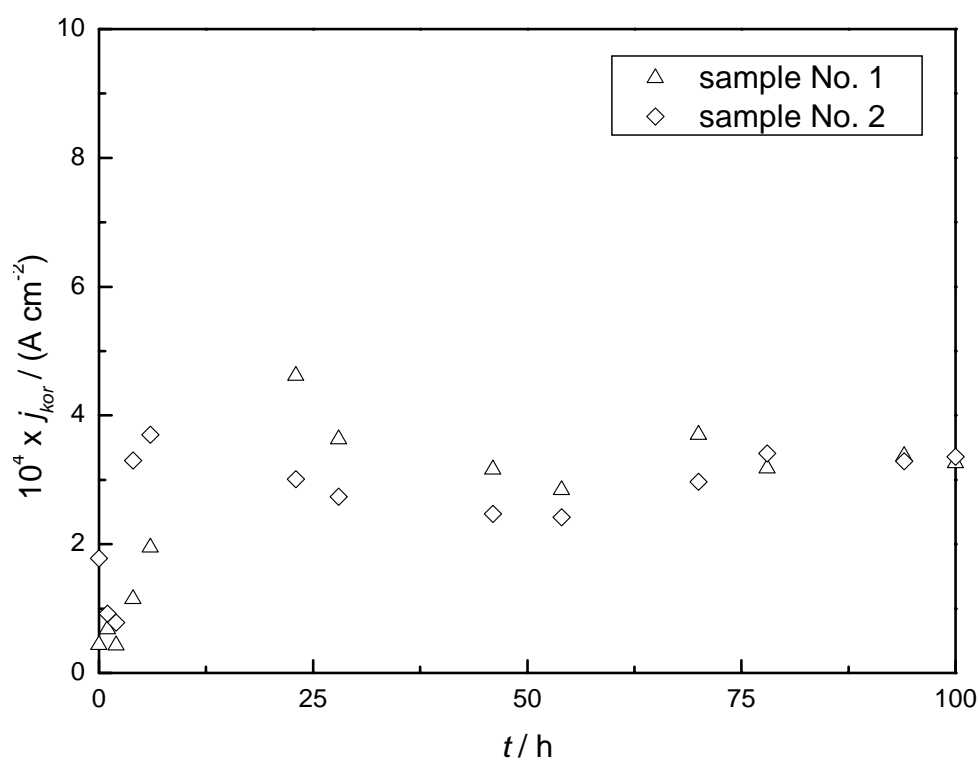


Fig. 3 The time dependence of the corrosion current density recorded during 100 h

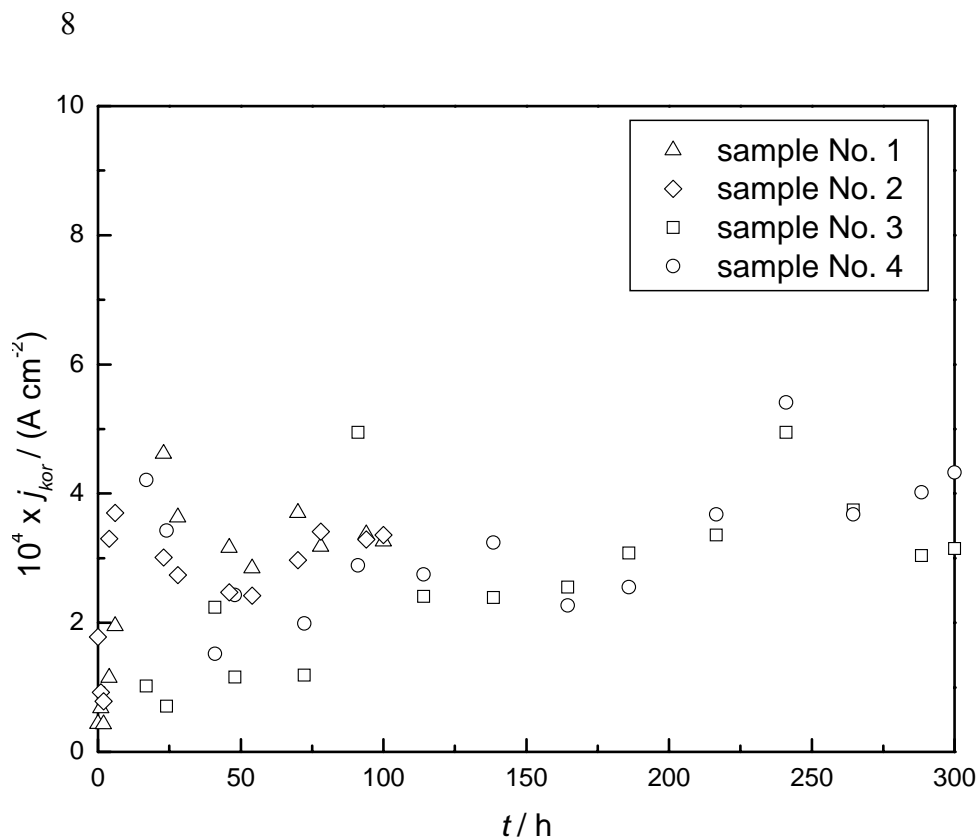


Fig. 4 The time dependence of the corrosion current density recorded during 300 h

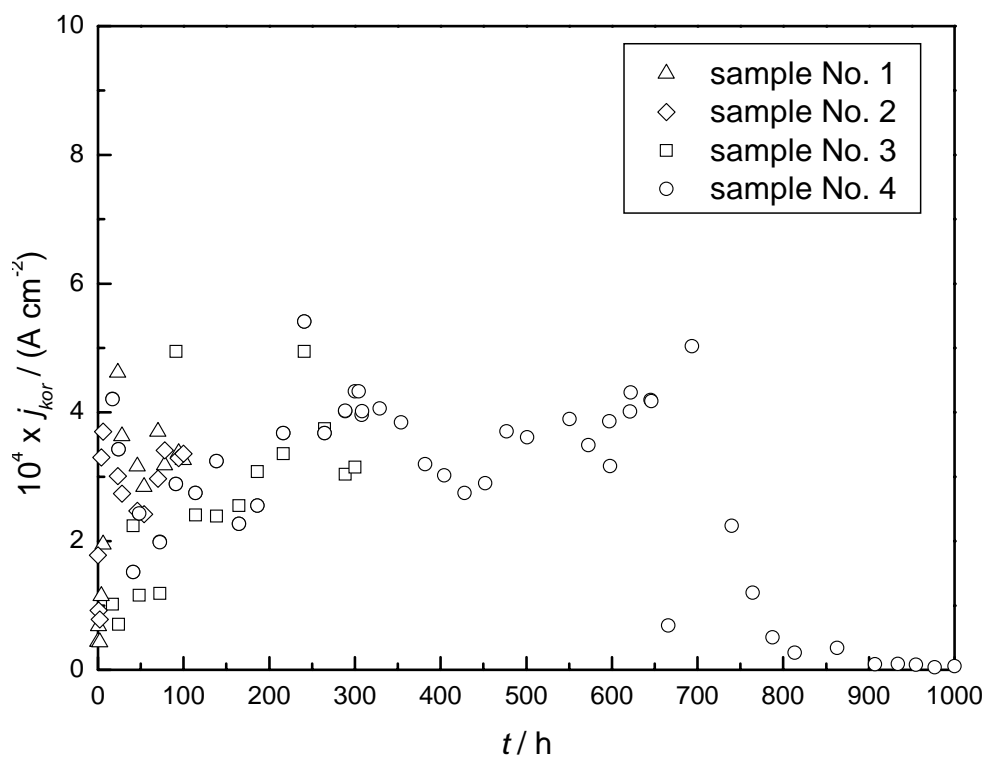


Fig. 5 The time dependence of the corrosion current density recorded for 1000 h

From Fig. 3, it can be seen that when the sample is exposed to the melt, the corrosion rate increases approximately during first 20 h. After this initial period it is almost constant for almost 200 h (see Fig. 4). Then the corrosion slowly increases and decreases with time. It can be seen that the corrosion rate oscillates around the value achieved after 100 h of exposition. However, after 700 h of exposition, the corrosion rate decreases by 2 orders (see Fig. 5). Explanation of this phenomenon can be revealed on the basis of chemical analysis of corrosion products. After the corrosion experiment, the layer of solidified electrolyte adjacent to the metal was analysed by X-ray powder diffraction. The layer consists of LiF, NaF, Na₃ZrF₇, Li₃ZrF₇, and Li₂ZrF₆. No free ZrF₄ was detected. In the case of 1000 h experiment, the layer contained also phases Zr₂Ni and NiF₂. Surface of the corroded metal was investigated also by AFM microscopy. Picture of the surface obtained with this technique is shown in Fig. 6. From Fig. 6, one can see that the corrosion is not homogeneous. In some places, melt penetrates deeper into the sample and the corrosion surface increases. AFM microscopy revealed the existence of fine crystals on the surface of the alloy exposed to the melt for 1000 h. Appearance of these crystals suggests that the melt is saturated with corrosion products which cover part of the surface. This may explain why the corrosion rate decreased after 700 h. For prove or disprove of this hypothesis further experiments are needed.

The corrosion rate expressed as loss of material caused by corrosion was calculated for two different assumptions:

1. rate of the corrosion decreases after 700 h
2. rate of the corrosion does not decrease and after the initial period it remains constant; the corrosion current density equals $3.17 \times 10^{-4} \text{ A cm}^{-2}$

In both cases we assumed that the 2 electrons take part in the corrosion reaction (e.g. oxidation of nickel to Ni²⁺). The results are summarized in Table 2.

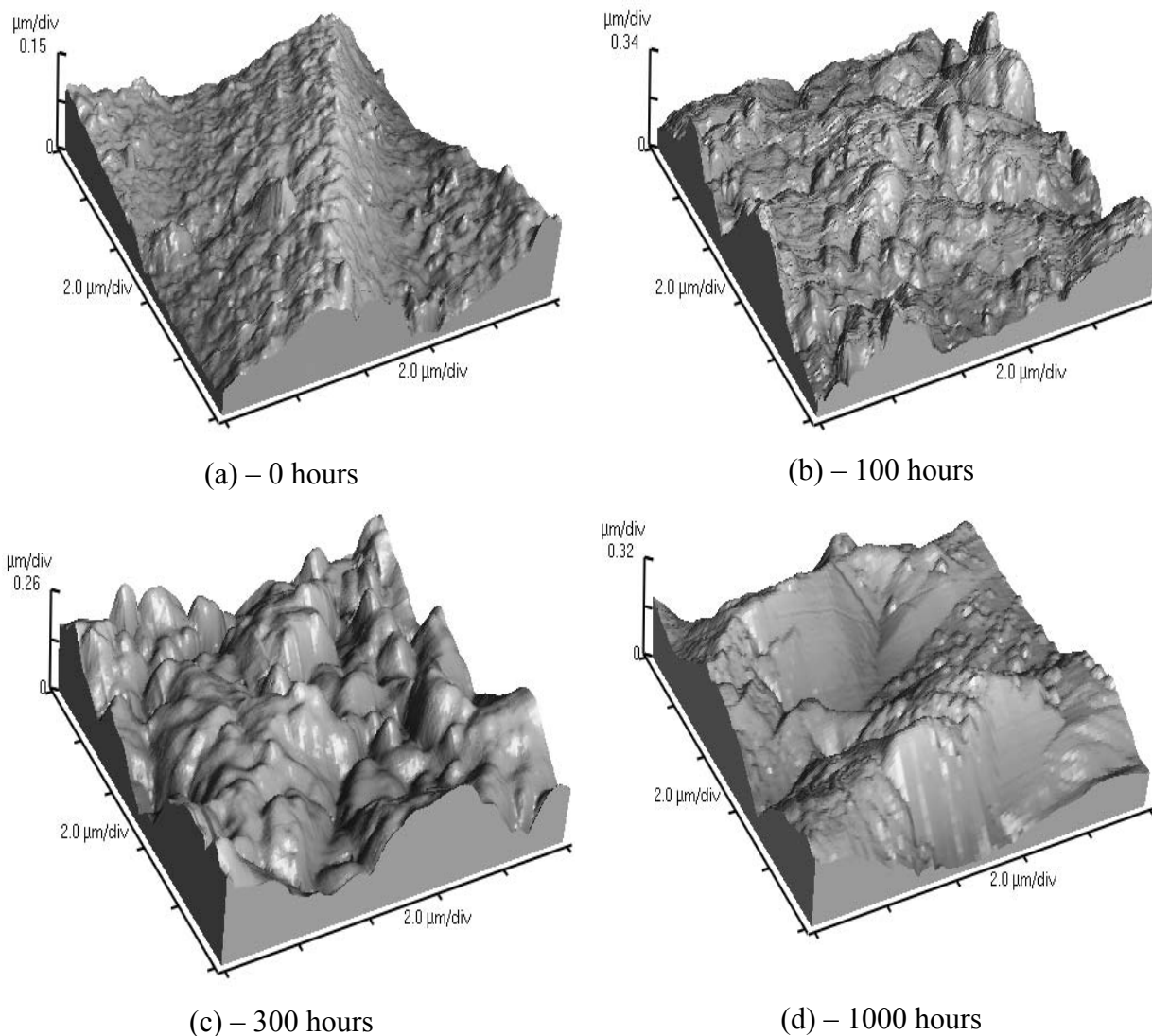


Fig. 6 Surface of samples after the corrosion experiments obtained by AFM microscopy

Table 3 Estimated corrosion losses of the tested Nickel 201 in the melt LiF – NaF – ZrF₄ at 680 °C

$\Delta m / (\text{g cm}^{-2} \text{ year}^{-1})$	$\Delta d / (\text{mm year}^{-1})^*$
Assumption 1: corrosion rate decreases after 700 h	
0.316	0.36
Assumption 2: corrosion rate remains constant	
2.98	3.34

*assumption of homogeneous corrosion

Conclusion

Corrosion rate of the tested Nickel 201 was investigated in the LiF – NaF – ZrF₄ melt at 680 °C for 100 h, 300 h, and 1000 h, respectively. Rate of corrosion was estimated on the basis of polarization resistance. After an initial period, the corrosion rate was 3.3 mm per year. However, when the layer of the melt adjacent to the studied sample was saturated with corrosion products (in our case after 700 h) the corrosion rate substantially decreased to about one tenth of its original value.

Acknowledgement

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