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The Analyses of the Rate of Pitting Corrosion of a NiTi Rod in a Natural Marine Environment

Abstract

The analysis of the behaviour of new materials in the natural environment is important for their application and commercial use. In order to explore the application of Shape Memory Alloys in the Maritime industry, this research focuses on the corrosive behaviour of the NiTi rod that was produced by means of a continuous casting process. The experiment included three samples of NiTi rods that were exposed to the marine environment for 6, 12 and 18 months at a depth of 3 metres below the surface. The morphological and chemical changes were analysed separately during the experiment. Ultrasonic thickness equipment and the Scanning Electron Microscope (SEM) technique were used for the tests that determined the corrosion rates and detected pitting. The changes in the chemical composition of the NiTi rod were investigated by means of an Energy Dispersive X-ray (EDX) analysis, in order to define the pitting behaviour of the rod`s surfaces during its exposure to seawater. The obtained research results prove that the rate of pitting corrosion follows a progressive curve – the minimum value of corrosion rate equalled 0.04 mm/month, while the maximum value was 0.12 mm/month.

Key words: NiTi rod, seawater, pitting corrosion, chemical composition, SEM, EDX

1. Introduction

Shape memory materials are now applied in various industries, such as the Automotive, Railway, Aircraft and Maritime industries, as well as in Medicine and Robotics [1]. The behaviour and various applications of these materials are researched in laboratories and natural settings. Although laboratory tests are necessary for the research on the basic physical and mechanical characteristics and chemical composition of materials, the practical application of materials requires research in natural environmental conditions over a longer period of exposure. The behaviour of materials and their susceptibility in different exploitation conditions can only be determined in natural settings.

Shape memory materials were discovered in 1932, and recognised for their thermo-mechanical properties, such as superelasticity, shape memory effect, high damping capacity and double shape memory effect [2]. The key thermo-mechanical properties were discovered on the basis of Ag, Au, Al, Cu, Fe, etc. However, the most significant applications are based on Cu, Al and Ni [3]. Binary, trinary and quaternary systems of alloys ensure good mechanical and chemical characteristics, as well as biocompatibility and corrosion resistance.

In addition to chemical composition, the process of alloy production is also very significant for the provision of their good performance. The main problem with the production is the possibility of further plastic deformation, especially cold drawing, that is caused by large grain size. New processing techniques, such as continuous casting and rapid solidification, can be used to prevent the formation of coarse grains on Shape Memory Alloys (SMAs).

NiTi alloys shaped like discs, wires and rods are applied frequently in different industries as a result of various production processes. Among the different production processes, including the melting process and the standard techniques for hot and cold working [4], casting processes are used most frequently for the production of NiTi alloys [5]. Continuous casting has recently emerged as a new production process of SMAs [6]. SMAs are characterised primarily by their capacity to restore their original dimensional integrity (pre-deformed shape and size) after undergoing substantial deformation when heated to a certain temperature [4]. This temperature induced strain recovery and other elasticity variants exhibited by SMAs make these materials suitable for use in various industrial applications.

The application of SMAs in the Maritime industry depends on the different conditions of their exploitation and characteristics. Corrosion is considered a dominant degradation process in seawater. More precisely, the corrosion 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.

There are different types of physical corrosion, e.g. intergranular, galvanic, crevice [7], stress, cavitation corrosion, corrosion fatigue, etc. However, the most frequent types in the Maritime industry are uniform and pitting corrosion [8]. For this reason, a number of studies calculated the corrosion potential of SMAs prior to their application. SMAs are based on two-phase changes, in which the corrosion rate of the austenitic phase is higher than the rate of the martensitic phase. Almost all SMAs are more resistant to corrosion than traditional alloys. This is the result of the hyperelastic behaviour of the polycrystalline structure [9]. Due to their pseudoelasticity, NiTi alloys show excellent resistance to cavitation erosion [10]. The appearance of different physical forms of corrosion requires research on the causes of corrosion, and determination of the extent and rate of the corrosion. Numerous corrosion models have been developed so far, and are based mainly on linear and nonlinear models [11].

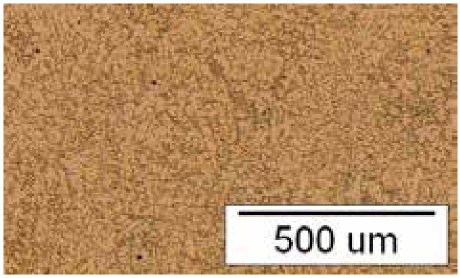
Experimental research in a real marine environment can best describe which forms of corrosion can occur and how intense the corrosion rate is. This paper indicates the intensity of pitting corrosion and chemical changes in the pitting itself, on its edge and in the hole of the pit for the case of NiTi alloys in the form of rods. In fact, it is a continuation of research work shown in the previous articles, where the behaviour of SMAs was presented in the marine environment [6, 11, 12]. In this study, the motivation was to determine the degree of pitting corrosion in seawater on a NiTi rod fabricated by a continuous casting process. After the introductory considerations and a description of the characteristics and corrosion of the NiTi rod, the second chapter analyses the NiTi rod and the research methodology. The third chapter presents the research results of the pitting corrosion rate, while the fourth chapter exhibits the concluding remarks.

2. Materials and Methods

2.1. The Characteristics of the NiTi rods

This paper analyses a NiTi rod whose diameter was d = 11,9 mm and a length of 50 mm (Figure 1a). The rods were produced by means of the vertical continuous casting process with a previous vacuum remelting. The production of the rod was based on the use of pure metal components - Ni and Ti - with a high degree of purity (99.99 %). All NiTi rod samples were ground after electro-erosion, so that they were cut longitudinally into two halves, thus obtaining a sample of a rod with a half cross-section (Fig. 1a). A notch was incised on this half-bar so that the samples could be dropped with a plastic wire to the desired test site at sea. Analyses of three rods samples in a natural marine environment were performed in this research. The initial analysis of the initial rod was based on the macro observation, and, in the second part, the microstructure was examined (Figure 1b) obtained by light microscopy (Nikon Epiphot 200, Japan), showing characteristic dendritic growth.

a)



b)

Figure 1. NiTi rod test samples: a) Both sides of the test samples of the NiTi rod (diameter of 11.9 mm), b) Dendritic microstructure [6]

In order to determine the chemical composition of the NiTi rod in seawater before testing, the samples were measured by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and X-Ray Fluorescence (XRF). The analysis of chemical composition of the NiTi rods detected a range of metals, as shown in Table 1 [6]. The difference in the desired chemical composition was due to the manufacturing process itself - remelting, where sufficient mixing of the melt was not provided. The induction melting furnace does not have the possibility of switching from medium to low frequency (1500 Hz), so a distinctly inhomogeneous NiTi rod was formed.

Table 1. The percentage composition of the NiTi rod analysed

Rod	% Ni		% Ti		% Fe	
	ICP	XRF	ICP	XRF	ICP	XRF
NiTi	62.6	62.5-62.6	35.9	35.9	1.4	1.4

2.2 Proposed Problem and Corresponding Methodology

However, this research focuses on the progress of pitting corrosion on the NiTi rod that was exposed to the influence of seawater. Namely, 3 samples of a NiTi rod were exposed to the marine environment for 6, 12 and 18 months. The samples were immersed into the sea near the coast, at a depth of three metres, over the maximum period of 18 months.

During the research between August, 2018 and March, 2020, the parameters of the seawater (temperature and salinity) were measured by the Institute of Biology at the University of Montenegro. Table 2 shows the relevant data on the minimum and maximum sea temperatures and salinity on the sea`s surface, which were measured during 2019 and 2020 in January and December. The previously published data [13] show a very small difference between the temperatures on the sea`s surface and at the depth of 5 m, while a more significant difference was noted in salinity on the surface and in shallow water, mostly during the rainy season.

Table 2. The values of marine parameters during 2019 and 2020 [14].

Year	**Temperature ^{0}C**	**Temperature ^{0}C**	**Max. Temp. ^{0}C**	**Min. Temp. ^{0}C**
2019	13.4 - January	12.88-December	25.42-September	11.7-February
2020	13.61 - January	15.41-December	25.90-August	13.0-March
Year	**Salinity** (‰)	**Salinity** (‰)	**Max. Salinity** (‰)	**Min. Salinity** (‰)
2019	32.8 - January	14.00-December	39.00-September	14.00-December
2020	38.20 - January	34.90-December	28.30-August	20.0-March

In Figure 2 can be see the conceptual model of the conducted research. In total three NiTi rods were exposed to seawater at a depth of three metres below the surface, close to the shore. After 6, 12 and 18 months of exposure the rod samples were tested by visual inspection, in order to identify surface corrosion. After visual inspection, the rod samples after 18 months of exposure were observed by a Scanning Electron Microscope (SEM), and chemical composition analysis was also performed on them using Energy Dispersive X-Ray (EDX) analyses. The first SEM inspections were used to calculate the corrosion rate, while the second EDX analyses enabled calculation of the chemical composition of the hole and the edge of the pitting.

Figure 2 shows the conceptual model of the research.

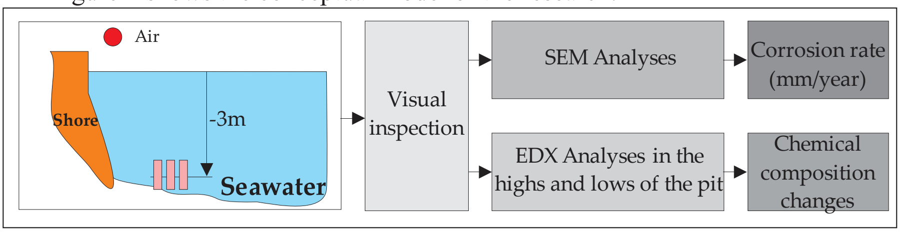


Figure 2. The scheme of the conceptual model of the research (location of the rod samples and type of characterisation)

2.2.1. The SEM Dimensional Analysis

The pitting corrosion depth was measured with a SEM microscope, Quanta 200 3D (FEI, USA). Figure 3 shows the measuring scheme of the pitting corrosion depth for the NiTi rods based on the SEM microscopy. Due to the irregular shape of the corroded sample, the corrosion depth was calculated based on the difference between the high and low focus areas on the corrosion features of the sample. The distance Z determines the distance from the SEM aperture to the focused feature. When the focus area is centred on an area above the corrosion pit, the SEM shows a smaller Z value than when the focus area is centred inside the corrosion pit. The focusing values are shown in this paper as Z high and Z low, as shown in Figures 3 and 5 and Table 2. The pitting depth was calculated as the distance between the low Z focus area minus the high Z focus area:

$$d_{pit} = Z_L - Z_H \tag{1}$$

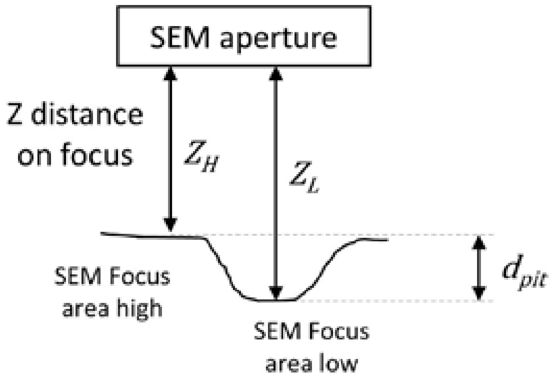


Figure 3. The scheme of focus measuring of the NiTi rods by the SEM microscope

The obtained values of pitting corrosion depth of the NiTi rods were subjected to statistical analysis in order to determine the beginning of the corrosive processes. The scientific literature investigated different corrosion models [15-20]. In this paper, statistical analysis was performed by fitting the usual corrosion linear models [21] to the data presented in Table 2. Accordingly, the linear corrosion model can be expressed as:

$$d(t) = c_1(t - T_{cl})^{c_2} \tag{2}$$

whereby the unknown coefficient (c_2) usually has the value of 1 or 1/3 [21]. This study examined the pitting corrosion depth as a linear model with the coefficient $c_2 = 1$. The statistical approach thus resulted in three different linear models, whose form was:

$$d(t) = c_1(t - T_{cl}) \tag{3}$$

whereby c_1 is the corrosion rate expressed in mm/month, $d(t)$ is the pitting corrosion depth measured in mm, T_{cl} is the time when the corrosion started expressed in the number of months, while t is the time of exposure to the environment expressed in the number of months. The fitted models were based on the assumption that corrosion starts immediately after the exposure of the samples to the environmental influences (T_{cl} = 0), or that corrosion starts after 6 or 12 months (i.e. T_{cl} = 6, and T_{cl} = 12) of exposure to the environment.

2.2.2. The EDX Analysis of the NiTi rod

All rod samples exposed to the influence of seawater at a depth of 3 metres were afterwards inspected visually. Fouling and surface corrosion were observed on the rod samples that were exposed to seawater for 6 and 12 months (Figures 4a and 4b). Pitting was observed on the rod sample that was exposed to seawater for 18 months (Figure 5b).

The chemical composition of the selected NiTi rod samples was determined by means of a high-resolution, field-emission SEM Sirion 400 NC (FEI, USA), which was equipped with an EDX detector - INCA 350 (Oxford instruments, UK), that enables extremely high magnifications (up to a million times) in high resolution (1 nm). The EDX semi-quantitative analysis determined the chemical composition of the NiTi rod after exposure to the marine environment, as well as the content of the elements on the pit edge and in the pit. The analysis included a total of 10 spectrums - five spectrums from the pit and five from the edge (Figure 5b).

a) b)

Figure 4. NiTi rods: (a) After 6 months of exposure, (b) After 12 months of exposure

3. Results

3.1. The Value of the Pitting Corrosion Rate

An illustration of the execution of the measurement by placing the sample in the SEM chamber of the microscope is shown in Figure 5a, while the corresponding values (Z high and Z low) and the calculated pit depth expressed in mm are shown in Table 3. Five pit depths were calculated by the measurement of the difference between the high and low SEM focus. Figure 5b shows the locations of the ten values (five on the pit edge and five in the pit) that were obtained by means of the SEM. The SEM views of sample edges and pits are presented in Figures 5c and 5d.

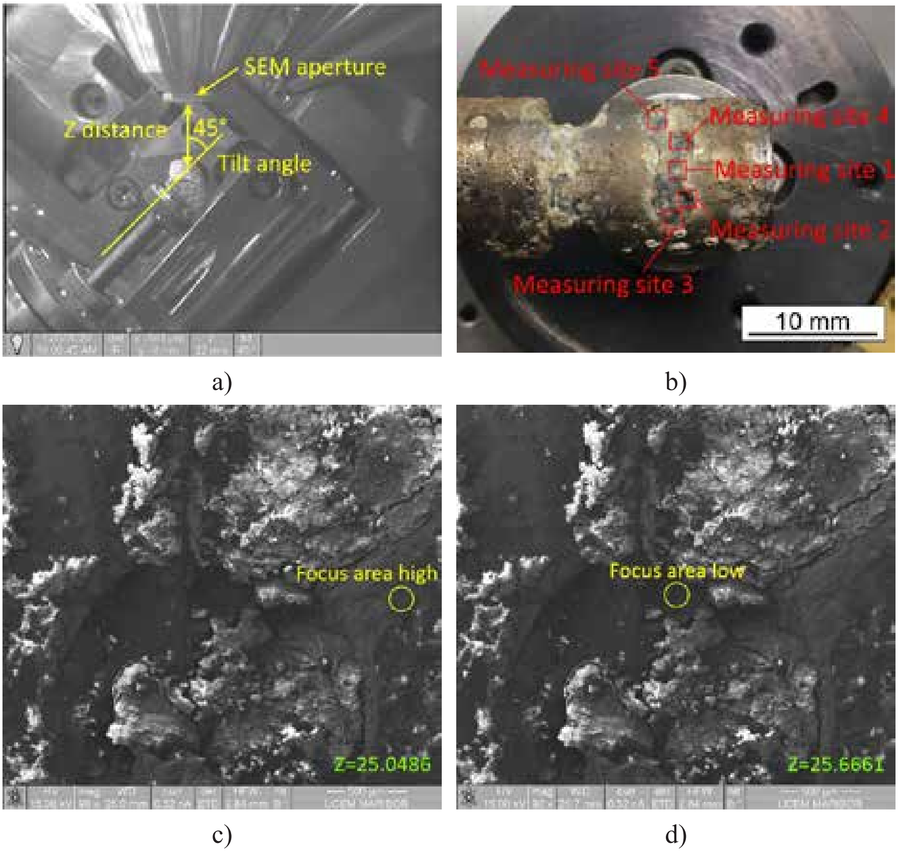


Figure 5. The NiTi rod after 18 months of exposure a) Measuring equipment b) The position of the measured pit c) High focus measuring - area 1 d) Low focus measuring - area 1

Table 3. Pit depth calculated by the SEM

	Z high Z_H	Z low Z_L	Pitting depth d_{pit}	
Measurement 1	25.0486	25.6661	0.6175	mm
Measurement 2	26.1029	26.5829	0.4800	mm
Measurement 3	30.0068	30.7716	0.7648	mm
Measurement 4	26.2902	26.5852	0.2950	mm
Measurement 5	30.6398	31.7052	1.0654	mm

Based on the fits of the linear models to the data shown in Table 3, the monthly corrosion rates equal 0.0414176 mm/month, 0.0621264 mm/month, and 0.124253 mm/month, assuming that corrosion starts immediately, or after six and twelve months of exposure (, , and months). More precisely, the depth of pitting corrosion in the three cases can be represented by the following linear corrosion models:

$$d(t) = 0.0414176t \tag{4}$$

$$d(t) = 0.0621264(t-6) \tag{5}$$

$$d(t) = 0.124253(t-12) \tag{6}$$

The three models can also be interpreted in terms of corrosion rates. Namely, expression (4) corresponds to the model whose monthly pitting corrosion rate was the lowest, expression (5) corresponds to the model with a moderate monthly corrosion rate, while expression (6) describes the model with the highest monthly corrosion rate.

The fitted linear models (4-6) are presented graphically in Figure 6, and show a functional dependence of pitting corrosion depth on the time of exposure.

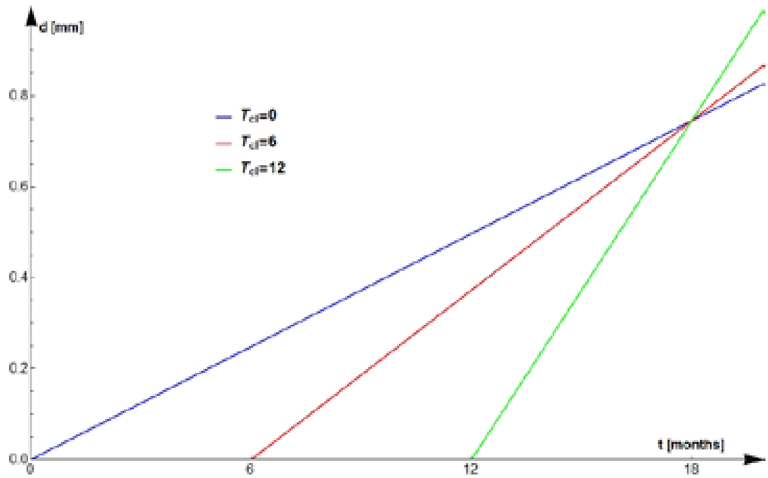


Figure 6. Fitted linear models

Figure 7 shows the residual plot of the models described by expressions (4) - (6). The graph shows if the residuals follow the normal distribution well. According to Figure 7, the fitting characteristics of models (4) and (5) are not good enough, as there are significant deviations from the straight line. On the contrary, in the case of model

(6) the probability plot is normal, and the points generally follow a straight line. There is no evidence of non-normality, outliers, or unidentified variables. This confirms that model (6) fits the data from Table 2 in the best way.

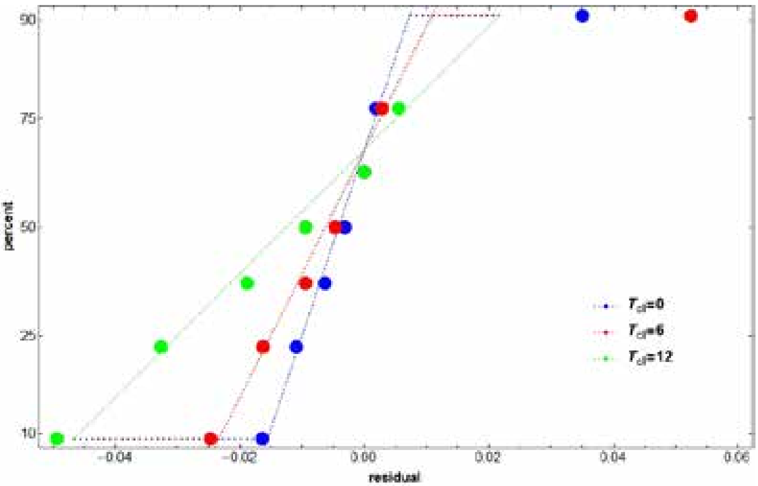


Figure 7. Normal residual plot of the fitted linear models

For the fitted model (6) in the case of , the variance around the fitted values is 0.0899699. More precisely, the calculated mean squared error is 0.0899699, which results in a low Standard Deviation value of the distance between the data values and the fitted values. The corresponding Standard Deviation equals 0.299950. The R squared (R^2) value of the model (6) is R^2=0.860677, which means that the variation of 86.07% in can be explained by a fitted model. In that sense, it can be concluded that the model represented by expression (6) describes the pitting corrosion values very well.

3.2. NiTi rod pitting chemical composition

The EDX analysis determined the chemical composition of the pit and the pit edge at 5 points on the NiTi rod. There were 6 spectra for each point scanned. Figure 8 shows the average chemical composition obtained by means of the EDX analysis for the pit and the pit edge.

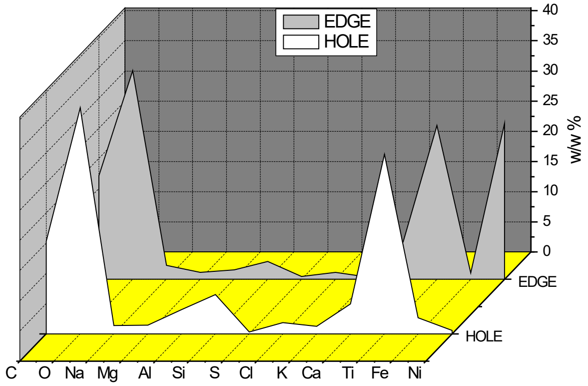


Figure 8. The average chemical composition of the pit edge and the pit based on the EDX analysis

As shown in Figure 8, the chemical compositions of the pit and the pit edge differ slightly in terms of the majority of the elements detected through the EDX analysis. A small increase in the oxygen content indicates slightly more intensive corrosion in the pit than on the edge, which was expected, considering that the corrosion flows with the formation of pitting.

Interestingly, according to Figure 8, there is another difference between the chemical compositions of the edge and pit - the pit has a rather increased content of aluminium and silicon compared to the edge, which can be attributed to the deposition of silicate (sand) in the pit.

The notable differences in the corrosive behaviour of the analysed NiTi rods at different pitting points can be attributed to the content of nickel. Namely, a slightly lower content of titanium on the edge compared to the pit, along with a significant difference in the average content of nickel on the edge (~ 26%) and in the (pit ~ 4.5%), indicate an excessive degradation or corrosion of the nickel during pitting. The presence of nickel could not be detected at most of the points measured.

4. Conclusion

This article investigated the behaviour of a NiTi rod in seawater at a depth of 3 m below the sea surface. The research relied on a linear corrosion model, and confirmed that the minimum corrosion rate was 0.04 mm/month, while the maximum corrosion rate was 0.12 mm/month. The presence of Si was observed in the pit, which accelerated the degradation of the pit. The whole process of corrosion of a NiTi rod in the sea is based on the fact that the degradation of Ni is more affected by pitting corrosion than the degradation of Ti.

Based on the statistical analysis, it was proven that the model with a moderate monthly corrosion rate, whose monthly corrosion rate was the highest, is also the most suitable for describing pitting corrosion depth on similar alloys. Statistical analysis shows that a NiTi rod in a seawater environment shows the tendency of a delayed onset of pitting corrosion i.e., corrosion occurs after 12 months of exposure to environmental influences. In that sense, rapid corrosive processes with intensive pitting start on the metal structures of a NiTi rod after 12 months of exposure.

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