Study of corrosion, crystal structure and magnetic properties on OL52 and OL52.4 steels in different seawaters

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The corrosion of OL 52 and OL52.4 steels exposed to seawaters (Black, Aegean and Mediterranean Sea) has been investigated by weight loss method and the corresponding corrosion rates in the three sea waters are calculated. Before and after immersion in the corrosive medium micrographic images are obtained. XRD and ponderomotive methods have been used to determine the influence of the seawaters corrosion processes on the structure and magnetization of the studied steels. Obtained results show that both OL52 and OL52.4 steels have good corrosion resistance in the studied seawaters.

In nuclear power, transportation, chemical processing, petroleum production, construction and metal processing equipment carbon steel is the most widely engineering materials used[1]. Many authors report also marine applications[2-7]. Corrosion of metals and alloy in the marine environment was studied at the beginning of the century. Scumacher[8] reported that the corrosion of steels, grey cast iron, alloy cast iron and austenitic cast iron is proportional the concentration of oxygen.

Structures like ships, platforms, pipelines, distribution systems and chemical processes from naval and petrochemical industries are affected by seawater corrosion. The content of chlorides and other salts in seawater is what corrodes most metals and alloys. Sea water is a complex chemical system affected by several factors, even if the main chemical parameters of seawater around the world are consistent. Sea water is a complex chemical system affected by several factors, even if the main chemical parameters of seawater around the world are consistent. It has been shown that in marine environments the corrosion of some steels starts very quickly and can reach high values[9]. The possible changes in the mechanism of degradation, considering the physico-chemical parameters of sea water were studied[10]. The international scientific community has great interest in the corrosion of metallic materials exposed to seawater, because there are a multitude of metal structures submerged in the sea. The variation of salinity, temperature, dissolved oxygen as well as the presence of other salts determines the geographical variation of the corrosivity of natural sea water. Chloride ion, Cl^-, has a strong influence on the corrosivity of structural steels. The Cl^- concentration of seawaters varies across different seas. Increasing the temperature and concentration of dissolved oxygen (DO) aggravates the rate of degradation of the structural material. Even if the *p*H of seawater is neutral to slightly alkaline, local acidity is developed due to corrosion products as well as crude petroleum products, which results in a lowering of *p*H.

The aim of this work is to investigate the corrosion of OL52 and OL52.4 steels in natural coast Black, Aegean and Mediterranean seawaters and to study of corrosion influence on the structure and magnetic properties of these steels.

Experimental Section

Materials and samples preparation

In this study we investigated two common carbon steels OL 52 and OL 52.4 (Romanian STAS: 500-68 respectively 500/2-80) of general purpose targets used in metallic constructions. The chemical composition

of these materials is: OL52: 0.2% C; 0.5% Si; 1.6% Mn; 0.05% P; 0.05% S; 97.60% Fe and OL52.4: 0.18 % C; 0.50% Si; 1.60% Mn; 0.04% P; 0.04% S; 0.25% Al; 97.39% Fe. Size samples of $50 \times 25 \times 5$ mm from both steels were used in the study after being prepared by mechanical grinding with SiC papers of P120, P180 and P220 grits successively to achieve a smooth surface. Using vernier calipers of high precision the length, breadth, and the thickness of carbon steel specimens were determined and the surface area calculated. The polished surface was cleaned thoroughly with distillated water and acetone to expose the microstructure, remove polishing residuals and possible grease. After being cleaned, the specimens were dried with a stream of warm air before further use.

The corrosion medium used was aerated natural seawater from Black Sea (Romanian coast), Aegean Sea (Turkey coast near Izmir) and Mediterranean Sea (Turkey coast near Anthalya).

Weight loss technique

The corrosion of OL52 and OL52.4 steels in seawaters was investigated at room temperature using weight loss (Δm) measurements. The test samples were suspended by means of glass hooks in 100 mL beakers containing 100 mL various test solutions, studied sea waters, and after each period of immersion, 30 days, the specimens were taken out, washed in running water, to get off the rust formed on the samples, and acetone, dried, and weighed using the electronic digital weighing balance Shimadzu D440400231 which has a sensitivity of 0.01 mg and a standard deviation of $\pm$0.02 mg. The samples were observed for 150 days and each sample was measured before and after each 30 days immersion time in order to obtain the Δm; measurements, procedures and precautions is described in[11-13].

Properties of sea water

In order to be sure of some properties of the seawaters in study, we measured pH, conductivity (κ) and total dissolved salts (TDS) by using a multicomponent Cyber Scan PCD6500-Eutech Instruments (USA) device.

Microstructural studies

X-ray diffraction (XRD) method and metallographic microscopy were used to determine the crystal structure and microstructures of mild steel surfaces before and after immersion in the seawaters.

Analysis of the studied samples by XRD was carried out on the modified and automated device "DRON-2" with CuK$_{\alpha}$-radiation in the $20° \leq 2\theta \leq 100°$ angle range at room temperature. XRD patterns are received with automatic recording of the reflexes intensities with a $0.03°$ scanning step and the exposure time of 2-3 s. For the purpose the crystal cell parameters determining were scanned the separate reflexes with a step of $0.01°$ with the exposure to 10 seconds. Phase composition of samples was identified using PCPDFWIN version 2.0. The processing of XRD patterns is carried out using the FullProf Suite program, which is based on the Rietveld method to clarify the parameters of the crystal cell. The lattice parameter determination error was $\pm$0.0001 nm. The average crystallite size is calculated by the Debye-Scherrer eq.[14,15].

$$B(2\theta) = k \cdot \lambda / d \cdot \cos\theta \qquad \qquad \ldots(1)$$

where: k is a constant taken as 0.94, λ is the wavelength of the X-ray radiation, CuK$_{\alpha}$ = 0.154242 nm, θ is the diffraction angle and B is the line width at half maximum height (FWHM), d is the full width at half maximum intensity of the peak, in Rad. Dislocation density is determined by the formula: $\delta = 1/d^2$. The microscopic images with different magnifications (from $100 \times$ to $800 \times$) were performed with an inverter microscope (NY Microscope Comp) with digital camera acquisition.

Magnetic characterization

The study of magnetic properties of samples is carried out using automatized setting, which works on base of a method of the ponderomotive force measuring. The method allows investigate temperature dependences of magnetization and magnetic susceptibility taking small amounts of substance. This makes it possible to achieve relatively fast the temperature equilibrium over the entire volume of the sample. It is obvious that the absence of the temperature gradient on the sample at the specific magnetization or susceptibility measurement moment provides the most accurate determination of their values. The specific magnetization temperature dependences were studied in the temperature range: 77-1100 K by ponderomotive method and details for this method were done before in[16].

Results and Discussion

Seawater properties

The amount of dissolved salts present in the water represents salinity; sodium and chloride ions are

predominant, and concentrations of calcium, magnesium and sulfate ions can be substantial [17]. Salinity level is described by the following water parameters: the conductivity (κ) and total dissolved solids (TDS).

Literature present that the salinity of the seawaters from this study, are: 17-22 $g \cdot L^{-1}$ Black Sea, 38-39 $g \cdot L^{-1}$ Aegean Sea and 38-40 $g \cdot L^{-1}$ Mediterranean Sea[18-20]. So both Aegean and Mediterranean seas had high salinity level. A most important feature of the Black Sea is that oxygen is dissolved only in the upper water levels and below a depth of about 70 meters there is no oxygen but the sea is contaminated by hydrogen sulfide, which results in a fully bacteria zone[18]. The determined values of *p*H, conductivity (κ) and TDS of the used seawaters are presented in Table 1. One can see from the data in Table 1 that all sea waters are lightly alkaline solutions (Aegean Sea being the most alkaline), with good conductivity (Mediterranean Sea having the highest value) and as for the TDS again the Mediterranean Sea has the highest value. Those data are in accordance with literature salinity data.

Corrosion behaviour

Δm measurement has been identified to be a good method for corrosion evaluation of metals in an immersion test [21-25]; in this investigation, the Δm method was used to assess the corrosion of OL52 and OL52.4 steel samples in the three seawaters medium. The cumulative Δm per area, cm^2, for the studied steels is presented in Fig. 1.

The evolution of Δm follows an upward trend almost linear with the immersion time for both steels studied. The equations of the lines in Fig. 1 are presented in Table 2 and a good linear correlation of mass loss is found (Adj.$R^2 > 0.99$). The highest mass lost was obtained for both OL52 and OL52.4 in the Mediterranean seawater, which is very normal as this seawater has the highest salinity.

The corrosion rate (CR) assists field engineers, scientists to envisage the lifetime of many metallic components in service. The CR, of a metallic material is evaluated by considering the, Δm, in g, the surface of the sample, S, in cm^2 and the time of immersion, t in h, using the following eq.:

$$CR = \Delta m / S \cdot t \qquad \ldots (2)$$

The CR of the studied mild steel samples was calculated at different intervals of exposure time and the data obtained were plotted in Fig. 2. The corrosion kinetics of the studied steel samples in the used sea waters as observed from Fig. 2 is composed of two
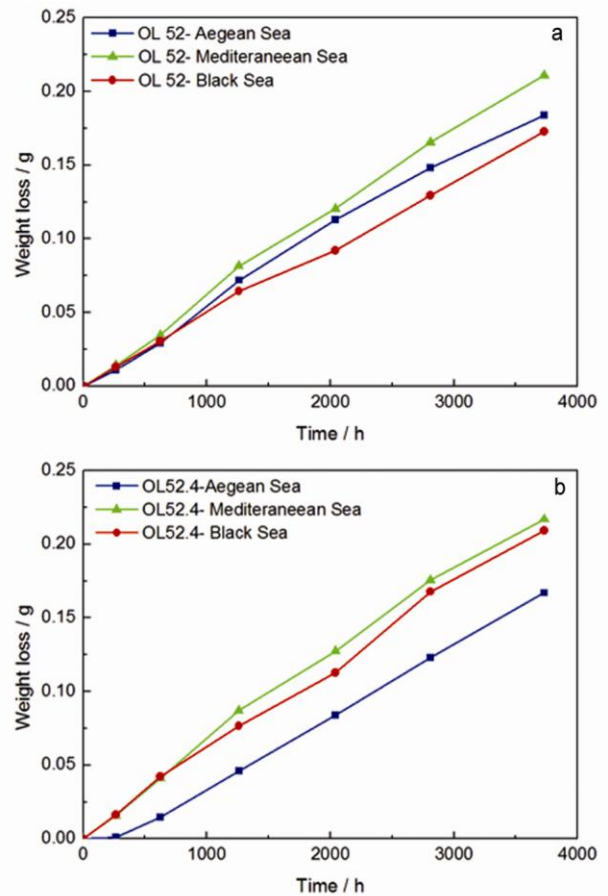

Fig. 1 — Cumulative weight losses *vs.* exposure time for OL52 (a) and OL52.4 (b) steels in seawaters

Table 1 — Some properties of seawaters in study

Sample of water	*p*H	K mS	TDS ppt
Black Sea	7.63	24.41	13.88
Aegean Sea	7.70	37.82	21.70
Mediterranean Sea	7.39	110.2	64.93

Table 2 — Weight loss equations along with the correlation factors (Adj. R^2)

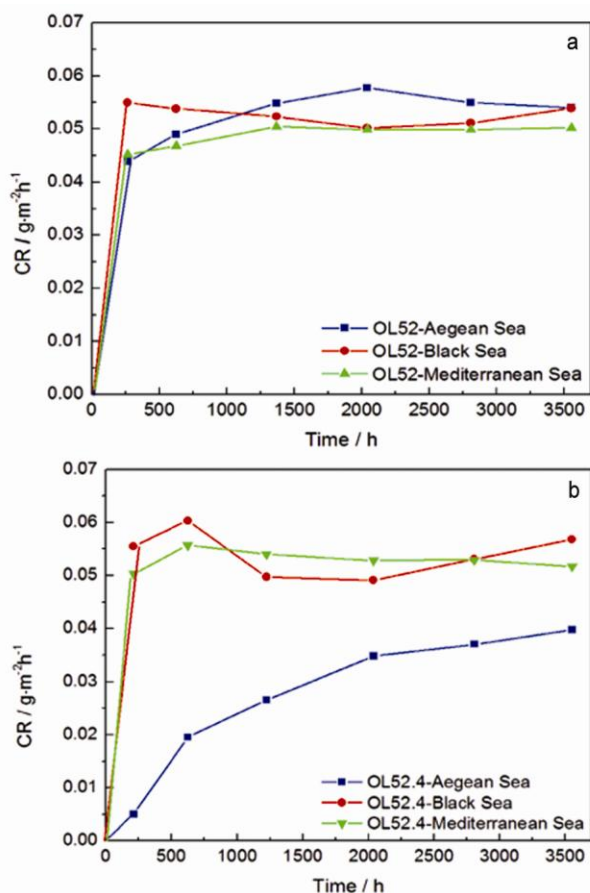| Sample	Corrosion media	Equation of mass loss	Adj.R^2
OL52	Aegean Sea	$\Delta m = -0.0010 + 5.2972 \cdot 10^{-5} \cdot t$	0.998
	Mediterranean Sea	$\Delta m = -0.0012 + 5.9599 \cdot 10^{-5} \cdot t$	0.999
	Black Sea	$\Delta m = -4.6614 \cdot 10^{-4} + 4.7481 \cdot 10^{-5} \cdot t$	0.997
OL52.4	Aegean Sea	$\Delta m = -0.0010 + 4.817 \cdot 10^{-5} \cdot t$	0.990
	Mediterranean Sea	$\Delta m = 0.0025 + 6.1297 \cdot 10^{-5} \cdot t$	0.997
	Black Sea	$\Delta m = -9.2452 \cdot 10^{-4} + 6.1626 \cdot 10^{-5} \cdot t$	0.992

Fig. 2 — Corrosion rate *vs*. exposure time for OL52 (a) and OL52.4 (b) steels in sea waters

phases. The first phase was the initiation phase which is characterized by a strong linear increase in CR, which started from the beginning of exposure time until the about 10th day for OL52 and 26th day for OL52.4 of exposure. The reason for this increase in CR can be attributed to the non-formation of a passive film on the surface of mild steel and so the degradation of the material is almost continuously. After this period the CR for both studied materials remain constant because of the passive protective layer formation that slowed down the CR. For OL52.4 we found that in the Aegean water there is a uniform variation of the CR and we believe that this behaviour is due to other forms of corrosion that occur on this steel (for example, pitting corrosion). It is also known that the most familiar corrosion of this type is the rusting of iron when exposed to such environment. The presence of Cl^- and S^{2-} ions, especially present in Black Sea, has an importance role in corrosion process, contributing to an accelerated corrosion reaction. The existence of Cl^- ions conduct to the formation of different forms of iron oxides[26-36].
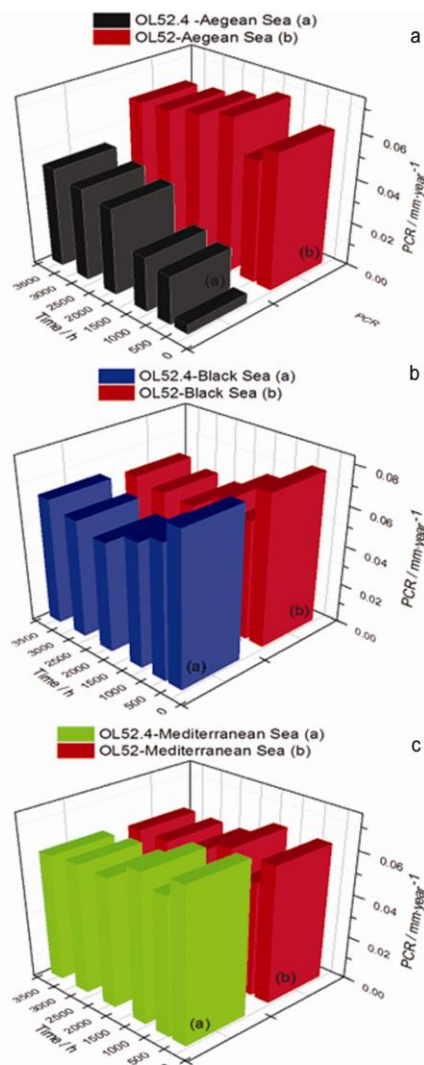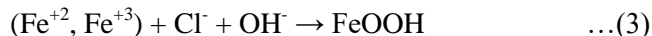

Fig. 3 — Corrosion penetration rate comparison for OL52 and OL52.4 in Aegean, Black and Mediterranean Sea

$$(Fe^{+2}, Fe^{+3}) + Cl^- + OH^- \rightarrow FeOOH \qquad …(3)$$

XRD analysis confirms the presence of iron compounds on these corroded steels.

Another important factor that accelerates the corrosion process could be the concentration of DO in the sea water. The presence of oxygen is influenced by the temperature and salinity gradient. The CR is going up with increasing salinity. Black sea is an exception as even if it's salinity is low, the rate of corrosion of OL52 and OL52.4 steels is similar to that in Mediterranean Sea. We believe that this behavior is a consequence of two factors: the presence of H_2S and the low or even absence of oxygen in the Black Sea[17].

Finally the corrosion penetration rate (CPR) was calculated for the studied steels corroded in seawaters and the results are presented in Fig. 3 and Table 3.

Table 3 — Calculated corrosion penetration rate for the OL52 and OL52.4 for the corrosion in sea water after 5 month total immersion

Sample	Corrosion media	CPR mm·year^{-1}
	Aegean Sea	0.0607
OL52	Mediterranean Sea	0.0606
	Black Sea	0.0564
	Aegean Sea	0.0447
OL52.4	Mediterannean Sea	0.0638
	Black Sea	0.0580

The CPR, in mm·year^{-1}, represents the depth to which the corrosion has penetrated the mass of the metal for one year and is calculated from the, CR, and the density of the metal, ρ, after the following formula:

$$P = (24 \cdot 365 \cdot CR)/(1000 \cdot \rho) \qquad \ldots(4)$$

Where, 24 represents the number of hours in a day; 365 is the number of days in a year; 1000 is the conversion factor of the units of measurement; ρ is the density of the metal being corroded, g·cm^{-3}.

Following the data from Table 3, the following are found regarding the corrosion resistance of the two steels in the studied sea waters:

1. In the Black Sea almost the same result was obtained for OL52 and OL52.4;

2. In the Mediterranean OL52 and OL52.4 also have similar corrosion resistance and

3. In the Aegean the corrosion resistance of OL52.4 is clearly superior to that for OL52 and as the composition of the two steels is very similar we tend to believe that this is due to the presence of Al in this steel.

Those data for both steels OL52 and OL52.4, show very good corrosion resistance as the CPRs determined are much lower than the allowable standard rate, 0.5 mm·year^{-1}.

XRD diffraction analysis for crystal structure

Figure 4 presents XRD patterns of OL52, OL52.4 samples before and after corrosion action of Black, Aegean and Mediterranean seas. XRD analysis before corrosion action showed that both samples have the same crystal structure based on the iron main phase.

On XRD patterns of alloys all reflexes are indicated on the basis of a cubic cell of Im3m space group; reflexes of XRD patterns are indicated in accordance with the ID 06-0696 of PCPDFWIN database, V.2.00 (a=0.2866 nm). The parameter of the crystal cell "a" is 0.2868 nm for OL52 steel and 0.2870 nm for OL52.4 steel, respectively. The XRD analysis showed that after the corrosion resistance
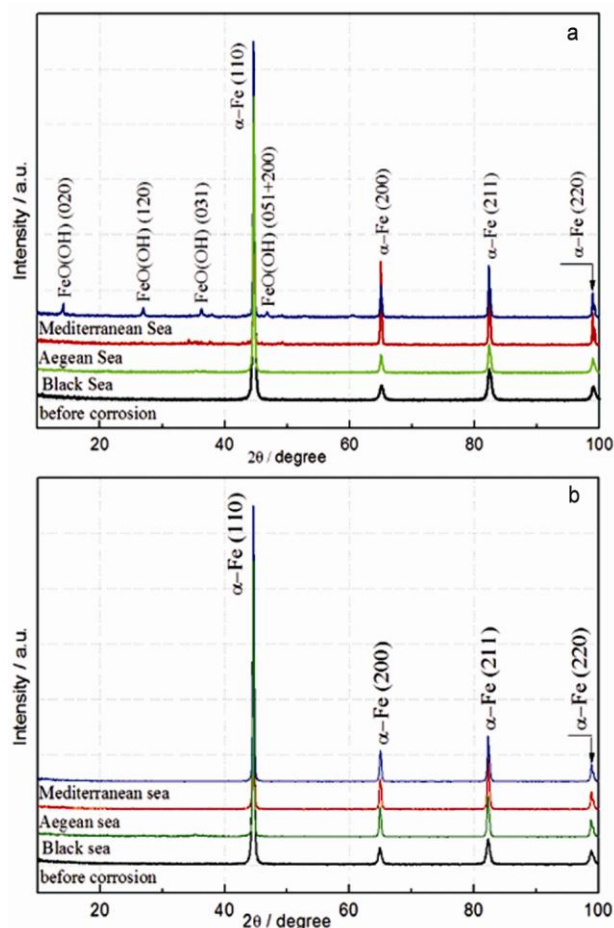

Fig. 4 — XRD-Analysis of OL52 (a) and OL52.4 (b) samples before and after corrosion in sea waters

studies by the gravimetric method the main phase of the Im3m type of iron remained, *i.e.* long exposure in the waters of the Aegean and Black Seas did not mainly affect the crystalline structure of stainless steels, Table 4. Only when Mediterranean water is used as a corrosive substance in the case of OL52 steel, the analysis of the XRD phase showed that on the surface of the sample the corrosion products have as major concentration iron oxide (especially FeOOH).

Microscopic study

Microscopic images presented in Figs 5 and 6 show that OL 52 and OL 52.4 steels have a fairly compact and homogeneous surface before corrosion and after corrosion the surface of these samples shows major changes due to the corrosiveness of marine medium. The microscopic images from pictures show that both OL 52 and OL 52.4 have a fairly compact and homogeneous surface in the initial state, before immersion in sea water. After corrosion in seawater,

the surface of these samples shows changes that can be seen even with the naked eye. From these figs. we can conclude that corrosion attacks the grain boundaries and this attack can be seen in the presence of white and grows grain boundaries along with red

Table 4 — Unit cell parameters, the crystallite size and the dislocation density of the OL52 and OL52.4 steels before and after corrosion in sea waters

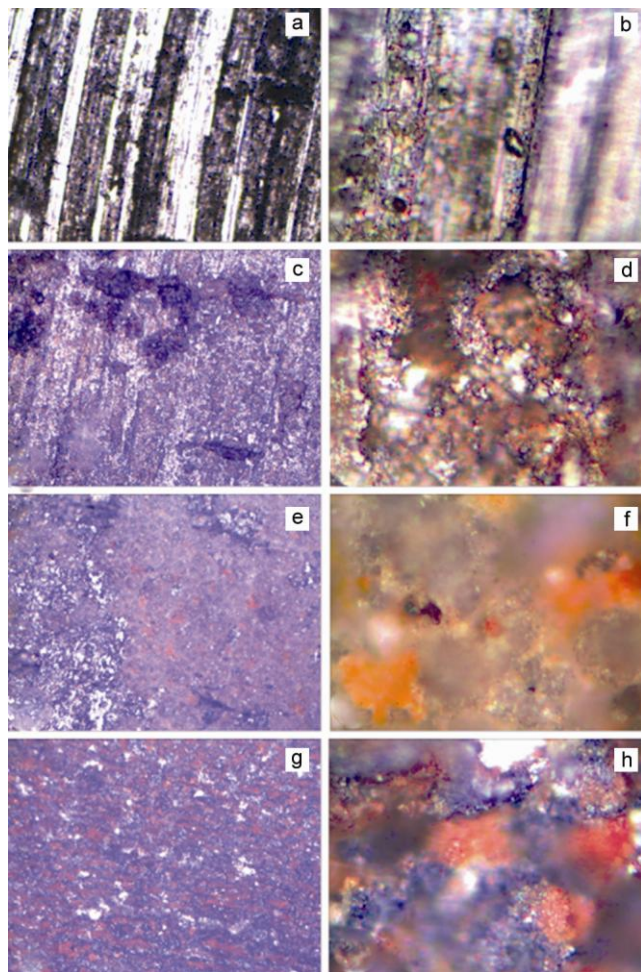| Sample	Corrosion media	A nm	Average crystallite size d, nm	Dislocation density δ 10^{-3}, nm^{-2}
OL52	Before corr.	0.2868	15.77	4.02
	Mediterranean Sea	0.2872	17.20	3.38
	Black Sea	0.2870	16.79	3.55
	Aegean Sea	0.2871	19.49	2.63
OL52.4	Before corr	0.2870	15.54	4.13
	Mediterranean sea	0.2871	19.31	2.63
	Black sea	0.2872	18.19	3.02
	Aegean sea	0.2871	17.38	3.31

Fig. 5 — Micrographic images of OL 52 with 100× and 800× magnifiers for: a,b) initial state and corroded state: c,d-Black Sea; e,f-Aegean Sea and g,h-Mediterranean Sea

rust. The images for corroded OL52.4 show some white parts which can be aluminium oxide formed in salt water .Those microscopic images sustain the Δm results.

Magnetic properties

Figure 7 presents the temperature behaviour of the specific magnetization, σ, for OL52 and OL52.4 before and after corrosion in the three seawaters in study. The inserts show the dependences $\sigma^2 = f(T)$, allowing a more accurate determination of the Curie temperatures, T_c. Steels have a similar nature of dependencies, confirming the presence of free iron. This fact is proved by XRD studies of the sample crystal structure and by chemical composition of studied alloys. In initial state before corrosion action at liquid nitrogen temperature the specific magnetization has a value of 200 $A·m^2·kg^{-1}$ for OL52 and 235 $A·m^2·kg^{-1}$ for OL52.4. It should be noted that the dependences σ=f(T) of these
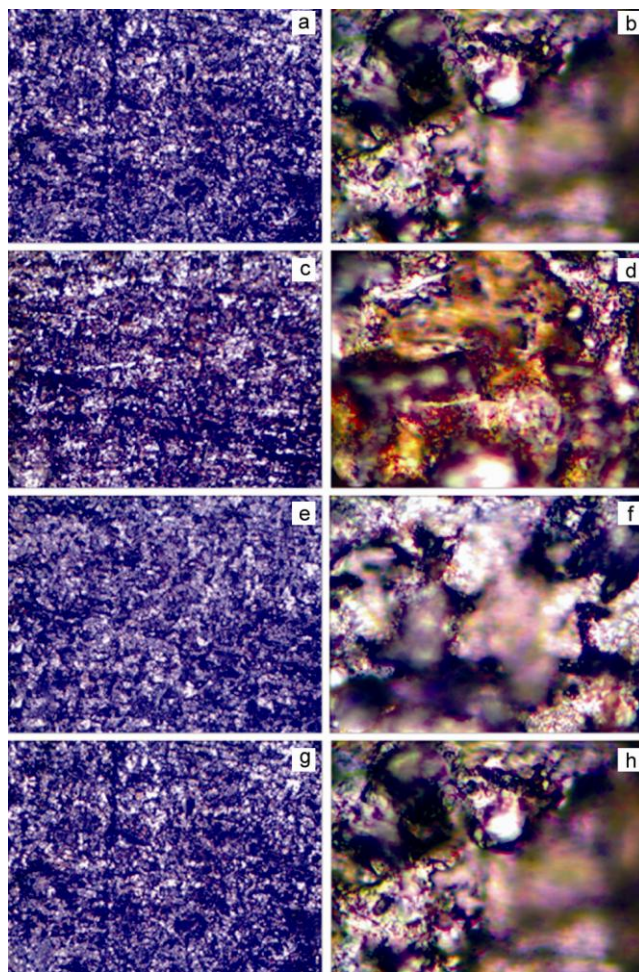

Fig. 6 — Micrographic images of OL 52.4 with 100× and 800× magnifiers for: a,b) initial state and corroded state: c,d-Black Sea; e,f-Aegean Sea and g,h-Mediterranean Sea
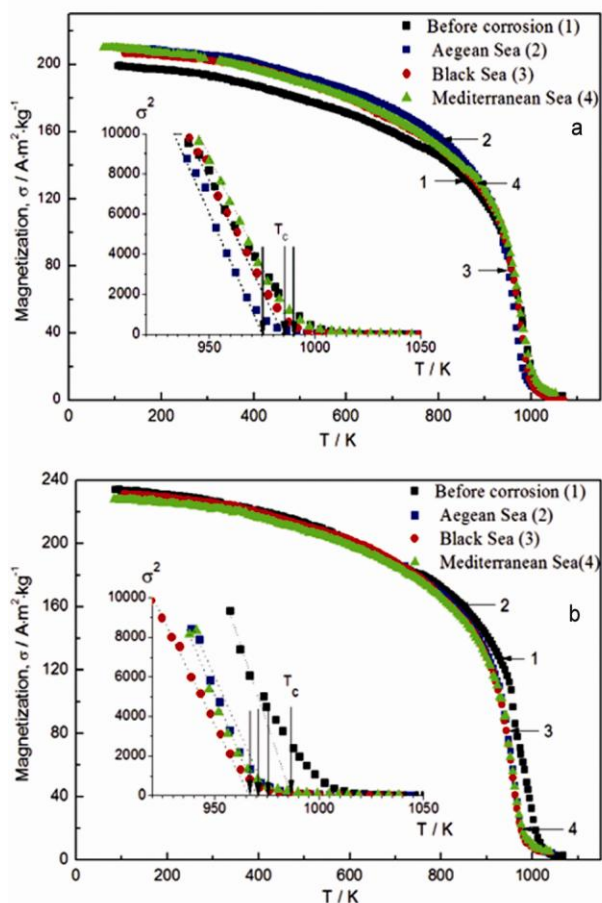
Fig. 7 — Temperature behaviour of specific magnetization for a) OL52 and b) OL52.4

Table 5 — Magnetic parameters of OL52 and OL52.4 alloys before and after the corrosive effects of sea waters

Sample	Corrosion media	T_c K	Σ A·m^2·kg^{-1}
OL52	before corrosion	990	203.1
	Mediterranean Sea	990	210.2
	Black Sea	985	206.7
	Aegean Sea	975	209.7
OL52.4	before corrosion	985	233.9
	Mediterranean Sea	970	227.9
	Black Sea	965	231.6
	Aegean Sea	970	228.3

two samples on cooling coincide with the dependences σ=f(T) on heating. T_c determined from the dependences σ^2=f(T) are 970 K for OL52 and 975 K for OL52.4. A comparative analysis of the specific magnetization temperature dependences and data of Table 5 before and after corrosion action of three sea waters types on OL52 and OL52.4 one can conclude the high corrosion resistance of the stainless steels magnetic characteristics.

The results of such a study can be useful for technologists and designers of constructions based on multifunctional alloys OL52 and OL52.4 in the case of their use in contact with seawaters of various salinity (for example, in the chemical, oil and shipbuilding industries). None of the data in this study could be compared with other data in the literature because this study is the first of its kind on these materials.

Conclusion

1. Weight loss measurements for OL52 and OL52.4 immersed in Aegean, Black and Mediterranean seas show a good corrosion resistance, so these steels can be used in constructions on or near the seawaters.

2. Values of corrosion penetration rate were found to be low (0.047-0.0638 mm·year^{-1}) and microscopic and XRD data sustain these results.

3. At room temperatures in CuK$_\alpha$-radiation the XRD analysis of functional alloys OL52 and OL52.4 samples before corrosion action of sea waters is carried out.

4. Samples of OL52 and OL52.4 alloys have a cubic crystal structure of Im3m sp. gr., with the free iron main phase. The unit cell parameter *a*=0.2868 nm for OL52 steel and *a*=0.2870 nm for OL52.4 steel.

5. The specific magnetization of OL52 and OL52.4 steels in the temperature range of 77-1100 K was studied by ponderomotive method in the 0.86 T magnetic field. It was found that both stainless steels are ferromagnets with a Curie temperature of 970 and 975 K, respectively. At liquid nitrogen temperature, σ=200 A·m^2·kg^{-1} for OL52 and σ=235 A·m^2·kg^{-1} for OL52.4. Both stainless steels are resistant to heating up to 1100 K: the temperature dependences σ = f(T) are reversible.

Acknowledgement

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