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COMPARATIVE STATISTICAL ANALYSIS OF CORROSION LAYERS OF TWO NI-TI ALLOYS FORMED UNDER DIFFERENT MARINE ENVIRONMENTS INFLUENCES

Špiro Ivošević[1], Nataša Kovač[2]

[1]University of Montenegro, Faculty of Maritime Studies Kotor, Put prve Bokeljske brigade, 85330 Kotor, Montenegro
[2]University of Donja Gorica, Faculty of Applied Sciences, Oktoih 1, 81000 Podgorica, Montenegro, natasa.kovac@udg.edu.me, spiroi@ucg.ac.me

ABSTRACT

This paper studies the corrosive processes caused by the influence of three different seawater environments on two Ni-Ti alloys produced by different technological processes. Statistical analysis is focused on monitoring changes in the base material as well as in the formed corrosive layer. Six samples of each Ni-Ti alloy were exposed to three different seawater environments for 6 and 12 months, after which the depth of corrosion was determined by the Focus Ion Beam method. In addition, the percentages of oxygen in the corrosive product that appeared on the surface of the alloys were determined on the same samples using semi-quantitative energy dispersive X-ray analysis. Statistical regression analysis was performed on the empirical databases formed in this way, which provided insight into the speed of development of Ni-Ti alloy corrosion processes. Different behaviours of alloys in marine environments were detected from the point of view of corrosion depth, corrosion rate, and percentage of formed oxygen, as well as the effects of the environments on the process of slowing down the corrosive degradation of the Ni-Ti alloys.

Keywords: linear regression, corrosion product, oxygen, shape memory alloy.

INTRODUCTION

The corrosion of metals and alloys is a process of spontaneous dissolution, which occurs as a process of interaction of solutions, melts, gases or the atmosphere on their surface. As a result of the corrosion process in different environments, the basic materials lose their weight and thickness, as well as lose some of the mechanical properties (strength, ductility, and impact strength). The impact of corrosion depends on the industry where it can occur, and considering published data, The World Corrosion Organization (WCO) estimates that the annual cost of corrosion worldwide is around USD 2.4 trillion (3% of the world's GDP) (Valasquez, Van Der Weide, Hernandez, & Hernandez, 2014).

The corrosion process begins on the surface of metals and alloys, from where it spreads faster or slower to the depth of the material, with a change in the chemical composition of the metal which causes the metal to dissolve completely or incompletely, or a layer of corrosion products forms on its surface. Corrosion is a degradation process of metal structures in seawater is an electrochemical process that occurs through the interaction between the metal surface, the seawater and the conductivity of the seawater. Depending on many influenced factors where the corrosion process exists, various forms of corrosion, such as general, intergranular, pitting, galvanic, crevice, stress, cavitation corrosion, corrosive fatigue, etc., can be found to date (Baumann, 2000). General corrosion and pitting are usually analysed corrosion forms. General corrosion can cover more surfaces of materials while pitting can go deep into the material (Ivošević, Vastag, Kovač, Majerič, & Rudolf, 2022a).

In that case, many techniques can identify the presence of different corrosion forms such as visual inspection, non-destructive testing (NDT) or surface analysis techniques (Caines, Khan, & Shirokoff, 2013).

To provide sustainable development and find better characteristics of materials in different industries, a lot of research was conducted in the last century to find new smart materials. One of those smart materials is shape memory materials. Since being discovered in 1932. (Jani, Leary, Subic, & Gibson, 2014), these materials have been used in different industries, such as Medicine, Aviation, Transport, Robotics, Traffic, Fashion, etc. (Huang, 1998).

One of the most attractive alloys is alloys on the base of Ni-Ti, usually called Nitinol. William Buehler and Frederick Wang (Mwangia et al., 2019), recognized and described the shape memory effect on a Ni-Ti alloy in 1962. (William, & Frederick, 1968).

The main characteristic of Ni-Ti alloy is its application at temperatures from -100 °C to 100 °C, hysteresis up to 30 °C and maximum recovery strain up to 8 % (Merola et al., 2017). The production process of this alloy is expensive and different production processes such as: Casting processes, vacuum induction melting, vacuum arc remelting, electron beam melting, plasma arc melting and electron beam melting are the most commonly used (William, & Frederick, 1968).

To analyse the behaviour of different production techniques and shape of Ni-Ti alloy, the previous research of the authors of this article analyses the behaviour of Ni-Ti alloys in different seawater environments (Ivošević, Majerić, Vukićević, & Rudolf, 2020; Ivošević, Kovač, Vastag, Majerič, & Rudolf, 2022b; Kovač, Ivošević, Vastag, Vukelić, & Rudolf, 2021; Ivošević, Vastag, & Kovač, 2022c).

The subject of this research is the compare corrosion behaviour (corrosion depth and change of corrosion product) of two different produced techniques and two different shapes of Ni–Ti alloys in a different seawater environment. The paper analyses the influences of different types of the marine environment (the atmosphere, tide, and sea) and the time of exposure. Using the Focus Ion Beam and Energy Dispersive X-Ray method, in this article we compare the corrosion depth on the alloy surface and analyse the changes in the chemical composition of the Ni–Ti alloy in different seawater environments after the 12 month exposure.

MATERIAL AND METHODS OF WORK

Materials

In this article, two shapes of Ni-Ti alloys were used. Pure metals were used to produce NiTi alloys: Ni (99.99 wt.%) and Ti (99.99 wt.%) delivered by Zlatarna Celje d.o.o. Slovenia. The Ni-Ti as cast in the shape of a disk was produced by classical casting and rolling while the NiTi CC alloy in the shape of a road was produced by a combination of vacuum remelting and the continuous casting method. A disc (diameter of 42.3 mm and thickness of 3.4 mm) and rod (diameter of 11.9 mm and a length of 50 mm) were presented in Figure 1. A total of 12 Ni-Ti alloy samples were used for this research (6 as Ni-Ti as cast alloy and 6 for Ni-Ti CC alloy samples) (Ivošević et al., 2020).

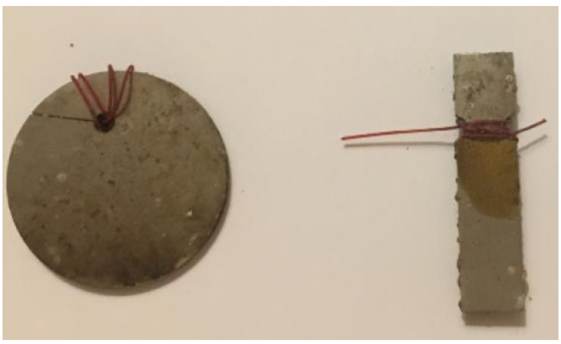


Figure 1. Ni-Ti alloy samples in the shape of disk and rod.

Related methodology

This paper studies the corrosive processes caused by the influence of three different seawater environments, as can be seen in Figure 2, on two Ni-Ti alloys produced by different technological processes. Statistical analysis is focused on monitoring changes in the base material as well as in the formed corrosive layer. Six samples of each Ni-Ti alloy were exposed to three different seawater environments for 6 and 12 months. The depth of corrosion was determined by the Focus Ion Beam method while the percentages of oxygen in the corrosive product that appeared on the surface of the alloys were determined on the same samples using semi-quantitative energy dispersive X-ray analysis (Ivošević, Kovač, Vastag, Majerič, & Rudolf, 2021). Statistical regression analysis was performed on the empirical databases formed in this way, which provided insight into the speed of development of Ni-Ti alloy corrosion processes. Different behaviours of alloys in marine environments were detected from the point of view of corrosion depth, corrosion rate, and percentage of formed oxygen, as well as the effects of the environments on the process of slowing down the corrosive degradation of the Ni-Ti alloys.

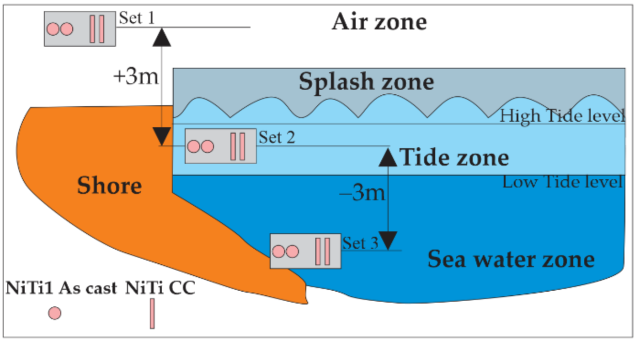


Figure 2. Scheme of related research on Ni-Ti alloys in different seawater environments.

2.3 Database

After the 6 and 12 months of exposure to the different sea environments, the depth of corrosion was measured using the FIB method and the chemical composition of the alloys was analysed using EDX analysis. Samples after 6 months of exposure were presented on Figure 3, while corresponding corrosion product and EDX analyses were presented on Figure 4, and appropriate databases were created for each alloy (Table 1).

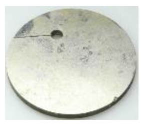
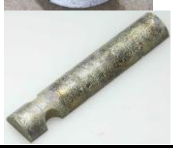
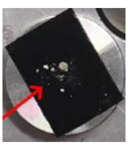
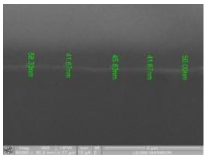
Alloys	ATMOSPHERE	TIDE	SEA WATER
Ni-Ti As cast			
Ni-Ti CC			

Figure 3. Examples of alloy samples after 6 month of exposure in the sea.

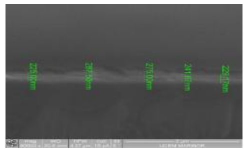


a)

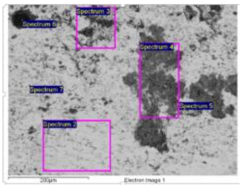
b)



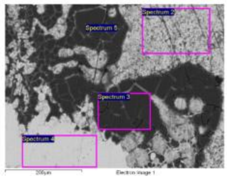
c)



d)



e)



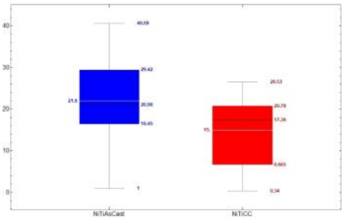
f)

Figure 4. The samples of the corrosion product that was formed in the seawater for 6 months of exposure (a – Ni-Ti As cast) and 6 months of exposure (b – Ni-Ti CC), the FIB method for Ni-Ti As cast (c) and Ni-Ti CC (d) and the corresponding EDX view of the sample ((e) - Ni-Ti As cast) and ((f) - Ni-Ti CC.

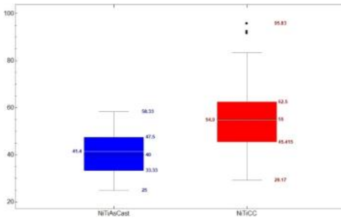
Table 1. The corresponding number of empirical data and the average depth of corrosion for the three types of the environment after 6 and 12 months for Ni-Ti As cast and Ni-Ti CC alloys.

Alloy	ATMOSPHERE	6	12	TIDE	6	12	SEAWATER	6	12
Ni-Ti As cast	No. of points	15	10	No. of points	20	20	No. of points	15	37
	Mean corrosion depth in nm	39.00	32.75	Mean corrosion depth in nm	39.	30.58	Mean corrosion depth in nm	48.75	404.05
	No. of points	12	12	No. of points	11	12	No. of points	12	12
	Mean of Oxyg. %	26.79	17.04	Mean of Oxyg. %	55.77	36.90	Mean of Oxyg. %	38.88	49.00
Ni-Ti CC	No. of points	22	24	No. of points	24	22	No. of points	24	22
	Mean corrosion depth in nm	35.8	66.36	Mean corrosion depth in nm	47.93	177.92	Mean corrosion depth in nm	144.27	239.28
	No. of points	12	12	No. of points	12	12	No. of points	22	16
	Mean of Oxyg. %	14.91	15.03	Mean of Oxyg. %	52.97	32.71	Mean of Oxyg. %	42.93	51.16

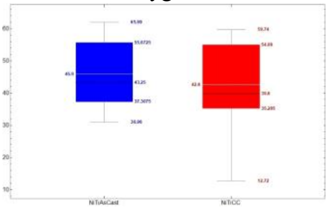
The empirical database consisting of the measured values of the amount of oxygen formed in the corrosion layer and the corresponding corrosion depth on the two observed Ni-Ti alloys (Ni-Ti As cast and Ni-Ti CC) is presented graphically in Figure 5 in the form of a box graph. Descriptive statistics related to the percentage amounts of oxygen formed in the corrosive layer are represented graphically in Figures 5a), 5c), and 5d), and the respective percentage values of oxygen formed on Ni-Ti alloys in the air, tidal and sea environments are shown respectively. Figure 5b), 5d), and 5f) show descriptive statistics for the depth of corrosion formed on Ni-Ti alloys under the influence of air, tide, and seawater environments. In all pictures, the graphic representation related to the Ni-Ti As cast alloy is shown in blue, while the Ni-Ti CC alloy is shown in red.



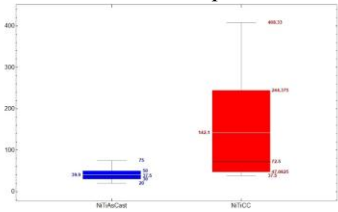
air: oxygen data



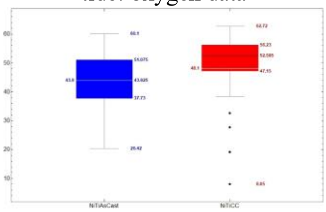
air: corrosion depth data



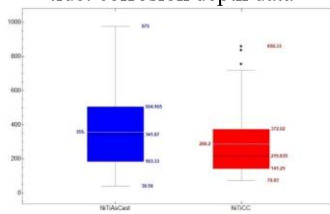
tide: oxygen data



tide: corrosion depth data



sea: oxygen data



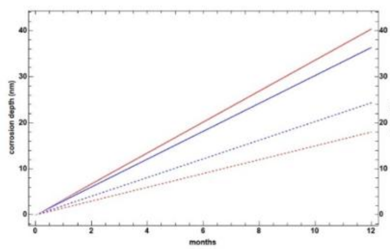
sea: corrosion depth data

Figure 5. Descriptive statistics of alloys' corrosion depth and oxygen rate in corrosion product in three types of the environment.

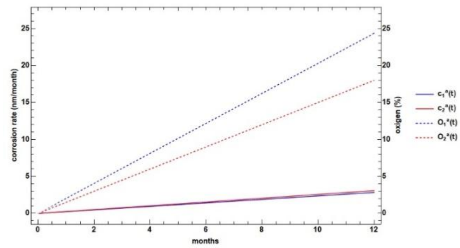
The minimum and maximum values from the empirical database, as well as the values of the first and third quartiles and the median (black line), are shown on the left side of the box graphic in Figure 5. The mean value (white line) is shown on the left side of each graph. Outliers are represented as dots on the graph.

RESULTS AND DISCUSSION

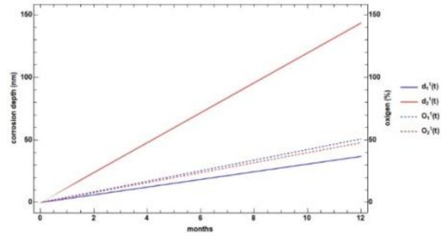
By applying linear regression over the empirical database related to the depth of corrosion and the percentage of formed oxygen in the corrosive layer in the three observed seawater environments, the diagrams are shown in Figures 6a), 6c), and 6e) were obtained, respectively. Linear regression was additionally applied to the calculated corrosion rate values. These results are shown with a comparative view of the oxidation of corrosion products after exposure in three marine environments in Figures 6b), 6d), and 6f). In this way, Figure 6 shows a set of diagrams showing the dependence of the corrosion rate (expressed in nm/month) on the percentage of oxygen content in the three investigated types of environments. In addition, Figure 4 shows the dependence of the corrosion depth (expressed in nm) on the oxygen content in the corrosion product in %(w/w). In all graphs, the Ni-Ti CC alloy is shown in red, while the blue colour is used for the Ni-Ti As cast alloy. The legends in Figure 4 have the following meaning: the exponent of the label indicates the marine environment in which the experiment was performed (a, t and s were used as labels for air, tide and sea, respectively); index 1 denotes Ni-Ti As cast alloy while index 2 represents Ni-Ti CC alloy; the symbol d is used for the depth of corrosion, O for the percentage of oxygen, while c represents the speed of corrosion. On the abscissa axis are shown months, i.e., the elapsed time of exposure of the alloy to the marine environment, while on the ordinate axis is shown the dependent variable (corrosion depth, corrosion rate, percentage of oxygen).



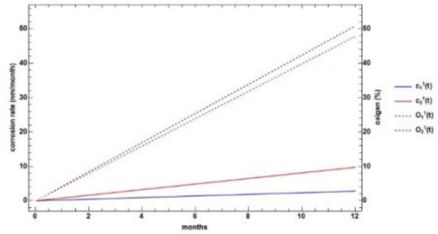
air: corrosion depth



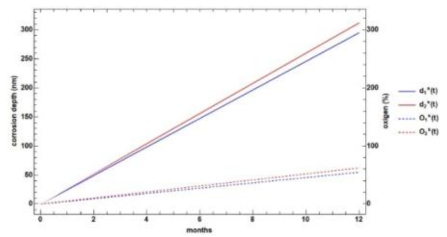
air: corrosion rate



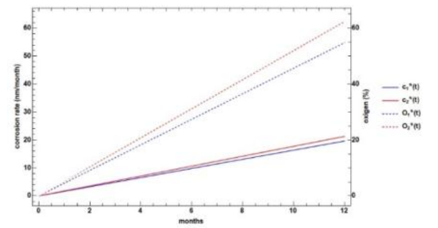
tide: corrosion depth



tide: corrosion rate



sea: corrosion depth



sea: corrosion rate

Figure 6. The corrosion depth and corrosion rate of the alloy and oxygen rate in corrosion product in three types of the environment.

The corrosion rate and depth of corrosion for both Ni-Ti alloys are the lowest in the air environment, and the highest in the sea environment. In these two environments, both alloys show similar behaviour, and there are no more mutual deviations in the values of corrosion depth and speed. The increase in corrosive values is accompanied by adequate increases in the percentage of formed oxygen in the corrosive layer of alloys. The lowest percentage of oxygen occurrence is manifested in both alloys in the air environment, while it is the highest in the sea environment. When alloys are exposed to the alternating influence of sea and air (tidal environment), the alloys show different behaviour in terms of depth and speed of corrosion. The Ni-Ti CC alloy is significantly more susceptible to corrosion processes in a tidal environment and shows significantly higher corrosion depth and speed values. However, the percentage of oxygen formed in the corrosion layer in both alloys remains approximately the same value. Moreover, the percentage of oxygen is slightly higher for the Ni-Ti As cast alloy when exposed to the influence of air and tide, compared to the Ni-Ti CC alloy. Only in the marine environment is the percentage of formed oxygen higher with the Ni-Ti CC alloy.

CONCLUSIONS

In this article, a comparative analysis of the corrosion process of two shape memory alloys based on Ni-Ti, which were produced by two different production processes and two shapes, was performed. All alloy samples used in this research were exposed to different influences of the marine environment for 6 and 12 months. A comparison was made between the corrosion depth of the base alloy and the changes in the chemical composition of the corrosion product formed on the surface of the alloy.

Based on empirical data and statistical analysis of the measured corrosion depth for the two observed Ni-Ti alloys, it can be concluded that in all three seawater environments Ni-Ti CC alloys show more intense corrosive processes. Namely, in all three environments, based on the figures, it can be seen that the depth of corrosion will always have a higher value for the Ni-Ti CC alloy compared to the Ni-Ti As cast alloy. In the air environment and the sea environment, both alloys have similar behaviour, which is reflected in approximately the same values of corrosion depth. In changing conditions with alternating exposure to air and sea, i.e., in tidal conditions, the observed alloys exhibit significantly different properties. The corrosion depth values are significantly higher (approximately four times) for Ni-Ti CC alloy compared to the measured corrosion depth values for Ni-Ti As cast alloy. The same properties and growth trends are shown when it comes to the corrosion rate of these alloys.

From the point of view of oxygen rate, the situation is somewhat different. Namely, the oxygen rate formed in the corrosive layer has lower values in Ni-Ti CC alloy compared to Ni-Ti As cast alloy when metal samples are released under the influence of air and tide. In the marine environment, the oxygen rate is slightly higher with Ni-Ti As cast alloy. The increase in oxygen rate in the corrosive layer follows the growth trend of corrosion rate in both Ni-Ti alloys. At the same time, the greatest imbalance between the relative value of oxygen and the depth of corrosion is observed in the Ni-Ti CC alloy in the air and tidal environment. In the marine environment, both alloys have large values of the relative ratio of the amount of oxygen and the value of the depth of corrosion. Based on this, it can be concluded that the amount of oxygen in the formed corrosive layer of Ni-Ti alloys that are exposed to the sea is relatively small, but that intensive corrosive processes are caused by other factors of the marine environment such as chlorides or salts!

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