

Corrosion of 12Cr18Ni10Ti steel in Ce-, Nd- and U-containing molten LiCl-KCl eutectic

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Abstract. The present work is aimed at the study of the 12Cr18Ni10Ti steel corrosion in the molten LiCl-KCl eutectic, which contains different proportions of CeCl₃, NdCl₃ and UCl₃.

The CeCl₃ and NdCl₃ concentrations varied within the interval of 0.2-5.0 mol.%, and the UCl₃ concentration varied within the interval of 1.0-2.5 mol.%. The temperature of the experiments was 500 °C. The composition of the melts under study was close to the composition of real electrolytes, which appear at the nitride SNF processing.

The basic method of study is the gravimetric method with the exposure time from 24 to 100 hours. Atomic-adsorption, micro X-ray spectral and X-ray structural methods were used for samples analysis.

The first component of selective dissolution in the steel under study was Fe. Chromium and manganese dissolution degrees were the smallest. The presence of UCl₃ in the melt was found to have the largest impact on corrosion. The corrosion rate is rather small. For example, in the melt containing 1 mol.% of NdCl₃ the corrosion is equal to 1.93 g/(m²·h), and in the (LiCl-KCl)_{eut.} + 1%CeCl₃+1%NdCl₃+ 1%UCl₃ melt it is 2.61 g/(m²·h).

The corrosion mechanism was found to be electrochemical.

Key Words: corrosion, cerium, neodymium, uranium.

1. Introduction

For a number of years alkali halide melts have been widely used in high-temperature metallurgical technologies and electrochemical devices. However, violent interaction of lithium, sodium, potassium molten chlorides and fluorides with metallic materials causes not only high efficiency of this process, but also for materials destruction. Therefore, corrosion of steels and alloys (total and local) in such molten salts is a serious problem to be solved.

It is commonly agreed that there are some ways to decrease the rate of corrosion. One of them is the injection of chromium, molybdenum, tungsten into steel; it diminishes corrosion losses in low-temperature electrolytes. At the same time, the corrosive behavior of alloyed steel has proved rather ambiguous [1-4]. It is necessary to focus on the Cr, Ni and Fe activities in the alkali chloride melt under pure argon atmosphere at 500-600 °C to achieve optimal corrosion characteristics.

The present paper makes use of the gravimetric, physicochemical and open circuit potential methods to target the weight and electrochemical characteristics of steel in the molten LiCl-KCl eutectic, which contains different proportions of CeCl₃, NdCl₃ and UCl₃. The emphasis is placed both on the interaction of a melt with metals and on quantitative corrosion characteristics. The experimental data were obtained observing the interaction of the alkali chlorides melt with metal. The experiments proved that the corrosion rate increased as the temperature rose, which is indicative of the temperature playing a significant role in the process. The greater was the concentration of added lanthanides/actinides, the greater was the corrosion rate.

2. Experiment

The present study involved steel samples under the interaction with a chlorides mixture.

The metal samples were carefully polished by a corundum paper and thoroughly washed with the ethanol-propanol mixture. The temperature of the experiment was varied from 500 to 600 °C. The samples were exposed to the alkali chlorides melt during 2-150 h. The gravimetical measurements were additionally performed, the open circuit potentials were determined. In order to evaluate the transfer of the metals into the melt, atomic-absorption analysis (Perkin-Elmer) of the resultant melts was performed when the melts were cooled to room temperature and grounded in a mortar with a pestle. Microstructural morphologies of the corrosion products were observed using secondary electron imaging (SEI) modification in a SEM (JEOL).

TABLE I: COMPOSITION OF 12Cr18Ni10Ti STEEL BY CHEMICAL ANALYSIS

Elements	Concentr. wt.%	Elements	Concentr. wt.%	Elements	Concentr. wt.%	Elements	Concentr. wt.%
Ag	<0.001	Eu	<0.0005	Na	<0.03	Sm	<0.008
Al	0.021	Fe	64.593	Nb	<0.004	Sn	<0.01
As	<0.03	Ga	<0.05	Nd	<0.005	Sr	<0.0002
Au	<0.005	Gd	<0.02	Ni	9.9692	Ta	<0.007
B	0.028	Hf	<0.004	P	<0.2	Tb	<0.01
Ba	<0.0008	Hg	<0.03	Pb	<0.03	Te	<0.02
Be	<0.0001	Ho	<0.0008	Pd	<0.008	Th	<0.003
Bi	<0.06	I	<0.4	Pr	<0.003	Ti	0.4360
C	-	In	<0.02	Pt	<0.06	Tl	<0.07
Ca	<0.007	Ir	<0.02	Re	<0.009	Tm	<0.0009
Cd	<0.002	K	<0.1	Rh	<0.005	U	<0.02
Ce	<0.02	La	<0.0009	Ru	<0.02	V	0.012
Co	0.044	Li	<0.002	S	<0.3	W	<0.03
Cr	19.7366	Lu	<0.0005	Sb	<0.06	Y	<0.0002
Cu	0.151	Mg	<0.01	Sc	<0.0002	Yb	<0.0001
Dy	<0.0008	Mn	1.3901	Se	<0.07	Zn	0.051
Er	0.5346	Mo	0.1292	Si	2.391	Zr	0.0020

A weighed portion of the pre-prepared salt (purified mixture of lithium chloride, potassium chloride and anhydrous chloride of the rare earth metal) was placed in aluminum oxide melting pot. A steel sample was put there on platinum current leads and was fixed in a roof of the cell. The prepared cell was connected to the air extraction system, which was turned on during 10 minutes, to prevent any leakage. The cell was then placed into a furnace, the temperature was measured using a chromel-alumel thermocouple, placed into a bag made

of aluminum oxide. As the desired temperature was reached the cell was filled with argon, purified from traces of moisture and oxygen. Samples were exposed from 1 hour to 24 hours in experiments with cerium- and neodymium-containing compositions. The duration of the experiment with the uranium- containing melt ranged from 72 to 150 hours to obtain more information about the corrosion process at this temperature. The corrosion potentials of the samples were measured relatively to the silver-chloride reference electrode using a potentiostat BioLogik SP-50 (France). The silver-chloride reference electrode was made of a quartz tube with a hole in the structural bottom, which was tightly clogged with asbestos and contained silver chloride and 1 mm-thick silver wire. The reference electrode, counter electrode, "chromel-alumel" thermocouple were placed into the aluminum oxide cover and the working electrode of the cold cell area was immersed into the melt. After each measurement the exposure was checked to stabilize of the potential. The experiments were carried out with the working electrode in the melt during 4 hours to assess the structural and chemical changes at the surface of steel during the corrosion of the melt.

To determine the corrosion potential of the examined steels the samples were measured relatively to the silver-chloride reference electrode during 4 h in the LiCl-KCl melt containing rare earth metal ions at 500 °C. Corrosion potentials are practically independent of the concentration of the additives. In the currentless mode microcracks appeared actively during dissolution processes, which limited the corrosion products diffusion in the liquid phase.

After the test the sample was removed from the melt and washed in different solutions (ethanol, ethanol-water, 0.1M nitric acid). The surface of the samples was investigated using the scanning electron microscope GEOL SM-5900 LV.

TABLE II: CORROSION OF 12Cr18Ni10Ti STEEL IN THE MELT LiCl-KCl-nCeCl₃

T, K	C, mol. %	t, h	ΔP, mg/sample	Corrosion rate, g·m ² /h	φ _K , V
723	1.0	4	5.38	3.36	-0.283
773	1.0	2	5.064	6.33	
773	0.2	4	8.71	5.44	-0.243
773	0.5	4	10.70	6.69	-0.245
773	1.0	4	26.70	16.69	-0.251
773	2.0	4	34.50	21.56	-0.259
773	5.0	4	50.03	31.27	-0.267
773	1.0	8	23.40	7.31	–
773	1.0	12	32.17	6.70	–
773	1.0	24	46.506	4.84	–
823	1.0	4	53.18	33.23	-0.243

The steel corrosion in cerium-containing melts regularly increased as the temperature and concentration of cerium in the melt increased. At 500 °C the corrosion rate began to decrease after ten hours of exposure in the melt.

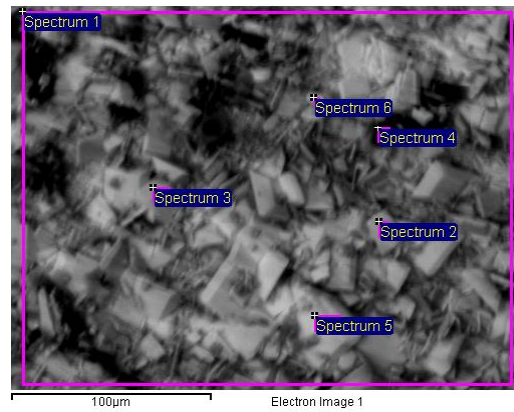


Fig. 1. Photomicrograph of the electrode surface of steel soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of cerium trichloride at 500 °C.

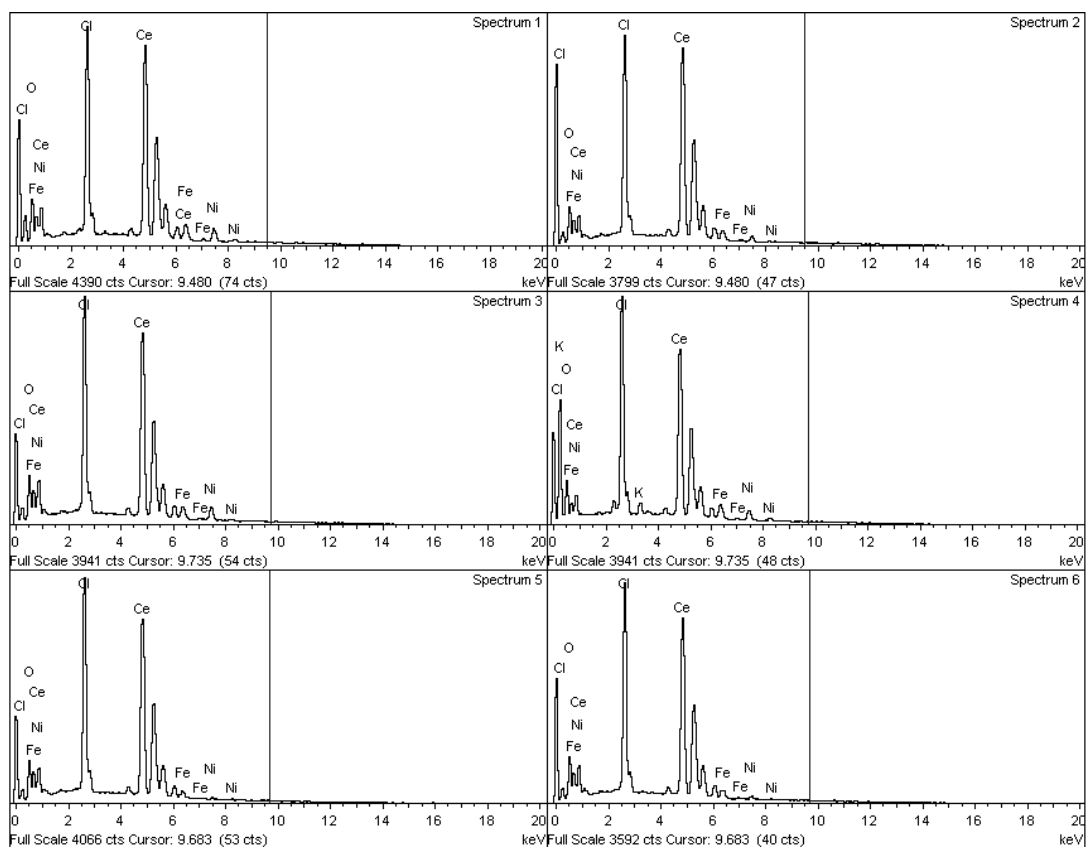


Fig. 2. Distribution of elements in the local areas of the surface of steel aged during 4 hours in the mixture of lithium and potassium chlorides containing 1 mol.% of cerium trichloride at 500 °C.

The surfaces of the steel electrode were different. The xenomorphic crystalline formations are combined with dark areas. In this case the spectral distribution of individual elements was approximately in the same place. Chromium was not detected on the surface.

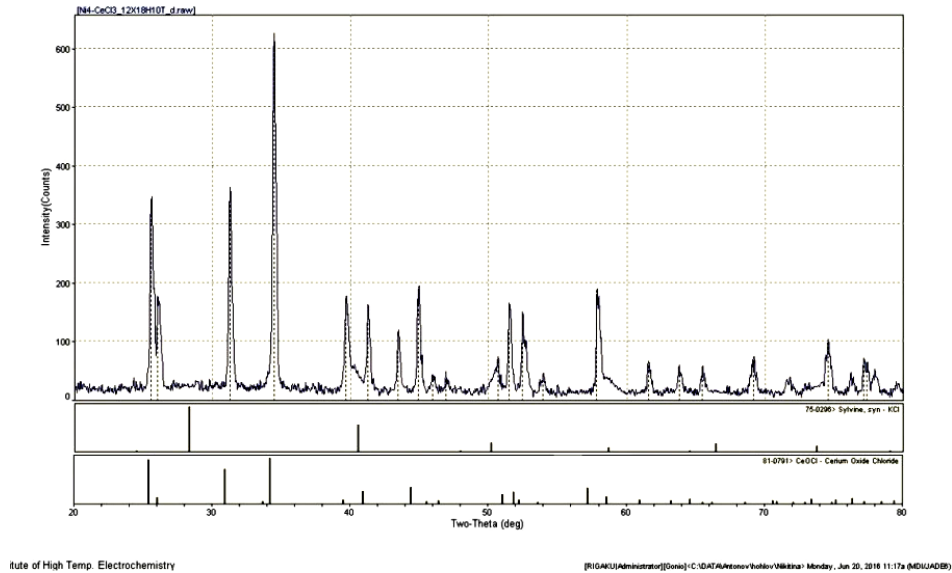


Fig. 3. XRD pattern of the steel electrode soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of cerium trichloride at 500 °C.

TABLE III: CORROSION OF 12Cr18Ni10Ti STEEL IN THE LiCl-KCl-nNdCl₃ MELT

T, K	C, mol, %	t, h	ΔP , mg/sample	Corrosion rate, g·m ² /h	ϕ_k , V
723	1.0	4	2.06	1.29	-0.238
773	1.0	2	6.09	7.61	—
773	0.2	4	6.35	3.97	-0.224
773	0.5	4	6.89	4.306	-0.239
773	1.0	4	7.51	4.69	-0.236
773	2.0	4	8.82	5.51	-0.241
773	5.0	4	14.07	8.79	-0.254
773	1.0	8	7.74	2.41	—
773	1.0	12	12.23	2.55	—
773	1.0	24	18.56	1.933	—
823	1.0	4	12.31	7.69	-0.217

Corrosion of steel in neodymium-containing melts regularly increased as the temperature and concentration of neodymium increased in the melt. At 500 °C the corrosion rate began to decrease after ten hours of exposure in the melt. Corrosion loss and corrosion rate were approximately twice lower as compared to the cerium-containing melt.

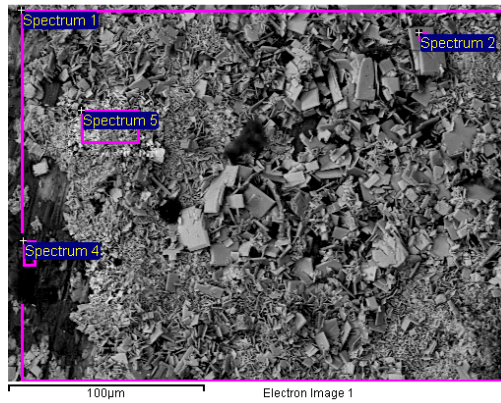


Fig. 4. Photomicrograph of the electrode surface of steel soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of neodymium trichloride at 500 °C.

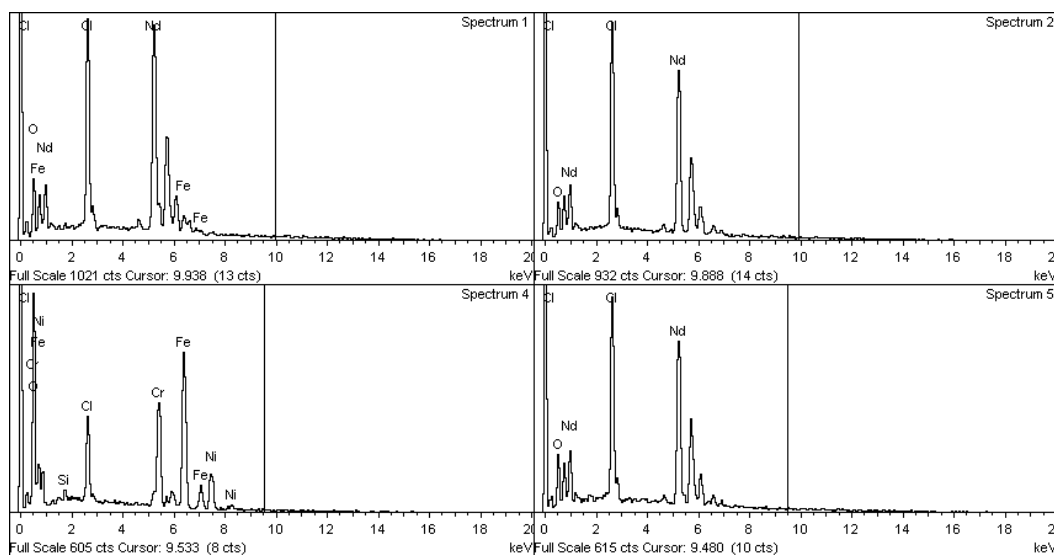


Fig. 5. Distribution of elements in the local areas of the surface of steel aged for 4 hours in the mixture of lithium and potassium chlorides containing 1 mol.% of neodymium trichloride at 500 °C.

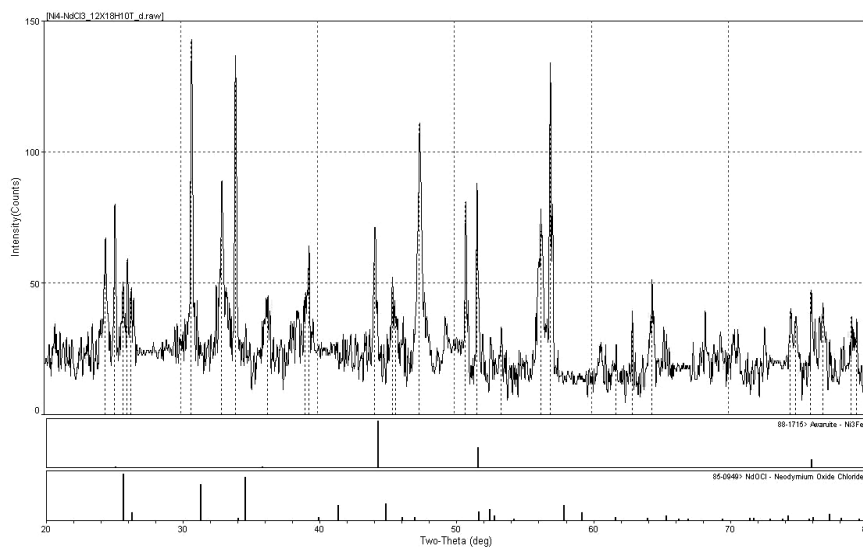


Fig. 6. XRD pattern of the steel electrode soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of neodymium trichloride at 500 °C.

TABLE IV: CORROSION OF 12Cr18Ni10Ti STEEL IN THE LiCl-KCl-0.5CeCl₃-0.5NdCl₃- nUCl₃ MELT AT 500°C.

C, mol, %	t, h	ΔP, mg/sample	Corrosion rate, g·m ² /h	C, mol, %	t, h	ΔP, mg/sample	Corrosion rate, g·m ² /h
1.0	1	0.0212	5.30	1.5	35	0.1287	0.919
1.5	1	0.041	10.25	1.0	42	0.1063	0.632
1.0	7	0.0428	1.53	1.5	42	0.1427	0.849
1.5	7	0.059	2.11	1.0	49	0.1154	0.589
1.0	14	0.06338	1.13	1.5	49	0.1652	0.843
1.5	14	0.0709	1.27	1.0	56	0.1327	0.592
1.0	21	0.1454	1.73	1.5	56	0.1691	0.755
1.5	21	0.1002	1.19	1.0	63	0.1449	0.575
1.0	28	0.0878	0.78	1.5	63	0.1749	0.694
1.5	28	0.1113	0.993	1.0	70	0.1459	0.521
1.0	35	0.1045	0.746	1.5	70	0.1885	0.673

Corrosion of steel of common uranium salt compositions increased with the concentration of uranium in the melt.

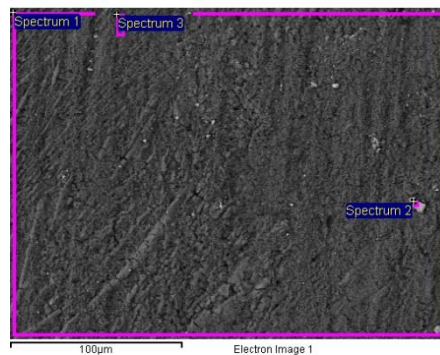


Fig. 7. Photomicrograph of the electrode surface of steel soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C.(washed with 0.1m nitric acid)

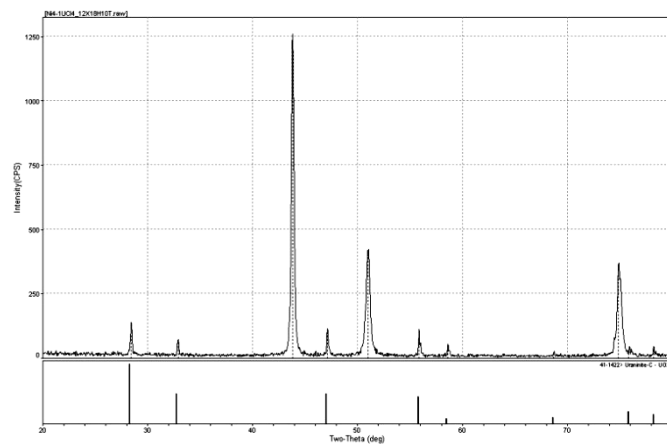


Fig. 8. XRD pattern of the steel electrode soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C (washed with 0.1m nitric acid).

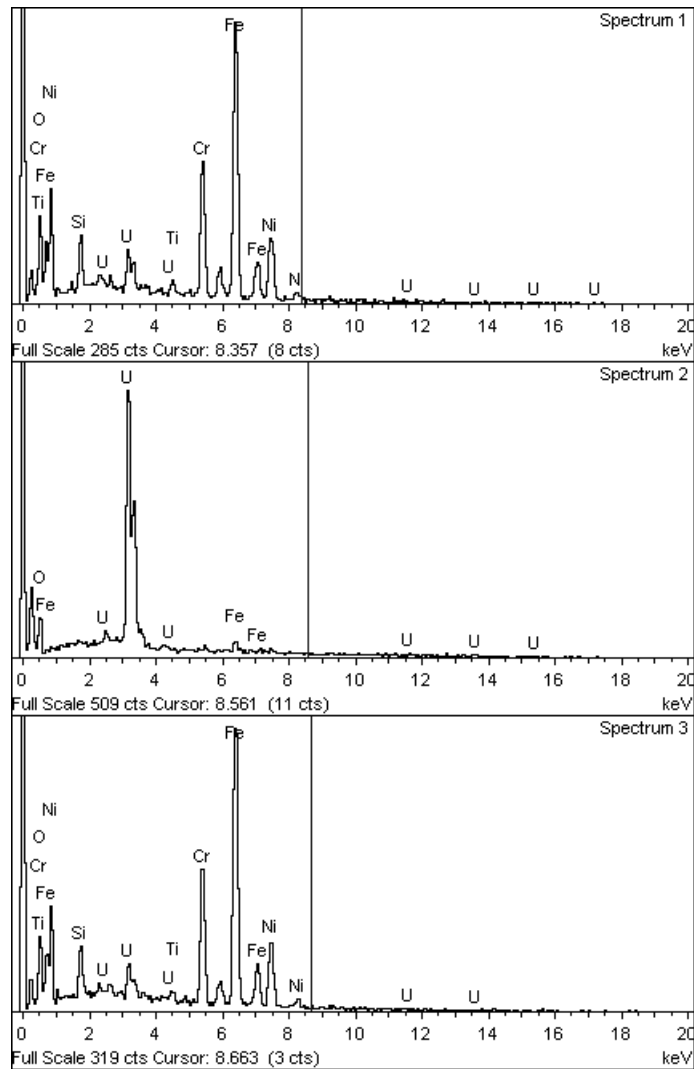


Fig. 9. Distribution of elements in the local areas of the surface of aged steel for 4 hours in the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C. (washed with 0.1M nitric acid)

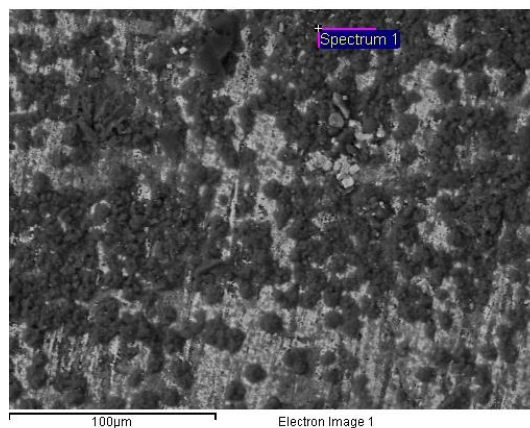


Fig. 10. Photomicrograph of the electrode surface of the steel soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C

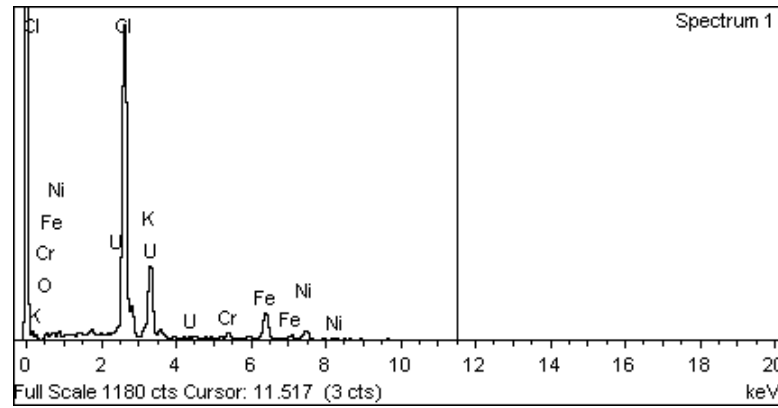


Fig. 11. Distribution of elements in the local areas of the surface of aged steel for 4 hours in the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C.

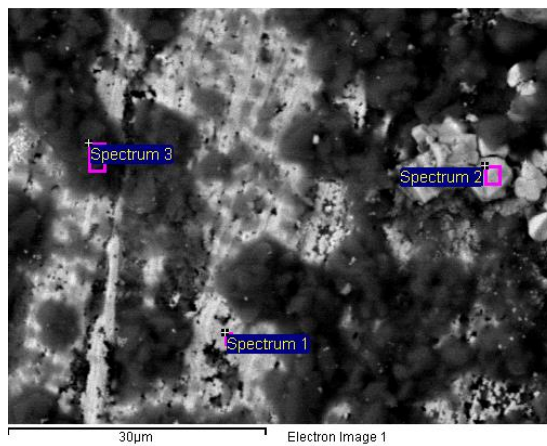


Fig. 12. Photomicrograph of the electrode surface of the steel soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C

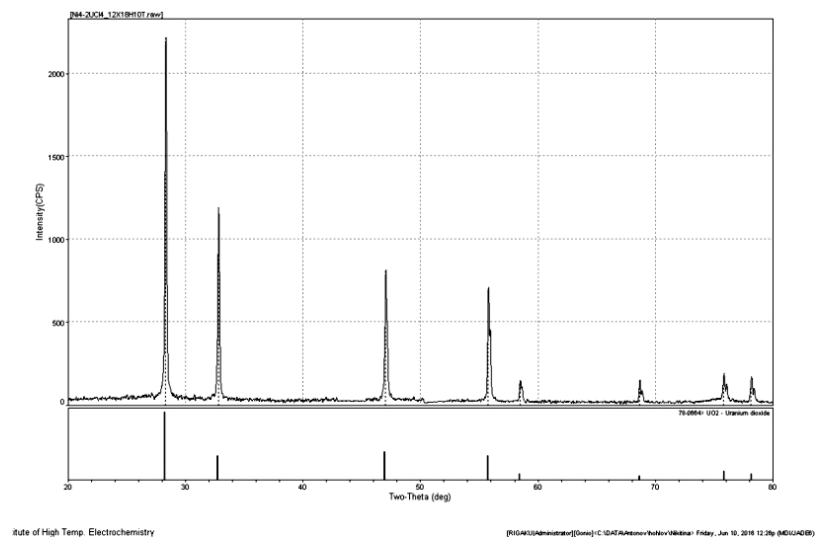


Fig. 13. XRD pattern of the steel electrode soaked for 4 hours into the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C.

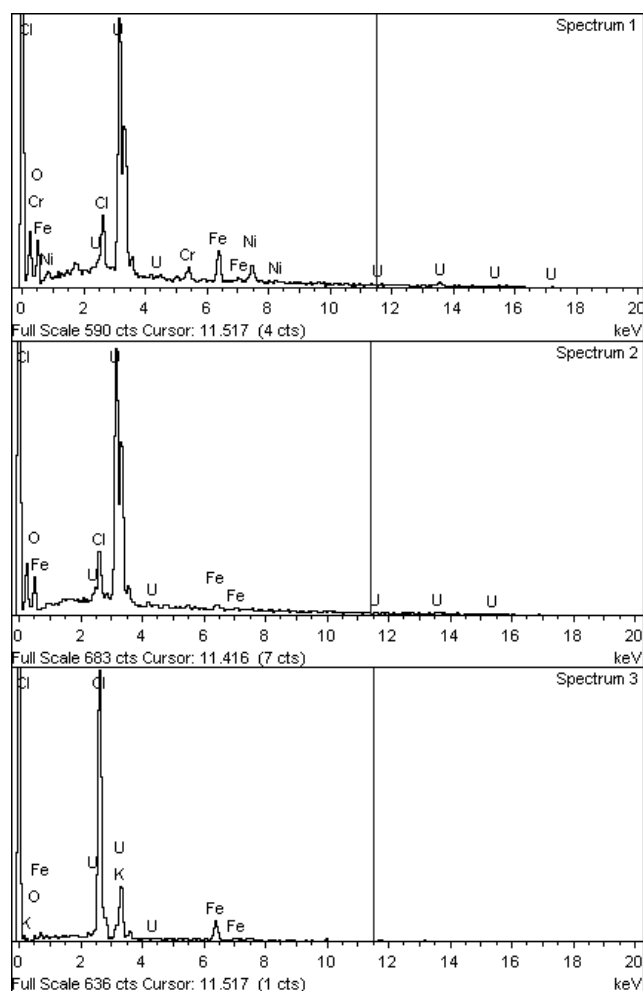


Fig. 14. Distribution of elements in the local areas of the surface of steel aged for 4 hours in the mixture of lithium and potassium chlorides containing 1 mol.% of uranium trichloride at 500 °C.

Conclusion

The ions of cerium and neodymium influence on the mechanism of the corrosion of metallic materials differently. Neodymium ions form intermetallic compounds with the materials under study. Cerium ions serve as mediators (carriers of electrons) from the oxidizing components of the alloys. The more attention is added to the lanthanides / actinides, the higher the corrosion rate.

Additions of CeCl_3 and NdCl_3 leads to a decrease of output of chromium from the steel into the melt. The presence of UCl_3 in the melt was found to have the largest impact on corrosion. For example, in the melt containing 1 mol.% of NdCl_3 the corrosion is equal to $1.93 \text{ g}/(\text{m}^2 \cdot \text{h})$, and in the $(\text{LiCl-KCl})_{\text{eut}} + 1\% \text{CeCl}_3 + 1\% \text{NdCl}_3 + 1\% \text{UCl}_3$ melt it is $2.61 \text{ g}/(\text{m}^2 \cdot \text{h})$.

It is necessary to conduct long-term corrosion experiments - more than 100h.

It is necessary that all corrosion experiments, which are directed to the choice of material for particular equipment, are carried out under conditions analogous to operating conditions.

In addition, corrosion-resistant materials in operating conditions and deformation mechanisms, internal stresses of the metal.

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