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CORROSION OF 42CrMo4 STEEL IN MARINE ENVIRONMENT USING SEM/EDS ANALYSIS

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Abstract:
Many steels are used in specific environments, while one of these is maritime applications. High-strength 42CrMo4 steel finds numerous applications in the marine industry, including shaft parts, crankshafts, connecting rods, drilling joints, pump parts, steam turbines, and salvage equipment. In order to provide performance reliability in the marine environment, it is essential to study the corrosion resistance of surfaces of 42CrMo4 steel components and parts. The steel's behavior is typically evaluated in a synthetic NaCl solution, which is prepared as a standard substitute for seawater. This paper is focused on the behavior of the steel samples under corrosion conditions in NaCl solution. The level of sample surface degradation which is caused by the corrosion over a 4-month exposure period was evaluated using SEM/EDS analysis. The mass loss increased during the testing period, following an almost linear model in all time periods.

Keywords*: corrosion, NaCl solution, mass loss, SEM/EDS analysis, degradation level*

1. INTRODUCTION

Corrosion is defined as the gradual degradation of metal properties caused by a chemical reaction or an electrochemical reaction with the surrounding atmosphere. The physical breakdown of metals is classified as damage, wear, and erosion. Metals decompose in contact with moisture/water (H_2O), bases (NaOH, $CaCO_3$, $NaHCO_3$, etc.), acids (HCl, H_2SO_4, HNO_3, etc.), salts (NaCl), liquid chemicals, aggressive metal varnishes and gases (formaldehyde, gases containing sulfur and ammonia) [1].
Seawater is a complex mixture of inorganic salts (mainly sodium chloride), dissolved gases (especially oxygen), suspended solids, organic matter, and organisms [2]. Seawater is a 3.5 to 4 percent solution of various salts, of which 86% is sodium chloride [3]. In addition to sodium and chloride ions, there are also magnesium, calcium and potassium ions forming strong alkalis, as well as sulfates and bicarbonates that create weak acids, which is why the pH is basic, around 8 [4]. Corosion rate in seawater depends on several factors: salt concentration, seawater flow, biofilm on the metal surface in the sea, dissolved oxygen concentration, and temperature [5].
Corrosion processes in seawater can be divided into four basic corrosion zones: atmospheric corrosion zone, tidal zone, underwater corrosion zone, and corrosion present in the mud zone [5]. The main factors affecting metal corrosion in seawater medium are chemical, physical, and biological factors [6]. Doubling the amount of oxygen doubles the rate of the corrosion process [5]. In this paper corrosion will be monitored using mass loss and SEM/EDS analysis.

2. EXPERIMENTAL

The following is a description of the materials to be used, their production and chemical composition, sample preparation that includes mechanical processing of the sampled material, and sample characterization showing characteristic sizes and their contribution to corrosion testing.

2.1 Material

The material used in this research is low alloy steel 42CrMo4, which was processed by classical casting – as cast. The chemical composition of the mentioned material was done at the Institute of black metallurgy in Nikšić is shown in Table 1.

Table 1. Chemical composition 42CrMo4 low alloy steel

42CrMo4					
Element (wt. %)	C	Cr	Mo	Mn	Si
	0.40	0.93	0.20	0.65	0.29
	Ni	Cu	Al	S	P
	0.03	0.04	0.044	0.003	0.009

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**Fe-balanced*

The steel was delivered by Kovintrade international trade d.d. Celje as hot rolled plates with dimensions of 10 mm × 1000 mm × 2000 mm according to the following procedure. After casting, the material in the form of billets was processed by hot rolling, the billets were heated to a temperature equal to 2/3 of the melting temperature of iron before hot rolling. After heating at 1024°C, the material passes through four flat rollers, and then the bars are straightened. Samples for corrosion testing were cut in the form of rectangles with dimensions of width and length of 20 mm × 20 mm. To obtain standardized samples, a 10-millimeter thick plate was processed on a milling machine and reduced to a thickness of 4 millimeters.

2.2. Corrosion testing

The corrosion behavior of structural steel 42CrMo4 was investigated by immersion, whose samples were immersed in a 3.5% NaCl solution according to ISO 11130 (E). The mass loss and SEM analysis were monitored at the beginning, after 30, 60, 90, and 120 days. Control of the metal surface consisted of examining the surface with a scanning electron microscope (SEM) at a magnification of 1000x. The elemental composition of samples was analyzed by the EDS method. The results of the mentioned tests gave an insight into the corrosion behavior of metals.

2.3. Mass loss

One of the criteria used to evaluate the results of the corrosion test, in which the samples were immersed in a salt solution, is mass loss. By weighing the specimen before and after cleaning (specimen should be weighed to three decimal places), the amount of metal loss can be determined. The mass of the samples was measured before and after each testing interval using an analytical balance with an accuracy of ± 0.1 mg, in accordance with the standard ISO 8407.

The degree or level of corrosion was measured as the mass loss of the steel samples before and after the corrosion tests. The samples were weighed and the mass loss was calculated using Equation (1) [7].

$$\text{Mass loss} = \frac{M_i - M_f}{M_i} \cdot 100 \quad (1)$$

Where M_i and M_f are the masses (in grams) of the sample before and after corrosion experiments, respectively.

3. RESULTS AND DISCUSSION

3.1. Mass loss

The relationship between the mass loss and the corrosion duration is shown in Figure 1. The mass loss increased during the testing period, following an almost linear dependence from 0 g for an uncorroded sample to 1.6 % after 120 days of immersion in a 3.5% NaCl solution.

The obtained mass loss results indicate that as the time spent in saltwater increases, more corrosion occurs. This suggests that there is a corresponding increase in corrosion with an increase in the time spent in saltwater.

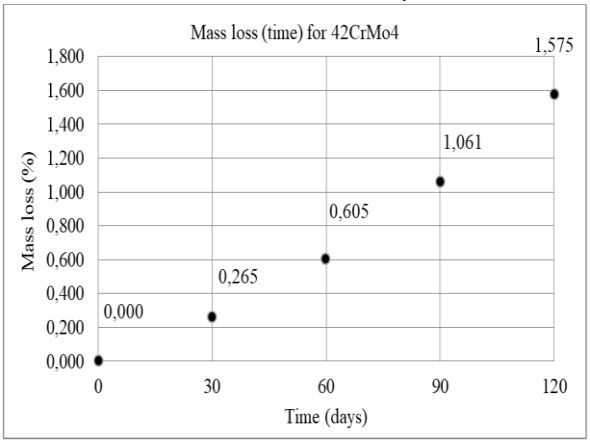
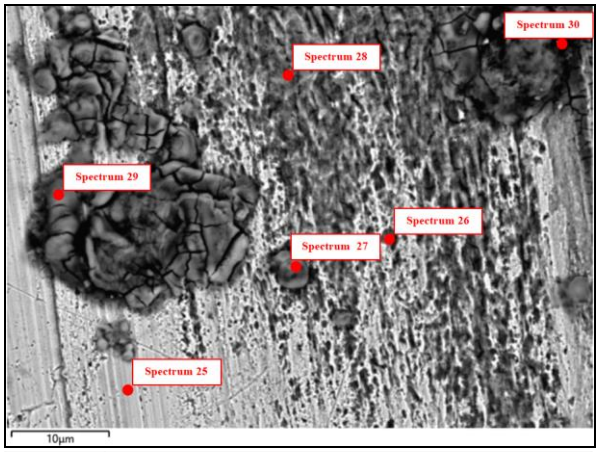


Figure 1. Mass loss for 42CrMo4 before and during testing

3.2. SEM/EDS analysis

SEM/EDS analysis was applied to monitor corrosion behavior of the samples. In Tables 2 and 3 results for samples after 30 and 120 days will be given, respectively.

Table 2. SEM images and elemental composition (on marked spots) of 42CrMo4 after 30 days

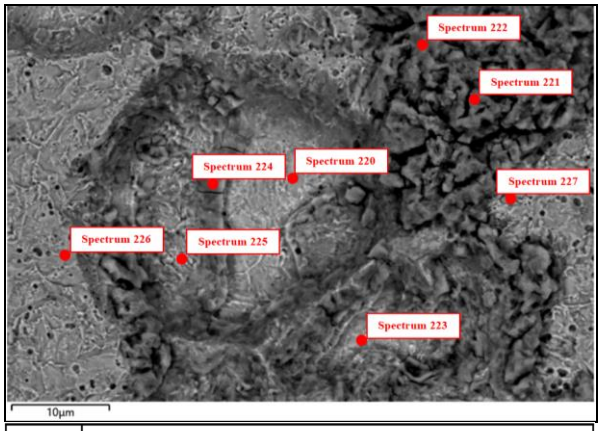


Element	Spectrum					
	25	26	27	28	29	30
	Wt. (%)					
Fe	94.95	84.13	66.75	79.63	65.28	92.45
O	2.84	12.07	30.62	15.72	33.07	2.74
Cr	0.95	2.33	0.69	3.10	0.31	2.12
Cl	/	0.08	0.65	0.14	0.69	1.52
Mn	0.70	0.57	0.45	0.56	0.52	0.82
Cu	/	/	/	/	/	0.19
Al	0.14	0.16	/	0.24	/	/
S	0.06	0.29	0.63	0.32	/	0.09
Si	0.36	0.24	0.11	0.20	0.13	0.06
Ni	/	0.13	/	0.11	/	/
Ca	/	/	0.09	/	/	/

Since the corrosion behavior is investigated, the presence of elements that could be a consequence of sample contamination are omitted, for example, the elements that make up the composition of seawater, namely Na, Cl, K, Mg, Ca, Sr, Br, and F because they do not exist in steel.

Table 2 shows SEM images and elemental composition (on marked spots) of 42CrMo4 after 30 days in 3.5% NaCl solution. Considering the chemical composition (Table 1), the EDS analysis gives almost the same elemental composition, with the omission of molybdenum, but increased content of oxygen (spectra 26-29) and Cr, are evident (spectra 26, 28 and 30).

Table 3. SEM images and elemental composition (on marked spots) of 42CrMo4 after 120 days.



Element	Spectrum							
	220	221	222	223	224	225	226	227
	Wt. (%)							
Fe	96.16	65.90	66.81	95.43	70.96	94.86	95.90	89.29
O	1.09	27.55	26.42	2.11	26.15	2.71	1.78	7.58
Cr	1.31	3.93	5.00	1.08	0.93	1.12	1.15	1.89
Cl	/	0.80	0.26	/	0.76	/	/	0.05
Mn	0.80	1.10	0.57	0.79	0.66	0.74	0.71	0.71
Al	/	0.19	0.23	/	/	/	/	0.10
Si	0.37	0.31	0.37	0.36	0.27	0.34	0.33	0.20
Mo	0.26	0.23	0.32	0.21	0.27	0.23	0.13	0.19

After 120 days of corrosion, content of oxygen is increasing, and specific corrosion zones rich with oxygen are formed (spectra 221, 222, and 224).

At the other zones, oxygen content is higher than after 30 days of corrosion testing. At the same spots Cr is detected with higher level compared to average. Some slightly increased level of Mo is also evident. These results indicate the cooperative influence of Cr and Mo, the corrosion, with whose oxides a passive layer is formed on the surface of the steel.

The morphology of the samples at the beginning and the changes that occurred later during the time period of the test were monitored. SEM analysis revealed that more corroded areas will appear on the surface of the samples after 120 days compared to 30 days exposure.

Studies of the cooperative effect of Cr and Mo on the corrosion resistance of superaustenitic stainless steels by Bingbing Li et all point to Pourbaix's graph showing that Fe, Cr, and Mo form stabilized complexes CrO_4^{2-}, Fe_2O_3, and MoO_4^{2-} under neutral conditions at 0.3 V [8]. While describing the electrochemical behavior of molybdenum by Klocke et al. of 42CrMo4 steel, the existence of models with different oxidation states in sodium nitrate and sodium chloride solutions was also taken into account. In this case, the molybdenum passivates as follows (Equation 2) [9]:

$$Mo + 3 \cdot H_2O \rightarrow MoO_3 + 6 \cdot H^+ + 6 \cdot e^- \quad (2)$$

This means that if Cr oxides as the oxides of the first alloying element do not provide sufficient corrosion resistance, molybdenum oxides are the ones that are passivated and thus protect the material.

4. CONCLUSION

Corrosion behavior in the marine environment of the selected steel (42CrMo4) sample was performed using NaCl solution.

Corrosion behavior was monitored using mass loss and EDS analysis. The time of exposure was selected to be 120 days.

Mass loss was almost linear dependent versus time of exposure, which indicates nearly the same rate of degradation.

SEM photographs could be used for morphology analysis of the level of degradation, and EDS results could be used to monitor the changes in chemical composition due to different oxides formation during the corrosion of the sample. The results of the EDS analysis of steel 42CrMo4 indicate the cooperative influence of of Cr and Mo, with whose oxides a passive layer is formed on the surface of the steel.

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