

Corrosion Behavior of Some Steels in Ionic Liquids Based on Choline Chloride

ELENA IONELA NEACSU¹, VIRGIL CONSTANTIN^{1*}, CRISTINA DONATH¹, KAZIMIR YANUSHKEVICH², ALIONA ZHIVULKA², ANATHOLY GALYAS², OLGA DEMIDENKO², ANA MARIA POPESCU^{1*}

¹ Ilie Murgulescu Institute of Physical Chemistry of the Romanian Academy, Laboratory of Electrochemistry and Corrosion, 202 Splaiul Independentei, 062043, Bucharest, Romania

² Scientific Practical Materials Research Centre of NAS Belarus, Laboratory of Physics of Magnetic Materials 19 P. Brovki Str., Minsk, 220072, BELARUS

The corrosion behaviour of special steels (OL44, OL52, SS1.4571) exposed to choline chloride (ChCl) based ionic liquids, has been investigated by polarization curves method at 80°C. Micrographic images before and after corrosion were obtained. The corresponding corrosion parameters in ChCl-Oxalic acid and ChCl-Malonic acid were calculated. The crystal structure was studied before and after the corrosion process by using X-ray diffraction method. The specific magnetization was investigated by ponderomotive method.

Keywords: Corrosion of steels, Ionic liquids, Polarization curves, Magnetization, XRD analyses, Micrography

In the conditions of the aggressive environment impact, for example of humid climate and high chloride content in the atmosphere, metallic materials that do not possess satisfactory corrosion resistance, quickly lose their external appearance, and then completely destroy. The result of the low-quality materials use is the necessity of frequent repairs of existing constructions or replacement of disabled parts. Currently, there are a number of industries in which the use of corrosion-resistant and heat-resistant steels and alloys on the basis of iron and nickel has no alternative. Alloyed steels are resistant to general corrosion, but they are inclined to various types of local one, such as pitting and intercrystalline corrosion. Therefore, modification of already available grades of stainless steels is necessary in order to increase the resistance to local corrosion types. Nickel-based alloys have not only higher implement of alloying elements in solid solution than other stainless steels and iron-based alloys, but preserve a good metallurgical stability. These factors have caused the development of production of nickel-based alloys with multiple alloying additions to provide a wide variety of applications in aggressive environments.

The results of investigation studies indicate the prospects of this direction [1-7], but a number of questions cannot be solved without a complex study of the crystal structure, magnetic properties and corrosion resistance of stainless steels for special purposes.

The term *ionic liquid* is most often used for salts with a melting temperature below 373 K [8]. Ionic liquids (ILs) are a new class of electrolytes with special properties and with many applications in various fields: media for electrodeposition of metals [9-11], fluids for thermal storage and exchange in solar concentrating power plants [12], use as solvents for chemical synthesis [13,14], supercapacitors [15,16], electrolyte for electrochemical devices such as battery [17]. ILs are ideal solvents for *green* chemistry, metals electrodeposition and recovery from electric and electronic waste [18-20]. The ILs involvement will minimize the environmental pollution, and synchronizes with the international technological development. However, reports on the corrosivity of ILs against engineering alloys are few in the technical literature. In all these applications ILs come into contact with different

materials and therefore must know the chemical activity and their interaction effects. Over the years the corrosion of metallic materials is a fairly studied in ILs [21-23], Uerdingen *et al.* [24] investigated the corrosion behavior of carbon steel, austenitic stainless steel, nickel based alloy C22 copper, brass, and aluminum in seven ILs with different chemical structure under flow conditions at temperature up to 363 K. Reddy *et al.* [25] investigated the thermal stability and corrosivity of various ILs against 316 stainless steel and 1018 carbon steel by electrochemical techniques at room temperature. Perissi *et al.* [26] studied the corrosion behavior of several metals and alloys (copper, nickel, AISI 1018 steel, brass, Inconel 600) exposed to a typical ILs, namely the 1-butyl-3-methyl-imidazolium bis-(tri-fluoromethanesulfonyl) imide ([C₄mim][Tf₂N]) by electrochemical and weight-loss methods. However, the question of interaction of ILs with the many metallic materials remains open.

In this study, we report the results of influence of corrosion process on different steels (OL44, OL52, SS1.4571) after long-term interaction with some ChCl based ILs.

Experimental part

Materials

In this study, we investigated the following steels: OL44, OL52 and SS1.4571. The steels as OL44 and OL52 (STAS 500-68 and SREN 10025-2) are carbon steels for general use and SS1.4571 an austenitic stainless steel with titanium stabilization (EN 10088-1). The chemical composition of these steels is: OL44 (0.17% C, 0.65% Mn, 0.04% S, 0.04% P, 99.1% Fe), OL52 (0.2% C, 0.5% Si, 1.6% Mn, 0.05% P, 0.05% S, 97.6% Fe) and SS1.4571 (16.5-18.5% Cr, 0-0.08% C, 2-2.5% Mo, 0.05% Si, 0-0.05% P, 10.5-13.5% Ni, 0.4-0.7% Ti, 0-0.03% S, 0-2% Mn, Fe balance).

Samples preparation

Samples were prepared for corrosion study according to ASTM-G31 standard practice. The sample preparation was done by polishing with abrasive paper of increased granulation, degreasing with acetone and rinsing in double distilled water, then with 50% sulfuric acid solution at a temperature of 323 K for 1-2 min, followed by washing

* email: virgilconstantin@yahoo.com, popescuamj@yahoo.com

again with double distilled water and finally directly immersed in the test solutions.

Potentiodynamic polarization measurements

Corrosion behavior of the samples (steels) was evaluated through potentiodynamic polarization tests in a standard three-electrode cell. The polarization tests were conducted in two systems of ILs ChCl-Oxalic acid (1:0.5 molar ratio) and ChCl-Malonic acid (1:2 molar ratio) at 353 K, using a Princeton Applied Research model PARSTAT 2273 potentiostat/galvanostat with a *Power Corr* software [27].

Both ILs used were prepared in our laboratory by mixing the choline chloride (Aldrich 98%, dried for 24-120 h at 353 K) with oxalic acid (Aldrich 99%) or malonic acid (Fluka 98%), heating in a baker the two components in 1:0.5 or 1:2 molar ratio at above 333 K for 30 min, until a homogeneous and colorless liquid was formed. We made no further purification on the substances used taking in account that water traces in hydrophobic ILs surprisingly proved to exhibit unusual corrosion inhibiting behavior by protecting copper and nickel under aerobic conditions [28]. The physico-chemical properties (density, viscosity and electrical conductivity) of the used ionic liquids were determined in previous published papers [29, 30].

A thermostatic glass cell was used for electrochemical corrosion tests. A 1 cm² surface area of the samples was used as the working electrode (WE); the counter electrode was a Pt plate (Radiometer) and as reference electrode Ag/AgCl (0.5M AgCl Radiometer) was used. The cell assembly was located at a Faraday cage to prevent electrical interferences. The samples were immersed in the electrolyte before the tests start and were allowed to reach equilibrium, which usually took around 20 min. Linear polarization curves were obtained by sweeping the electrode potential in the range of ± 20 mV versus OCP starting from cathodic region, after a constant value of OCP was achieved. Tafel polarization experiments were performed with a constant scan rate of 0.166 mV $\times$ s⁻¹, while the potential was shifted within ± 250 mV versus E_{OCP} [31]. To achieve reproducible results, each determination was made three times.

Structure and micrographic characterization

The crystal structure of stainless steels was characterized by X-ray diffraction (XRD) using X-ray diffractometer (model DRON-2) with Cu-K α radiation ($\lambda=0.154$ nm) working at 2 kW at room temperature. X-ray patterns were obtained by the automatic recording of reflection intensities using a 0.03° scanning step and 2-3 s time per step. The obtained XRD data were analyzed with the Rietveld-type refinement FullProf program. The average

size of crystallites (d) was calculated using the Debye-Scherrer equation [32, 33]: $B(2\theta)=k \times \lambda/d \times \cos\theta$, where k is a constant taken as 0.94, λ is the wavelength of the X-ray radiation (Cu-K α =0.15406 nm), θ is the diffraction angle and B is the line width at half maximum height (FWHM) [34,35]. Dislocation density, δ , is determined by equation: $\delta=1/d^2$.

The micrographic images with x100-x800 magnifications were obtained with a metallurgical microscope (New York Microscope Comp.) with camera acquisition.

Magnetic characterization

The temperature dependence of the specific magnetization was studied in the temperature range of 77-1100K by the ponderomotive method in the field of 0.86 Tesla [36].

Results and discussions

Electrochemical test results

The open circuit potential (OCP) of OL44, OL52 and SS1.4571 steels is expected to be dependent on the characteristics of resulted oxide, such as oxide thickness, composition, conductivity, structure, etc. After 7-10 min time of immersion at 80°C in the ILs corrosive environment the studied steels present OCP potential values varying from -0.029V for SS1.4571 sample in ChCl-Oxalic acid to -0.250 V for OL52 sample in ChCl-Malonic acid. The OCP values are listed in table 1.

Figure 1 show the Tafel plots obtained from the polarization curves of the steel samples in the two ILs used. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) derived from the polarization curves using Tafel extrapolation are summarized in table 1. Corrosion rate (CR) expressed as penetration index in millimeter per year was calculated from the product: $87.6 \times i_{corr}/(\rho \cdot z \cdot F)$, where ρ is the steel density (8 g $\times$ cm⁻³), $z=2$ number of transferred electrons and F is the Faraday constant.

The plots and the corrosion data indicate that all steels studied have good corrosion protective properties with corrosion rates ranging from 0.1-27.3 μ m/yr. The SS1.4751 sample has the lowest corrosion rate in both ChCl-Oxalic acid and ChCl-Malonic acid. From the shape of Tafel curves we can see existence of the passivity and transpassivity domains for all types of steels. Steels OL44, OL52 show more intense corrosion, which highlights the fact that the passive films deposited on these samples are very thin.

The stainless steel SS1.4571 has a good corrosion resistance so it can be said that the passive layer formed on its surface is more stable and resistant. Regarding the aggressiveness of these ILs we can mention that the ChCl-

Corrosive media	Sample	E_{OCP} (V)	E_{corr} (V)	i_{corr} (μ A $\cdot$ cm ⁻²)	CR (μ m $\cdot$ year ⁻¹)
ChCl-Oxalic acid (1:0.5 molar ratio)	OL44	-0.195	-0.201	1766.00	27.30
	OL52	-0.202	-0.188	903.41	11.99
	SS1.4571	-0.029	-0.33	5.13	0.10
ChCl-Malonic acid (1:2 molar ratio)	OL44	-0.246	-0.283	1505.00	17.66
	OL52	-0.250	-0.268	778.40	10.34
	SS1.4571	-0.093	-0.110	32.48	0.64

E_{OCP} =rest potential; E_{corr} =corrosion potential; i_{corr} =corrosion current density; CR=corrosion rate

Table 1
CORROSION PARAMETERS
FOR THE STUDIED STEELS IN
IONIC LIQUIDS AT 80° C

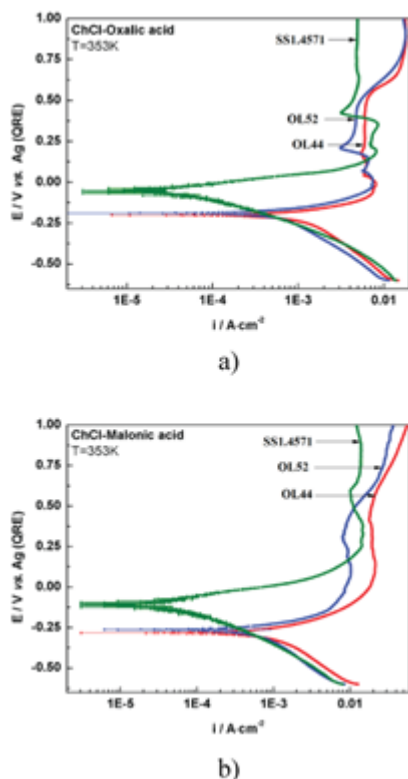


Fig. 1. Potentiodynamic polarization curves of OL44, OL52 and SS1.4571 steels in ionic liquids at 80°C

Oxalic acid mixture is much more aggressive for OL44 and OL52, while for SS1.4571 the corrosivity of ChCl-Malonic acid is more evident.

Microscopic study

Microscopic images in figures 2 and 3 show that OL44 and OL52 steels have a compact and homogeneous surface before corrosion and after corrosion the surface of these samples shows some changes due to the corrosiveness of ILs.

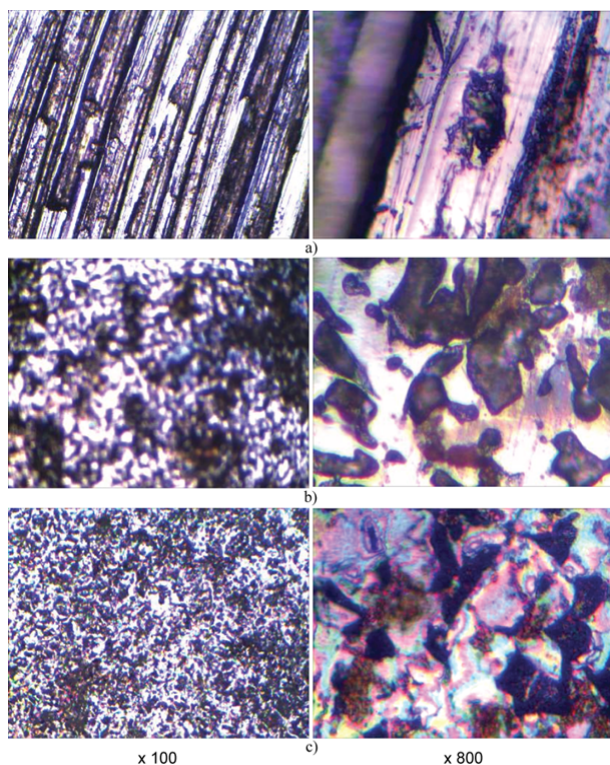


Fig. 2. Micrographic image of OL44 sample: a) initial stage; b) corroded in ChCl-Oxalic acid; c) corroded in ChCl-Malonic acid.

The microscopic images show also that for both samples OL44 and OL52 the corrosion in ChCl-Oxalic acid is stronger. For the images in figures 2c and 3c we believe that the identified colored phase originates from ILs itself due the fact that the samples were not well washed from the ILs. On the whole, microscopic data are in perfect correlation with electrochemical results.

For the SS1.4571 steel sample the microscopic images before corrosion (fig. 4a) present a surface that is not homogenous, even with formation of degradation products that can generate corrosion points. The SS1.4571 austenitic steel contains an addition of molybdenum and titanium that gives it improved in corrosion resistance. This is particularly apparent for pitting and crevice corrosion in chloride environments. The images of this sample after corrosion in ILs (fig. 4b, 4c) show that in the warm environment (80 °C) of choline chloride-carboxylic acids, the crevice corrosion is produced. However the corrosion is not very different in ChCl-Oxalic acid or ChCl-malonic acid, results which are in good agreement with electrochemical corrosion data.

XRD diffraction analysis for crystal structure

X-ray diffraction patterns of OL44 and OL52 stainless steel samples before and after corrosion action are shown in figures 5 and 6 respectively. The analysis showed that the two samples have the same crystal $Im\ 3m$ type structure with the presence of a significant proportion of the iron phase, that correlate with chemical composition of these steels. Reflexes of diffraction patterns were indexed according to ID 06-0696 of PCPDFWIN data base (V.2.00, 1998) ($a=0.2866\text{ nm}$). The unit cell parameter (a) is equal to 0.2868 nm for OL44 and OL52 steels. After corrosion action on X-ray diffraction patterns is not observed the appearance of new lines, this means that is not revealed the crystal structure changing. In case of stronger ChCl-Oxalic acid corrosion action the crystal cell parameter is equal to 0.2870 nm for OL44 steel and 0.2869 nm for OL52 steel.

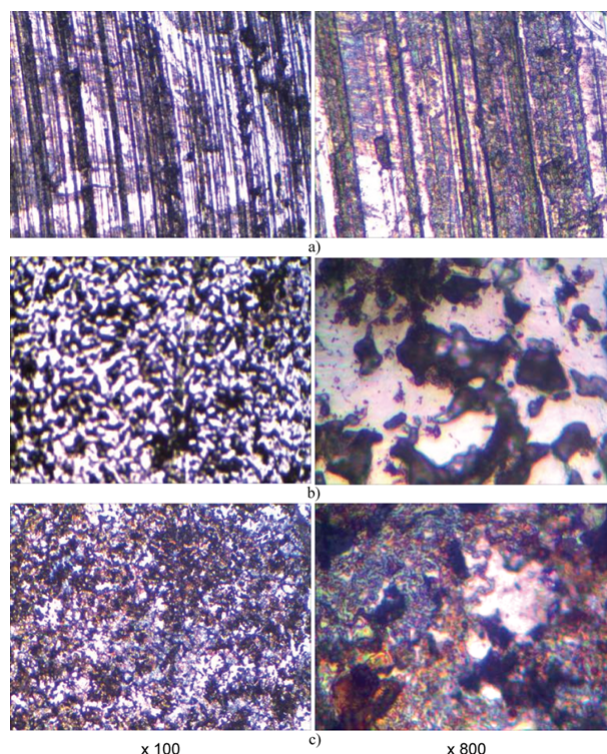


Fig. 3. Micrographic image of OL52 sample: a) initial stage; b) corroded in ChCl-Oxalic acid; c) corroded in ChCl-Malonic acid.

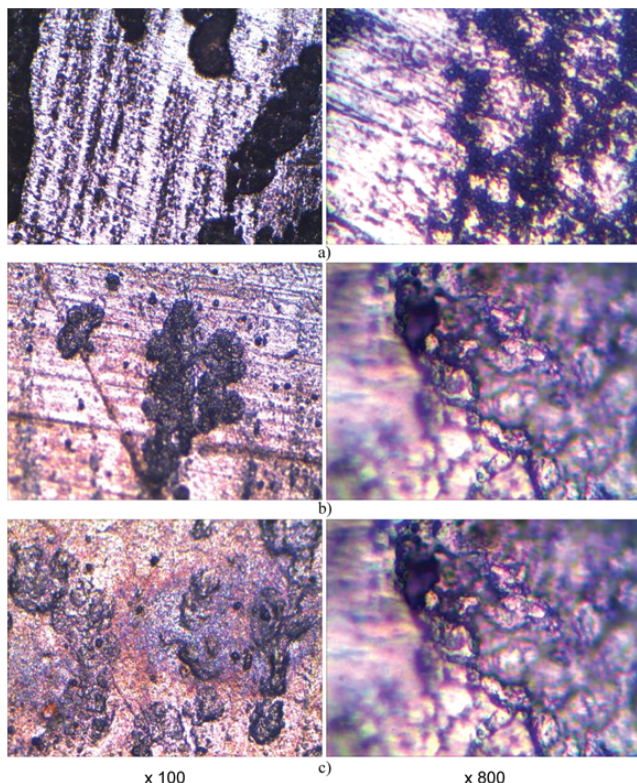


Fig.4 Micrographic image of SS1.4571 sample: a) initial stage; b) corroded in ChCl-Oxalic acid; c) corroded in ChCl-Malonic acid

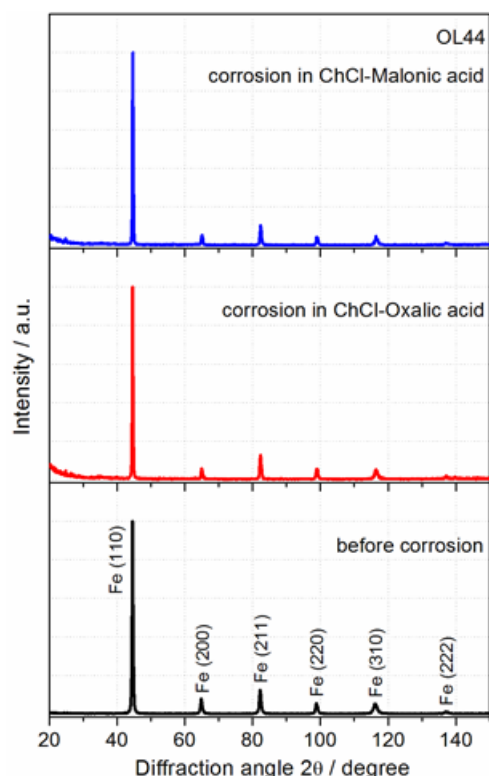


Fig. 5. XRD spectra of OL44 sample before and after corrosion at 80°C

X-ray diffraction pattern of SS1.4571 stainless steel sample is represented in figure 7. This sample also has a similar cubic unit cell, but a different space group (Fm3m). Reflexes were indexed on basis of FeNiCr phase according to ID 33-0945 ($a=0.3554$ nm). Unit cell parameter a is equal 0.3599 nm. In this case the presence of chromium and nickel in steel does not lead to the appearance of new lines accordingly to the crystal structure change. A redistribution of the intensities of the diffraction lines is observed. This may indicate the presence of a textured

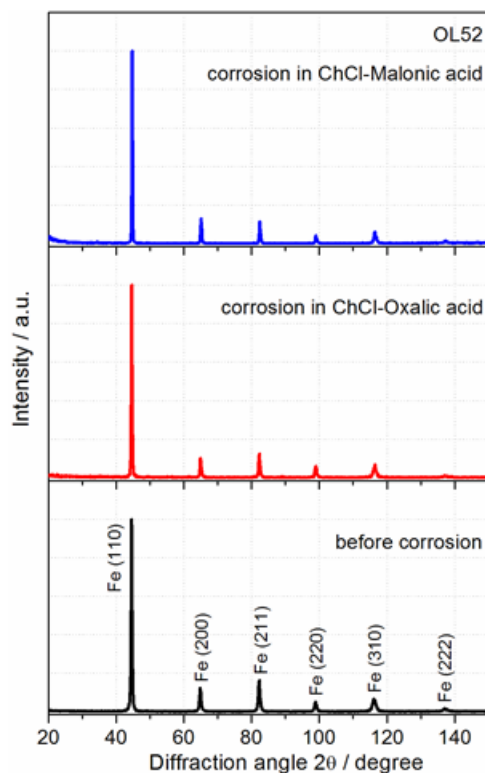


Fig. 6. XRD spectra of OL52 sample before and after corrosion at 80°C.

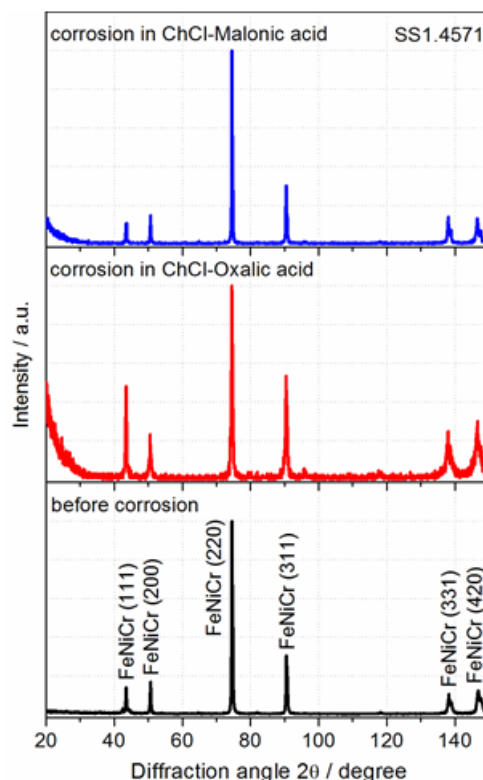


Fig. 7. XRD spectra of SS1.4571 sample before and after corrosion at 80°C

state due to deformation of crystal cell as a result of doping by nickel and chromium. As in case of OL44 and OL52, the corrosion action of ChCl-Malonic acid and ChCl-Oxalic acid does not has a significant influence on stainless steel samples crystal structure. For SS1.4571 stainless steel crystal the cell parameter a is equal 0.3600 nm after corrosion action of both ILs.

The crystal parameters of all investigated steels before and after corrosion action are presented in table 2. After the corrosion process one can see from figures 5-7 and table 2 that there are no significant changes in the XRD

Sample	Unit cell parameter a (nm)	Average size of crystallites d (nm)	Dislocations density, $\delta \cdot 10^{-3} \text{ (nm}^{-2}\text{)}$	σ_{77} ($\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$)	T_c (K)
OL44*	0.2868	15.60	41.11	208.50	975
OL44 (I)	0.2870	16.69	35.88	210.00	965
OL44 (II)	0.2871	17.18	3.85	210.50	985
OL52*	0.2868	15.02	44.3	200	980
OL52 (I)	0.2869	16.76	35.59	205	983
OL52 (II)	0.2868	17.61	32.24	203.50	990
SS1.4571*	0.3599	22.37	19.98	8.04	795
SS1.4571 (I)	0.3600	20.79	23.14	8.27	785
SS1.4571(II)	0.3600	23.34	18.35	8.10	805

*-before corrosion, (I)-corrosion in ChCl-Oxalic acid, (II)-corrosion in ChCl-Malonic acid

Table 2
CRYSTAL
PARAMETERS AND
MAGNETIC
PARAMETERS OF
STAINLESS STEELS

patterns, unit cell parameter, average size of crystallites or dislocations density, which means that the used ILs do not exceed an important corrosion process on these steels.

This XRD study confirmed that for steels OL44 and OL52 the main phase is iron, while for SS1.4571 is a Cr-Ni alloy. This fact explains the corrosion data, as iron is very susceptible to corrosion. Presence of nickel and chromium increases corrosion resistance of austenitic steels in acidic solutions that is proved by results of corrosion measurements.

Magnetic properties

Figure 8 presents the comparison of specific magnetization vs. temperature dependences for OL44, OL52 and SS1.4571 steels before and after corrosion action of ILs during heating at 827 C. The OL44 and OL52 steels have a similar character magnetic confirming the presence of free iron. At liquid nitrogen temperature the specific magnetization (σ) is $209 \text{ A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$ for OL44 and $200 \text{ A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$ for OL52. It should be noted that cooling and heating dependences $\sigma=f(T)$ of the two samples are identical. The Curie temperature, defined from dependences $\sigma^2=f(T)$, is 975 K for OL44 and 980 K for OL53.

For SS1.4571 stainless steel there is another character of the temperature dependence of the specific magnetization. At liquid nitrogen temperature the value of σ is $8.1 \text{ A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$, and the Curie temperature is 795 K. Heating of this sample up to 1000 K and subsequent measurements of samples with slow cooling led to decreasing of the specific magnetization to a value about $3.0 \text{ A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$ at room temperature.

The magnetic curves from figure 8 show that such influence of corrosivity of ChCl-Malonic acid and ChCl-Oxalic acid ILs has only surface influence and has not significant effect on specific magnetization values of these samples. The parameters of magnetization curves are presented also in table 2.

Correlating XRD, magnetic and corrosion data, one can say that the OL44 and OL52 steels exhibit higher corrosion rates in both ILs (the presence of Fe from XRD diagrams confirm this fact), while SS1.4571 stainless steel has a low corrosion rate due to the presence of FeNiCr combination which gave a good corrosion resistance.

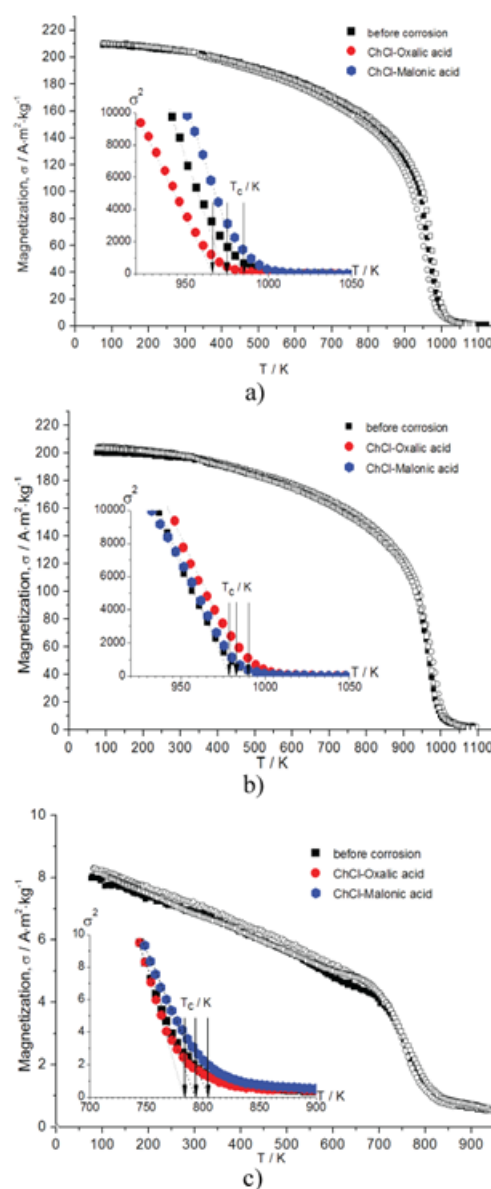


Fig. 8. The comparison of temperature dependence of specific magnetization for: a) OL44, b) OL52, c) SS1.4571 stainless steels before and after corrosion action of ionic liquids

Conclusions

The study of crystal structure and specific magnetization of OL44, OL52, SS1.4571 steels before and after corrosion action of ChCl-Malonic acid (1:2 molar ratio) and ChCl-Oxalic acid (1:0.5 molar ratio) ionic liquids was successfully carried out.

XRD data confirm that the main phase of OL44 and OL52 steels is iron and of SS1.4571 steel is Fe-Cr-Ni alloy.

All investigated OL44, OL52, SS1.4571 steels are ferromagnets with a phase transition temperatures of 975, 980 and 795K, respectively. The OL44 and OL52 steels are resistant heating up to 1100 K, while the heating of SS1.4571 steel reduces 2.3 times the specific magnetization at room temperature.

It is revealed that corrosion action of ChCl-Malonic acid and ChCl-Oxalic acid ILs not have a significant effect on the crystal structure and specific magnetic characteristics of studied steels.

Aknowledgement: The work was carried out within the program: Electrode processes, materials for electrochemical processes and corrosion of the Institute of Physical Chemistry and was supported by the Romanian Academy and the Academy of Sciences of the Republic of Belarus Foundation for Basic Research (project 2016-2017). Authors equally contributed to this work.

References

1. SOUZA, E.C., ROSSITTI, S.M., ROLLO, J.M.D.A., Mater. Charact., **61**, 2010, p. 240.
2. SHERIF, E.S.M., ALMAJID, A.A., BAIRAMOV, A.K., AL-ZHRANI, E., Int. J. Electrochem. Sci., **6**, 2011, p. 5430.
3. UNNIKRIISHNAN, R., IDURY, K.S.N.S., ISMAIL, T.P., BHADARIA, A., SHEKHAWAT, S.K., KHATIRKAR, R.K., SAPATE, S.G., Mater. Charact., **93**, 2014, p. 10.
4. SOTOMAYOR, M.E., de KLOE, R., LEVENFELD, B., VAREZ, A., J. Alloys Compd., **589**, 2014, p. 314.
5. WANG, S., DING, J., MING, H., ZHANG, Z., WANG, J., Mater. Charact., **100**, 2015, p. 50.
6. BIRCAKOVA, Z., KOLLAR, P., WEIDENFELLER, B., FUZER, J., FABEROVA, M., BURES, R., J. Alloys Compd., **645**, 2015, p. 283.
7. ABRIKOSOV, I.A., PONOMAREVA, A.V., STENETEG, P., BARANNIKOVA, S.A., ALLING, B., Curr. Opin. Solid State Mater. Sci., **20**, 2016, p. 85.
8. HOLBREY, J.D., SEDDON, K.R., Clean Prod. Proc., **1**, 1999, p. 223.
9. ENDRES, F., Chem. Phys. Chem., **3**, 2002, p.144.
10. LIN, Y.F., SUN, I.W., Electrochim. Acta, **44**, 1999, p. 2771.
11. TAKAHASHI, S., KOURA, N., KOHARA, S., SABOUNGI, M.L., CURTISS, L.A., Plasmas Ions, **2**, 1999, p. 91.
12. MOENS, L., BLAKE, D.M., RUDNICKI, D.L., HALE, M.J., J. Sol. Energy. Eng., **125**, 2003, p.112.

13. PERISSI, I., BARDI, U., CAPORALI, S., LAVACCHI, A., Corros. Sci., **48**, 2006, p. 2349.
14. WELTON, T., Chem. Rev., **99**, 1999, p. 2071.
15. UE, M., TAKEDA, M., TORIUMI, A., KOMINATO, A., HAGIWARA, R., ITO, Y., J. Electrochem. Soc., **150**, 2003, p. A499.
16. BALDUCCI, A., BARDI, U., CAPORALI, S., MASTRAGOSTINO, M., SOAVI, F., Electrochem. Commun., **6**, 2004, p. 566.
17. BRENNECKE, J.F., MAGIN, E.J., AIChE J., **47**, 2001, p. 2384.
18. KUSTOV, L.M., BELETSKAYA, I.P., Ross. Khim. Zh., **48**, 2004, p. 3.
19. POPESCU, A.M., DONATH, C., NEACSU, E.I., SOARE, V., CONSTANTIN, I., BURADA, M., DUMITRESCU, D.V., YANUSKEVICH, K., CONSTANTIN, V., Rev. Chim. (Bucharest), **68**, 2017, no. 9, p. 1963.
20. ANICAI, L., COSTOVICI, S., COJOCARU, A., MANEA, A., VISAN, T., Transactions of the IMF, **93**, 2015, p. 302.
21. PERISSI, I., CAPORALI, S., FOSATTI, A., LAVACCHI, A., Chapter 12 in Advanced in Chemistry Research, vol.6, ed. TAYLOR, J.C., Nova Science Publishers Inc., NY, 2011, p. 315.
22. KITIK, A.A., RUBLOVA, Y.D., PROTSSENKO, V.S., DANILOV, F.I., in: BARSUKOV, V.Z., Promising Materials and Processes in Applied Electrochemistry, 1st ISE Regional Student Meeting in Ukraine, Kyiv National University of Technologies and Design, Kyiv, 2017, p. 313.
23. PERISSI, I., BARDI, U., CAPORALI, S., FOSSATI, A., LAVACCHI, A., VIZZA, F., Russ. J. Electrochem., **48**, 2012, p. 434.
24. UERDINGEN, M., TREBER, C., BALSER, M., SCHMITT, G., WERNER, C., Green Chem., **7**, 2005, p. 321.
25. REDDY, R.G., ZHANG, Z., ARENAS, M.F., BLAKE, D.M., High.Temp. Mater. Processes, **22**, 2003, p. 87.
26. PERISSI, I., BARDI, U., CAPORALI, S., FOSSATI, A., LAVACCHI, A., Sol. Energy Mater. Sol. Cell, **92**, 2008, p. 510.
27. NEACSU, E.I., CONSTANTIN, V., SOARE, V., OSICEANU, P., POPA, M.V., POPESCU, A.M., Rev. Chim. (Bucharest), **64**, 2013, p. 994.
28. LEBEDEVA, O., JUNGUROVA, G., ZAKHAROV, A., KULTIN, D., CHERNIKOVA, E., KUSTOV, L., J. Phys. Chem. C, **116**, 2012, p. 22526.
29. POPESCU, A.M., CONSTANTIN, V., FLOREA, A., BARAN, A., Rev. Chim. (Bucharest), **62**, 2011, p. 5310.
30. POPESCU, A.M., DONATH, C., CONSTANTIN, V., Bulg. Chem. Commun., **46**, 2014, p. 452.
31. KRUGER, J., Chapter 12 in Uhlig's Corrosion Handbook, 3-rd ed, John Wiley & Sons Inc, Hoboken, NJ, USA, 2011.
32. SCHERRER, P., Nachr. Ges. Wiss. Gottingen, **26**, 1918, p. 98.
33. LANGFORD, J.I., WILSON, A.J.C., J. Appl. Cryst., **11**, 1978, p. 102.
34. BARAKAT, M.A., HAYES, G., ISMAT SHAH, S., J. Nanosci. Nanotechnol., **5**, 2005, p. 759.
35. OSKAM, G., NELLORE, A., LEE PENN, R., SEARSON, P.C., J. Phys. Chem., **B 107**, 2003, p. 1734.
36. POPESCU, A.M., YANUSKEVICH, K., DEMIDENKO, O., CALDERON MORENO, J.M., NEACSU, E.I., CONSTANTIN, V., Cent. Eur. J. Chem., **11**, 2013, p. 1137.

Manuscript received: 29.01.2018