STUDIA UBB CHEMIA, LXVII, 2, 2022 (p. 67-77)
(RECOMMENDED CITATION)
DOI:10.24193/subbchem.2022.2.04

STRUCTURE, MAGNETIC PROPERTIES, CORROSION RESISTANCE OF 1.4541 STAINLESS STEEL IN SURFACE SEAWATERS

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ABSTRACT. We investigated the phase structure, magnetic properties, corrosion resistance, microstructure of 1.4541 (V2A) stainless steel through X-ray diffraction (XRD), magnetic measurement device, gravimetric/electrochemical methods, metallographic microscopy. Corrosion resistance was evaluated in natural seawaters of Mediterranean, Black and Aegean seas. The results show that crystal structure and specific magnetic characteristics are resistant to corrosion action of all seawaters at a temperature of 295 K. The greatest corrosive effect on studied alloy has the Mediterranean Seawater, corrosion penetration is about 0.1290 mm/year. Microscopy confirmed corrosion data.

Keywords: *text, Stainless steel, Sea waters, Corrosion, Micrography, XRD analyses, Magnetization.*

INTRODUCTION

Most metal products are used in corrosive natural environments, so on an industrial scale, there is little alternative to nickel-based steels and alloys that are resistant to corrosion. Stainless steels have a wide industrial application in heavy, energy, mechanical and electronic industries. A very actual problem is the corrosion resistance of such materials in marine media. Therefore, the key to a significant economy is the existence of accurate data on the resistance to marine corrosion, as well as the physical, mechanical, stability properties of stainless steel. Knowledge of processing and operating temperature ranges, as

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well as operating conditions, is also very important information in the widespread use of these steels in corrosive environments. Stainless steel containing 13% chromium and additionally alloyed with nickel, as well as a small amount of silicon and manganese, shows high anti-corrosion properties [1,2]. High chromium content stainless steels have as their main property corrosion resistance, which is very important knowing that corrosion losses can be enormous in some cases. The chromium content in steel over 12% provides high resistance to oxidation and heat resistance [3,4]. It was found that varying the carbon content in the range of 0.08-0.25% affects the quality characteristics and changes the properties. The extension of the study of this issue is generated by the ambiguity of the published results.

The problem of corrosion resistance of stainless steels and alloys based on chromium and nickel, like nickel-based alloy 1.4541(V2A), is still relevant. Therefore, leading research centers carry out comprehensive studies of such materials [5-8]. From the scientific references found we have not been able to get explanation and prediction of the corrosion resistance of the steels that can be used in seawater.

Considering the wide use of 1.4541(V2A) steel in various parts and components that are used in the marine environment, as well as the lack of systematic studies of corrosion of this material in the marine environment, we considered appropriate and interesting the study his corrosion behavior in different seawaters.

In this study, we aim to study structure and magnetic properties of functional nickel-based alloy 1.4541(V2A) along with the corrosive effects of sea waters with different salt content (respectively seawaters from Black Sea, Aegean Sea and Mediterranean Sea). In the same time structure of this stainless steel were studied before and after corrosion process in seawaters. To our knowledge, this study is original, being the first of its kind. Our purpose and objectives are relevant for having a long life in the aggressive marine environment, materials with specific characteristics of the crystalline structure must be used, which leads to the increase of the corrosion resistance in aggressive environments.

RESULTS AND DISCUSSION

X-ray phase analysis of the alloy 1.4541(V2A) (Fig. 1) showed that the alloy contains two phases – γ-phase of iron austenitic $Fm\bar{3}m$ sp. gr. and α'-phase ferrite $Im\bar{3}m$ sp. gr. The unit cell parameter was 0.3595 nm for γ-phase and 0.2877 nm for α'-phase of iron with a phase ratio of 6/1. The average crystallite size is 16.86 nm, and the dislocation density is $3.52 \cdot 10^{-3}$ nm^{-2}.

Figure 2 shows the temperature dependence of the specific magnetization of the 1.4541(V2A) alloy before corrosive action. The inset shows the dependences σ^2=f(T), which allow more accurately determining the Curie temperature. At liquid nitrogen temperature, the specific magnetization is 12.4 $A{\cdot}m^2{\cdot}kg^{-1}$. Curie temperature determined from dependence σ^2=f(T), equals 890 K. It should be noted that the σ=f(T) dependence at cooling is completely different from σ=f(T) at heating, that is, the heating of the 1.4541(V2A) alloy to 1060 K is irreversible. The specific magnetization values at nitrogen temperature decrease 5.5 times and amounts to 2.25 $A{\cdot}m^2{\cdot}kg^{-1}$. As X-ray phase analysis showed that two phases are present in the alloy, it can be assumed that a sharp decrease in the magnetization is associated with the restoration of the stable structure of austenite by high-temperature treatment.

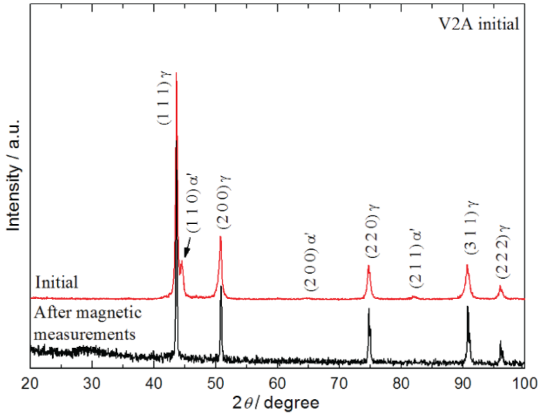

Figure 1. X-ray patterns of 1.4551(V2A) before and after high-temperature annealing

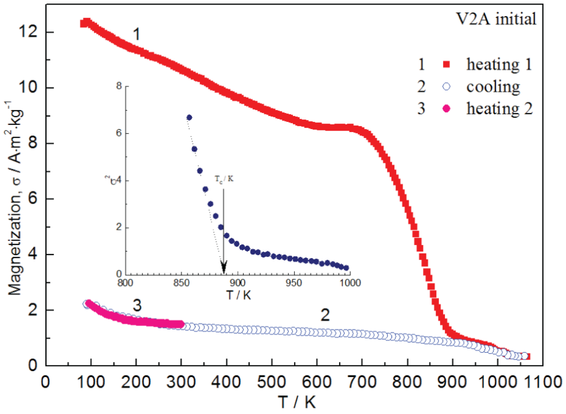

Figure 2. Temperature dependences of the specific magnetization of the 1.4541 (V2A) stainless steel before the corrosive effect of studied sea waters

For understanding this fact, it was carried out an X-ray study of 1.4541 samples after high-temperature annealing during specific magnetization measurements, the results of which are presented as a comparison in Fig. 1. This treatment causes the transformation of α' – γ phase into the austenitic γ phase as shown by the X-ray phase analysis. Slow cooling of the alloy leads to recrystallization of the alloy, the average grain size increases to 41.71 nm, and the dislocation density increases to $5.75{\cdot}10^{-3}$ nm^{-2}. Magnetic hysteresis loops at 77 K and 300 K (Fig. 3) also confirm the presence of only austenitic γ-phase. By heating, to 1100K the alloy becomes completely austenitic by the disappearance of the martensitic phase of the iron.

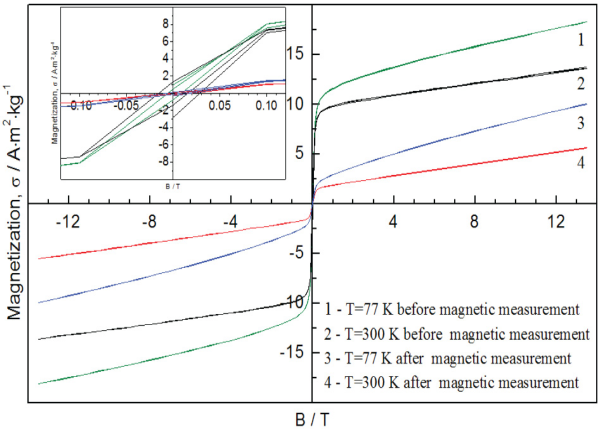

Figure 3. Magnetic hysteresis loops for the 1.4541(V2A) stainless steel before and after high-temperature annealing at 77 K (1 and 2) and 300 K (3 and 4)

The experimental data for mass loss corrosion study of 1.4551(V2A) stainless steel in three seawaters shows a mass loss of 0.0001-0.0004 g at 31 days of immersion in seawaters, followed by a big increase in the mass loss (0.0005-0.0007g) at 65 days of immersion. After that the mass loss (Δm) remains almost constant up to 277 days of immersion. From 308 days of immersion the mass loss has again a lower value and at 365 days the Δm was 0.0004 g in Mediterranean and Aegean sea and 0.0003 g in the Black sea. Finally, the mass loss was in accordance with the salinity of the three seawaters in study.

The calculated corrosion rate (CR=Δm/S×t; Δm, in g, the surface of the sample, S, in cm^2 and the time of immersion, t in h), was the same in the Mediterranean and the Aegean sea, which is normal as the two seawaters have almost the same salinity (38-40 g×L^{-1}). For the Black sea, the corrosion rate is lower as the salinity of that seawater is also lower (17-22 g×L^{-1}). Finally, the corrosion penetration rate (CPR) was calculated for the studied steels corroded in seawaters and the results are presented in Table 1. 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: CPR=(24×365×CR)/(1000×ρ), 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}. Those data, presented in Table 1, show a very good corrosion resistance as the CPRs determined are much lower than the allowable standard rate, 0.5 mm×year^{-1}.

Table 1. Calculated corrosion parameters of 1.4541(V2A) stainless steel corrosion in seawater after a total immersion of 365 days.

Corrosion media	Mass loss Δm(g)	Corrosion rate (g·cm^{-2}·h)	CPR (mm·year^{-1})
Mediterranean Sea	0.0004	7.1×10^{-9}	7.9×10^{-9}
Aegean Sea	0.0004	7.1×10^{-9}	7.9×10^{-9}
Black Sea	0.0003	5.3×10^{-9}	5.9×10^{-9}

Figure 4 shows the Tafel plots obtained from the polarization curves of the 1.4541(V2A) steel (in the initial state and after the weight loss study) in the tree seawater in the study. The plots corrosion *vs.* time respects a logarithmic law [9]. Corresponding corrosion parameters rates calculated are summarized in Tables 2 and 3.

Table 2. Corrosion parameters for electrochemical corrosion measurements in the water of different seas for 1.4541(V2A) stainless steel in the initial stage.

Corrosion media	E_{OCP} (V)	E_{corr} (V)	i_{corr} (A)	$CR_{init.}$ (mm/year)
Black Sea	-0.325	-0.204	$3.21\cdot10^{-6}$	0.0006
Aegean Sea	-0.101	-0.370	$16.24\cdot10^{-6}$	0.0122
Mediterranean Sea	-0.172	-0.465	$19.62\cdot10^{-6}$	0.1323

Table 3. Corrosion parameters for electrochemical corrosion measurements in the water of different seas for 1.4541(V2A) stainless steel after long-term corrosion.

Corrosion media	E_{OCP} (V)	E_{corr} (V)	i_{corr} (A)	$CR_{corr.}$ (mm/year)
Black Sea	-0.051	-0.465	$3.49\cdot10^{-6}$	0.0128
Aegean Sea	-0.125	-0.595	$8.65\cdot10^{-6}$	0.0583
Mediterranean Sea	-0.012	-0.983	$17.44\cdot10^{-6}$	0.1490

The highest corrosion rate (in both situations: initial and corroded) was obtained in the Mediterranean seawater. In general, the corrosion rate increases with increasing salinity and with decreasing pH. So we measured the pH and TDS for the three seawaters [using a multicomponent Cyber Scan PCD6500-

Eutech Instruments (USA) device] and we present the obtained values in Table 4. The high values of the corrosion rate obtained in Mediterranean seawater are confirmed by the highest value of salinity and a low pH.

Table 4. Some properties of seawaters in the study.

Sample of water	pH	TDS ppt
Black Sea	7.63	13.88
Aegean Sea	7.70	21.70
Mediterranean Sea	7.39	64.93

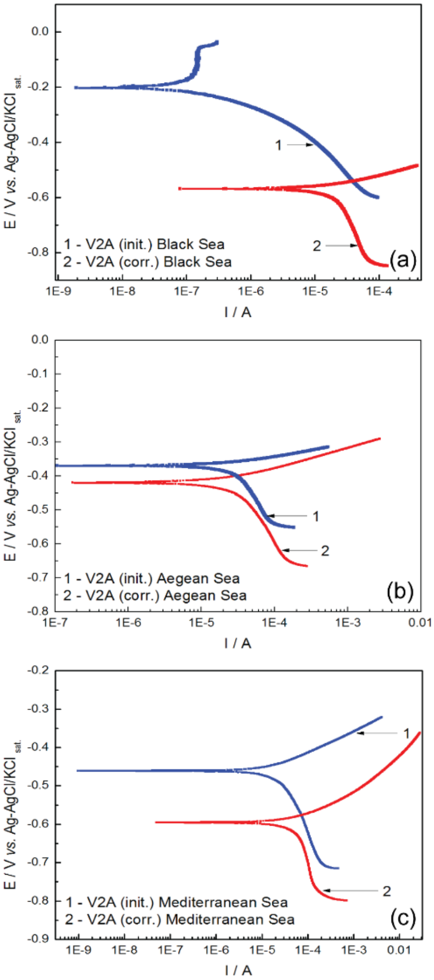

Figure 4. Tafel plots for 1.4541(V2A) corrosion (initial and after gravimetric long term corrosion) in different natural seawaters.

Figure 5 shows the diffraction patterns of the 1.4551(V2A) stainless steel before the corrosion action of different sea waters and after the corrosion resistance studies by gravimetric and potentiodynamic methods in seawater. The analysis of the diffraction patterns showed that the crystal structure of 1.4551(V2A) in case of longtime exposure in seawater has good corrosion resistance, the structure of the alloy was preserved. Table 5 shows the crystal cell parameters of the α' and γ-phases of 1.4551(V2A) alloy, as well as the average grain size and dislocation density. We did not observe any iron oxides or hydroxides be formed on the surface of the samples.

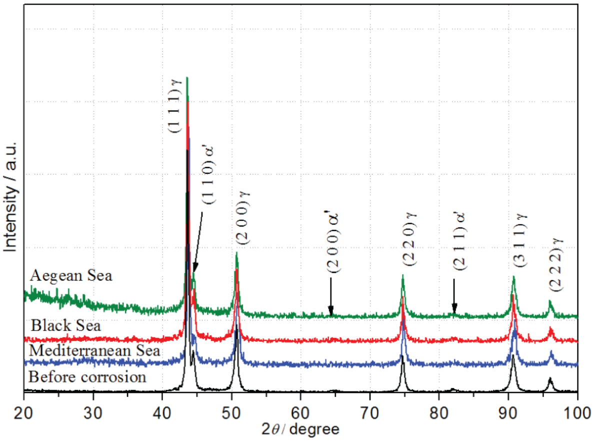

Figure 5. X-ray patterns of 1.4551(V2A) before and after corrosion action of seawaters.

Table 5. Crystal cell parameters of the α 'and γ-phases of the 1.4551(V2A) stainless steel, the average grain size, the density of dislocations.

Corrosion media	**γ-phase *a* (nm)**	**α'-phase *a* (nm)**	**average crystallite size d (nm)**	**dislocation density $\delta \cdot 10^{-3}$(nm^{-2})**
Before corrosion	0.3598	0.2879	16.86	3.52
Mediterranean Sea	0.3596	0.2874	16.08	3.86
Black sea	0.3589	0.2870	16.61	3.62
Aegean sea	0.3597	0.2879	16.15	3.83

Figure 6 shows metallographic images of the 1.4551(V2A) stainless steel surface before and after corrosion studies. The analysis of the micrographic images shows that at small magnifications (×100) the effect of the corrosion of the seawater is observed very little. At high magnifications, it is found that Mediterranean and Aegean seawaters have a profoundly visible effect on the surface of 1.4551(V2A) samples. The Mediterranean Sea has the greatest corrosive effect (one can see in that on the surface of V2A appears many caves). We believe that the corrosion resistance of this stainless steel alloy is given by the content of Cr and Ni. Because we have more austenitic phases than ferrite ones (Fig. 1 and 5) the stainless steel should exhibit good corrosion resistance, as ferrite phases are more susceptible to cracks. From the micrographs, one can see that nickel is mainly extracted during the corrosion process (green areas). The initiation of crevice corrosion may be done in the defect zone of the alloy which helps propagation of corrosion. The metallographic microscopy study supports the corrosion data.

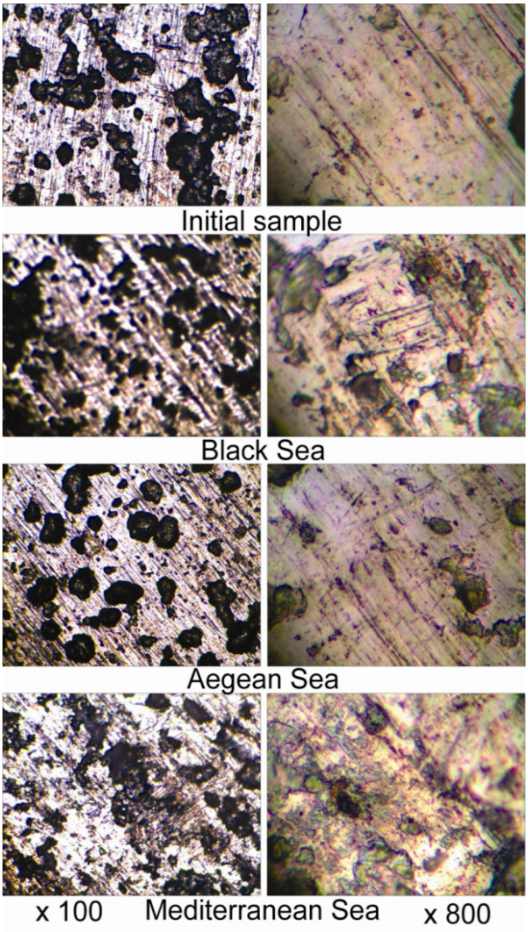

Figure 6. Surface of 1.4541(V2A) alloy samples before and after corrosive action of seawaters: the Mediterranean, Black and Aegean seas (resolution ×100 and ×800)

CONCLUSIONS

It was found that 1.4541(V2A) alloy has two crystalline phases – austenitic γ-phase Fm$\bar{3}$m sp. gr. and ferritic α'-phase Im$\bar{3}$m sp. gr. The cell parameter a before corrosion action is 0.3595 nm for the γ-phase and 0.2877 nm for α'-phase with a phase ratio of 6/1. X-ray patterns analysis after different seawater electrochemical actions showed that in all cases 1.4541(V2A) alloy structure was preserved. Any iron oxides or hydroxides were not observed to be formed on the surface of the samples. The magnitude of the specific magnetization, at nitrogen temperature, decreases 5.5 times and amounts to 2.25 $A\cdot m^{2}\cdot kg^{-1}$. X-ray phase analysis showed that two phases are present in the alloy. Thus, it can be assumed that a sharp decrease in magnetization is associated with the restoration of the stable structure of austenite by high-temperature treatment.

Analysis of the corrosion parameters showed that the greatest corrosive effect on studied alloy has the Mediterranean Sea water with a corrosion rate of 0.1323 mm/year, which is confirmed by the results of a study of surface morphology.

EXPERIMENTAL SECTION

Chemical composition of investigated 1.4541(V2A) samples was: 0.08% C, 67.70% Fe, 18% Cr, 11% Ni, 2% Mn, 0.03% S, 0.04% P, 1% Si. 0.15% Ti .

The alloy was used to investigate before and after corrosion by X-ray diffraction of the automated apparatus "DRON-2" in CuKα in angle range 20 ° ≤ 2θ ≤ 100 ° at room temperature. To obtain the XRD pattern, the recording of the reflex intensities takes place automatically with a scan step of 0.03 ° and exposure time of 2-3 s. Using a step of 0.01 ° with exposure at 10 seconds it was determined the parameters of the crystal cell. The FullProf Suite program, which is based on the Rietveld method to clarify the parameters of the crystal cell, was used to process experimental X-ray data. The lattice parameter determination error was ± 0.0003 nm and the average crystallite size is calculated with the Debye-Scherrer formula. The temperature dependences of the specific magnetization were studied in the 77 – 1100 K temperature range by the ponderomotive method in a magnetic field of 0.86 T. The relative error in determining the specific magnetization value is about 4%. Dependences of magnetization on a vibration magnetometer of the universal measuring system

"Liquid Helium Free High Field Measurement System" from "Cryogenic Ltd." at 77 and 300 K in fields up to 14 T were studied. Corrosion resistance studies of functional 1.4541(V2A) alloy were carried out at a temperature of 25^{o}C by two methods: the weight loss and the potentiodynamic method. The corrosive media used was natural seawater from Black, Aegean and Mediterranean seas. Literature [10-12] presents that the salinity of those sea waters is: 17-18.5 g/L the Black Sea, 38 g/L the Aegean Sea, 37-39 g/L the Mediterranean Sea.

The size of the steel samples used for weight loss (Δm) corrosion, were 50 mm × 25 mm × 5 mm. They were cleaned wet-polished with 2000# grade SiC paper, then cleaned in alcohol and acetone, after which they were dried, weighed, stored in a desiccator until use. The test samples were suspended using 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 ±0.02 mg.

The samples were observed for 367 days and each sample was measured before and after each 30 days immersion time to obtain the Δm; measurements, procedures, precautions are described in [13-15]. After that, the samples were subjected to the potentiodynamic polarization method in a standard three electrodes cell. The polarization tests were conducted using a Princeton Applied Research-PAR, model PARSTAT 2273 potentiostat/galvanostat with "Power Corr" software. The Tafel polarization measurements were performed at ±250mV *vs.*OCP with a scan rate of 0.166 mV/s. The glass working cell is connected to a thermostated bath for temperature control. A specific area (1cm^2) of the alloy sample was used as the working electrode (WE); a platinum sheet and Ag-AgCl/KCl(sat.) were employed as a counter (CE) and respectively reference electrode (RE).

A polarization corrosive study was also done on 1.4541(V2A) samples before being subject to long-term corrosion (initial state). Tafel polarization curves analysis was carried out, and the corresponding electrochemical parameters of corrosion were calculated.

Surface images before and after corrosion exposure with different magnifications (from ×100 to ×800) were performed with an inverted microscope (NY Microscope Comp.) with digital camera acquisition.

ACKNOWLEDGMENTS

Text, The financial support of the Romanian Academy and the Research Foundation of NAS of Republic Belarus (bilateral project 2018-2020) is acknowledged.

REFERENCES

1. S. S. M. Tavares; J. M. Pardal; T. R. B. Martins; M. R. da Silva; *J. Mater. Eng. Perform.*, **2017**, *26*, 2512-2519.
2. B. Liu; X. Wei; W. Wang; J. Lu; J. Ding;, *Sol. Energy Mater. Sol. Cells*, **2017**, *170*, 77-86.
3. L. Taleb; C. Keller; *Int. J. Mech. Sci.*, **2018**, *146-147*, 527-535.
4. Z. Wang; T. A. Palmer; A. M. Beese; *Acta Mater.*, **2016**, *110*, 226-235.
5. S. S. Sawant; B. D. Gajbhiye; S. Tyagi; C. S. Sona; R. Divya; C. S. Mathpati; A. Borgohain; N. K. Maheshwari; *Indian Chem. Eng.*, **2017**, *59*, 242-257.
6. S. Wang; J. Ding; H. Ming; Z. Zhang; J. Wang; *Mater.Charact.*, **2015**, *100*, 50-60.
7. V. V. Zelenskiy; S. V. Nesterenko; L. P. Bannikov; *Coke Chem.*, **2014**, *57*, 167-176.
8. A. A. Lukhvich; V. I. Sharando; A. K. Shukevich; K. I. Yanushkevich; *Russ. J. Nondestruct. Test*, **2015**, *51*, 131-137.
9. J. Kruger; *Passivity*, in: *Uhlig's Corrosion Handbook*, 3-rd ed., R.W. Revie Ed.; NJ: John Wiley & Sons Inc., **2011**, Chapter 12, pp.151-155.
10. https://water.fandom.com/wiki/Black_Sea
11. D. Velaoras; V. Zervakis; A. Theocharis; *The physical characteristics and dynamics of the aegean water masses.* in*: The handbook of environmental chemistry*, D. Barcelo; A. G. Kostianoy Eds.; Springer, Berlin, Heidelberg, Germany, **2021**, Chapter 1, pp.1-29.
12. https://www.esa.int/ESA_Multimedia/Images/2017/05/Mediterranean_Sea_salinity.
13. X. H. Chen; C. S. Chen; H. N. Xiao; F. Q. Cheng; G. Zhang; G. J Yi; *Surf. Coat. Technol.*, **2005**, *191*, 351-356.
14. H. A. Sorkhabi; N. G. Jeddi; F. Hashemzadeh; H. Jahani; *Electrochim. Acta*, **2006**, *51*(18), 3848-3854.
15. B. Jabeera; S. M. A. Shibli; T. S. J. Anirudhan; *Appl. Surf. Sci.*, **2006**, *252*(10) 3520-3524.