

Corrosion Behaviour of CuAlNi SMA in different Coastal Environments

Gyöngyi Vastag^{1,*}, Špiro Ivošević², Danilo Nikolić², Goran Vukelić³, Rebeka Rudolf⁴

¹ University Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia

² Faculty of Maritime Studies Kotor, University of Montenegro, Put I Bokeljske brigade 44, 85330 Kotor, Montenegro

³ University of Rijeka, Faculty of Maritime Studies, Studentska 2, 51000 Rijeka, Croatia

⁴ University of Maribor, Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia

*E-mail: djendji.vastag@dh.uns.ac.rs

Received: 3 March 2021/ Accepted: 30 September 2021 / Published: 10 November 2021

Recently, the usage of different Shape Memory Alloys (SMAs) in the coastal environments has been registered increasingly, so knowledge of their corrosion behaviour is crucial. In accordance with this, the corrosion behaviour of CuAlNi SMA was monitored in different coastal environments after 6 months of exposure time. The corrosion effect of CuAlNi SMA was evaluated by the changes in chemical composition of the surface by using Energy-Dispersive X-ray spectroscopy (EDS). The measured chemical compositions were correlated by using linear regression analysis and selected chemometrics methods (Cluster Analysis and Principal Component Analysis – CA, PCA) with the aim to identify the impact of the environment on the corrosion behaviour of CuAlNi SMA, and to find the correlations between the formatted corrosion products, depending on the given conditions. The obtained results show that the used multivariate methods have the ability to register the impact of selected environments on the corrosion behaviour of CuAlNi SMAs.

Keywords: Shape Memory Alloy, CuAlNi, corrosion, coastal environment, chemometrics

1. INTRODUCTION

One of the major material losses worldwide are the losses resulting from corrosion of the structural materials, raw materials, products, or semi-finished products. The latest estimates indicate that the damage caused by the corrosion of the material (predominantly metals) is about 3-4% of the Gross National Income of developed countries [1-2]. Therefore, there is an understandable high interest in reducing the degree of the structural materials` corrosion.

With the increasing utilisation of marine resources, a large number of different fixed and mobile metal constructions are put to use in coastal environments. On the other hand, corrosion of structural

materials at coastal conditions is very pronounced, since, in addition to the usual corrosion factors, high humidity and air salinity further contribute to increasing the degree of structural materials' corrosion [3]. Due to the complexity of the marine conditions, metal structures exposed to coastal environments are exposed to different types of corrosion, predominantly it is electrochemical corrosion, but very often microbiological corrosion can also occur, as well as stress corrosion, etc. [4-6]. In order to protect the materials adequately against corrosion, it is first necessary to become aware of the corrosion behaviour of a material under the given conditions and if it is possible to predict it [7]. Moreover, the knowledge of the chemical composition of the corrosion products also may indicate their impact on the environmental pollution.

Shape Memory Alloys (SMAs) represent a relatively new group of smart materials, whose application in medicine and different types of industry sectors shows great potential. The main characteristic of the SMAs is that they can recover their original shapes when heated above a certain characteristic transformation temperature [8]. The Shape Memory Effect (SME) is a phenomenon which represents transformation of the solid state from martensite to austenite, and vice versa. [9]. Numerous researches have been performed to investigate the key thermo-mechanical properties of SMA (Shape Memory Effect, superelastic and pseudoelastic effects, high damping capacity and double Shape Memory Effect), and also the corrosion resistance in different environments [10-14], for the reason that these traits are key factors for their applications in a various fields of industry.

NiTi SMA is one of more functional, successful, commercial and useful alloys with SME [15-17]. However, their commercial application is limited, due to some of their disadvantages, such as a low transformation temperature, difficulty in production and processing, complexity and cost. Because of that, an increase interest in copper and iron based SMAs has been observed. These type of SMAs compared to NiTi alloys have lower production costs, but they still dispose of good shape-memory properties and also good process ability [18]. The major feature of iron based SMAs is easy and simply manufacturing and good workability. Cu-based SAMs have simpler and less expensive production processes [19] than iron-based shape memory alloys but still have an excellent shape memory behaviour [20].

Recently, the usage of different SMAs in the coastal environments has been registered increasingly [21], so the interest in their corrosive behaviour has also increased. For that reason, the aim of this study was to monitor the corrosion behaviour of CuAlNi SMAs in different coastal conditions. After 6 months of CuAlNi SMA exposure, the corrosion behaviour of the different environments on the chemical composition was investigated by using EDS. In order to identify the influence of the marine environments on the degradation of CuAlNi SMAs, and to find the correlations between the most important degradation products of this alloy in the given conditions, the results obtained by EDS were correlated by applying linear regression analysis and selected chemometrics methods (CA, PCA).

2. EXPERIMENTAL

2.1. Materials

A continuously cast CuAlNi SMA rod with a diameter of $2r = 7$ mm (Fig. 1a) and with average composition w/w: 12.20 % Al, 3.99% Ni and 83.91% Cu was used for the study [22]. The rod was cut

by electro-erosion to the selected dimensions of samples. In the final step all samples were ground to remove the remnants of erosion cutting and possible impurities. For microstructure investigation the samples were prepared metallographically (Figs. 1b-d) and observed with light microscopy (a Nikon EPIPHOT 300 light microscope).

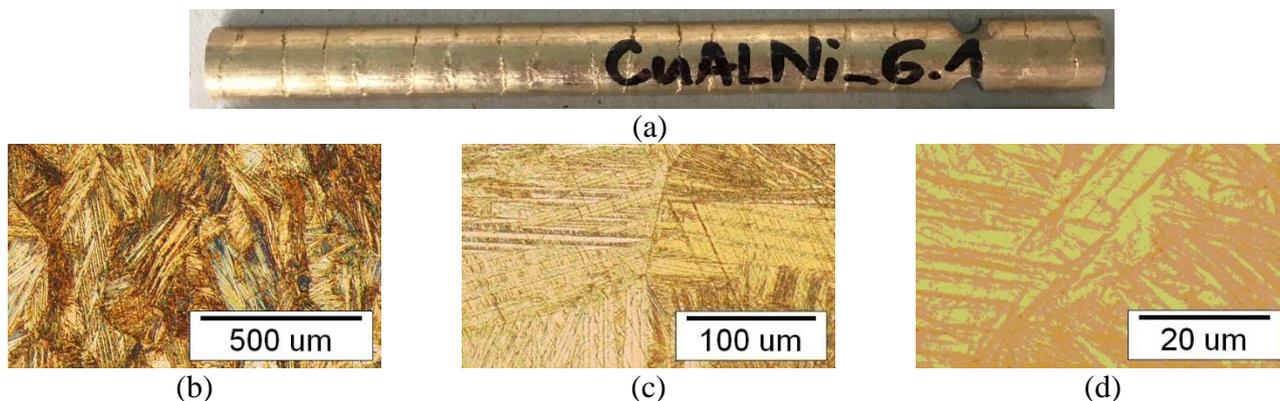


Figure 1. (a) CuAlNi SMA rod ($2r=7\text{mm}$), (b-d) Characteristic microstructure

2.2. Coastal environment place and parameters

The experiment – exposure to different coastal conditions - was carried out in such a way that the samples were placed in the three different environmental zones with a time period: in 1st September 2018 and taken out in 1st March 2019 (Fig. 2). In total three samples of CuAlNi alloy were placed in such a way that one was placed on the shore near the sea at a height of 3 m from the sea surface (Atmosphere), the second was placed in mixed conditions on the sea surface (Tide zone) and the third was placed in the sea at a depth of 3 m (Seawater).



Figure 2. Macroscopic presentation of CuAlNi SMA morphologies after 6 months exposure: (a) Atmosphere; (b) Tide zone; and (c) Seawater

During the research, the parameters of the environment were not measured, but on the basis of the available and published data from relevant sources [23], the key environmental parameters were followed, such as air temperature and the temperature, conductivity and salinity of the seawater for the area of Boka Kotorska Bay, where the research was conducted [23]. Based on the available data, it can be pointed out that the average value of the air temperature was in range from 20.5°C (September) up to 7.5°C (February), while the average minimum month temperature was 6.7°C (January) [23]. Data for

the seawater average month temperature on the depth of 0.5 m from sea surface show that it ranged from 23.2⁰C (September) to 13.0⁰C (February), while lowest average seawater temperature was 11.4 ⁰C (January). Average month conductivity of seawater was in the range from 54.5mS/cm (September) to 33.4 mS/cm in (February), while average month salinity was in range from 36.0‰ (September) to 21.6‰ (February) [23].

2.3. Methods

The surfaces of the CuAlNi SMA samples were analysed before and after exposure, using a high-resolution (1nm) Field Emission Scanning Electron Microscope SIRION 400C. The microscope has an Energy Dispersive Spectrometer (EDS) - Oxford INCA 350 and the Schottky electron source. In this research, three places were selected on the surface of each sample, where several spectra were measured (approximately 6).

The obtained EDS spectra were processed by applying the Origin 6.1 software, and the chemometric calculations were made by using the Statistics 13.5.017 software (StatSoft Inc., Tulsa, OK, USA). Results in the calculation were marked as: Seawater - S, Atmosphere – A, and Tide zone- T. The number behind the abbreviation point out the sample, and the second is the number of the spectrum within the sample.

3. RESULTS AND DISCUSSION

3.1. Analysis of the EDS results

The SEM characteristics microstructures of the CuAlNi SMAs for 3 selected places after half year exposure to selected environments are presented in Fig. 3. These places are areas where EDS analysis was performed (visible as Spectrum 1- Spectrum 6).

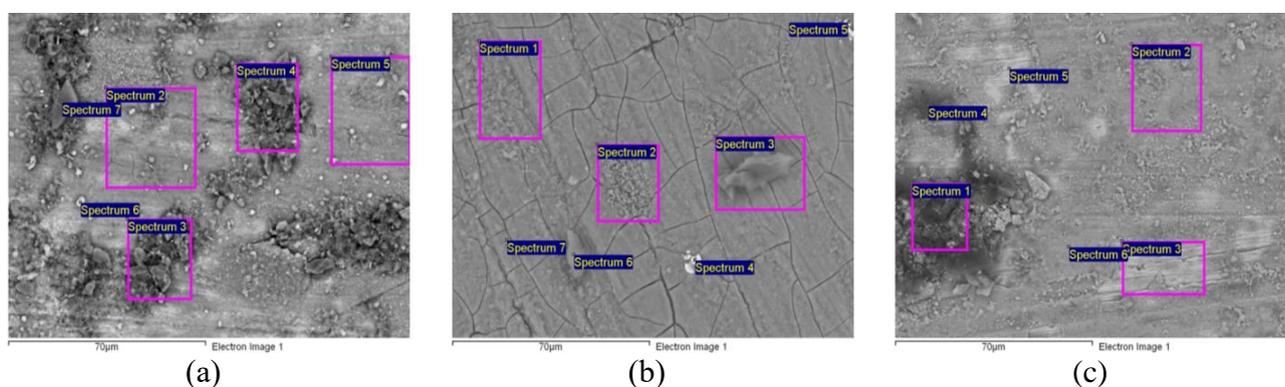


Figure 3. Characteristic microstructure of CuAlNi SMAs after 6 months exposure in: (a) Seawater; (b) Tidal zone; (c) Atmosphere

From Fig.3 it is evident that the degradation process leaves behind quite a heterogeneous surface of the CuAlNi SMA. The microstructure which was exposed to sea effects for 6 months (Figure 3a)

shows that corrosion products and an inorganic salt (heterogeneous composition of: Ca, Mg, K, Na, Cl, SO_4^{2-}) was precipitated on the CuAlNi SMA's surface. Moreover, these products did not cover the CuAlNi SMA's surface uniformly, as a result of which it was unable to provide future corrosion protection [24]. The obtained results also indicated that, during this time, no separation of algae or deposits of any organic origin can be observed on the CuAlNi SMA's surface [25,26]. Fig. 3b shows the surface of the CuAlNi SMA after tidal zone corrosive effects. The surface seems much more uniform than with seawater, but, based on the EDS result (Fig. 4), it is also heterogeneous, and has a very similar composition as the surface after the seawater's effects. On the basis of this, the effects of the localities cannot be distinguished. What can be pointed out as a difference is that the protective layer on the CuAlNi SMA surface has cracked into the tidal zone, which can be attributed to the action of the wave strikes [27].

In the atmosphere zone (Fig. 3c), as was expected, the corrosion products on the CuAlNi SMA's surface were thinner and more compact. Also, as in the case of the other environments, a certain amount of inorganic salts were registered, which reached the surface thanks to the high Relative Humidity (RH) level of the marine atmosphere environment [28], though vapour condensed or adsorbed on the active sites and formed an electrolyte layer on the surface [25, 28, 29].

3.2. Comparison of results obtained after 6 months of exposure of CuAlNi SMAs in different coastal environments

Fig.4 shows the total metals' content (Cu + Al + Ni) after corrosion at the tested locations.

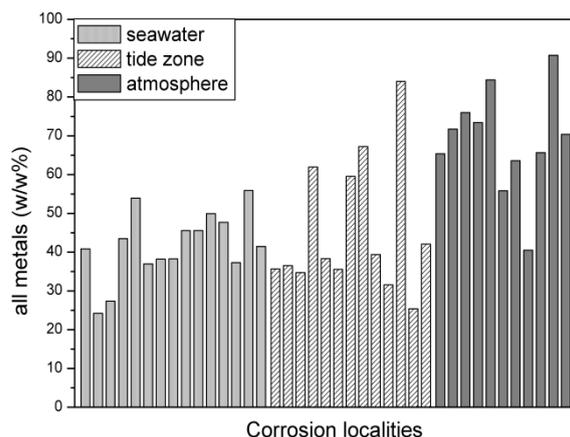


Figure 4. Total metal content after corrosion of the investigated CuAlNi SMAs at the tested locations.

It is clearly evident from Fig. 4 that, between individual measuring points, a large difference in the metal content was registered in all of the tested corrosion environments. In cases like this, it is difficult to estimate the true impact of the tested marine localities on the corrosion. Regardless of this fact, on average, it can be said that the least metal was lost in the atmosphere, while about the same amount of metal dissolution was registered by the tide zone and in the seawater.

Considering the corrosion of each individual metal (Figs.5a-c), the following can be concluded:

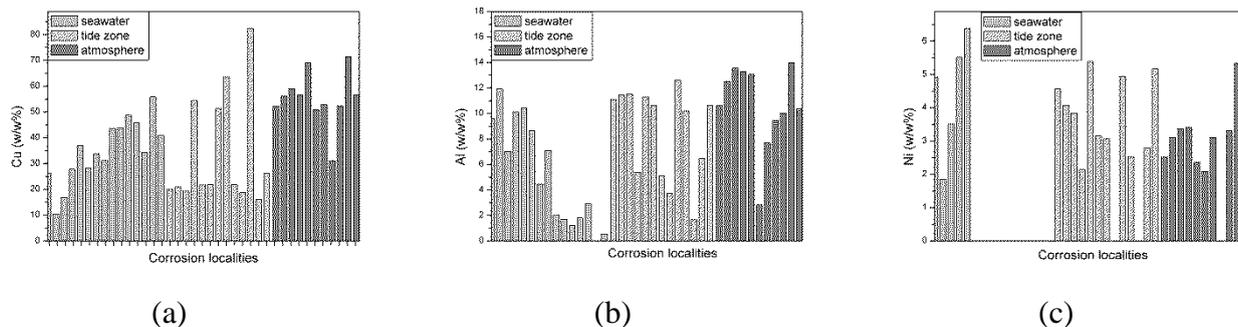


Figure 5. Content of (a) Copper, (b) Aluminum and (c) Nickel after corrosion of the investigated CuAlNi SMAs at the tested locations.

Despite the large heterogeneity of the analysed data, from Fig.5 it is evident that the nickel dissolution (c) in the seawater was the most intensive, and in many of the measuring places it was completely dissolved, while, on average its content at the tides and in the atmosphere was approximately equal. In the case of the aluminium (b), the most intense corrosion also happened in the seawater, unlike the copper (a), which was the most intensively corroded by the tide zone. The corrosion range of each metal within the CuAlNi SMAs was, as expected, evidently the lowest in the atmosphere (Figs. 5a-c) [27] due to the CuAlNi SMA not being exposed directly to the seawater.

Fig.6 shows the total amount of the two dominant anions (oxide and chloride) generated during the corrosion at different locations.

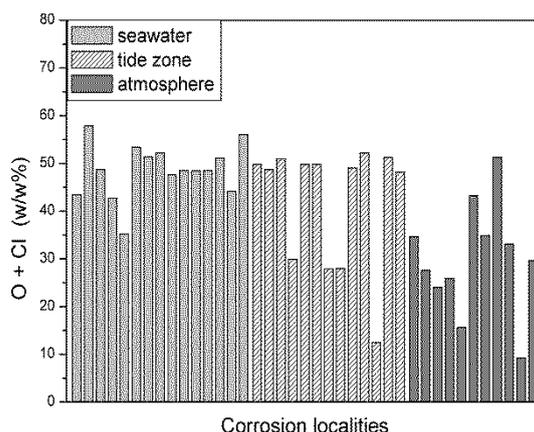


Figure 6. Content of anions after corrosion of the investigated CuAlNi SMAs at the tested locations.

When the total amount of anions formed during corrosion was observed (Fig.6), which was approximately equal with the corrosion products formed on the CuAlNi SMA's surface, it can be seen that the least formed in the marine atmosphere, much more by the tide zone and the highest in the seawater. The obtained results are in line with the dissolved metal amounts during the corrosion in the tested locations.

Figs.7a-b show separately the amount of individual anions on the corroded surfaces of the CuAlNi SMAs in all the tested locations.

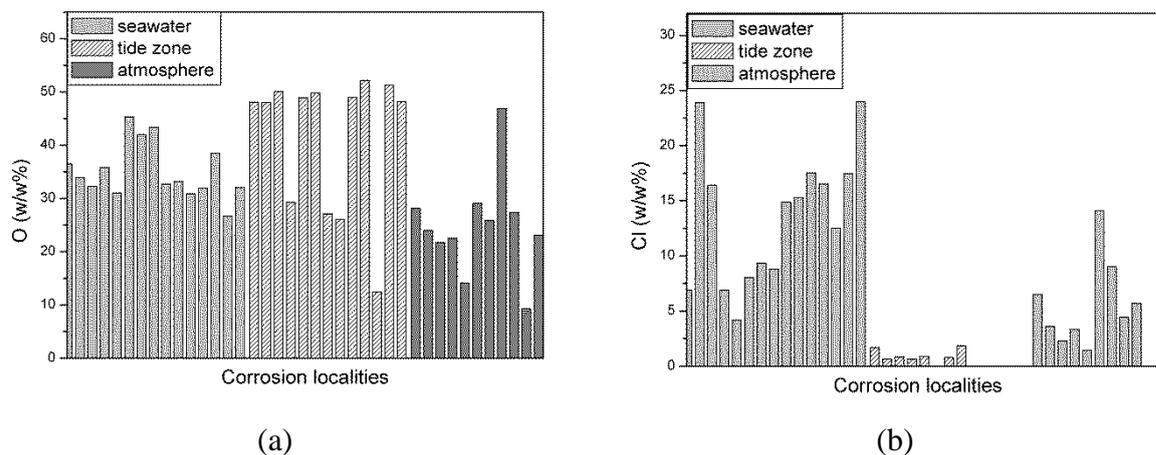


Figure 7. Content of (a) Oxygen and (b) Chloride after corrosion of the investigated CuAlNi SMAs at the tested locations.

Fig. 7a shows that the amount of oxide formed on the CuAlNi SMA's surfaces during the corrosion was the smallest in the atmosphere and the highest by the tide zones. This can be explained because, in marine tidal zones, CuAlNi SMA is exposed alternately to wet-dry conditions and, consequently, the exposed parts of the CuAlNi SMAs in tidal zones are anode and the others are cathode, thereby forming the structure of a small anode and large cathode [27]. Therefore, greater oxygen concentration is available on the surface than in the seawater and the atmosphere zone.

If the change of the chloride content at different locations is analysed (Fig. 7b), it can be seen that it forms most on the surface of the CuAlNi SMA which was exposed to the seawater effects, less in the atmosphere, and extremely low for the tide zones. This kind of behaviour suggests that it is much easier to wash off more soluble chlorides from the alloy surface than the oxides of the given metals.

As we have already said, due to the large scattering of the obtained results within each sample in all the investigated marine zones, it is very difficult to make the right conclusions about the real impact of each tested environment on the corrosion behaviour of this CuAlNi SMA. Because of that, in order to better understand the effect of the corrosion medium on the behaviour of individual metals of the tested CuAlNi SMA, the results of the elemental analysis obtained during EDS were analysed additionally in different ways.

3.3. Analysis of different environments' influence on the corrosion of the tested CuAlNi SMAs using multivariate methods

Given the large heterogeneity of the results obtained from the corrosion measurements, (Figs. 3-7) the idea was to apply multivariate analysis methods to facilitate the detection and accurate interpretation of the corrosion effects of different environments on the CuAlNi SMA alloy. The selected

chemometric methods can help, as they can reveal highly differentiated results that may need to be discarded in further analysis to recognise the real effects of corrosion.

In modern science, cluster analysis (CA) and principal components analysis (PCA) belong to the most commonly used chemometrics methods for qualifying and classifying data obtained in different ways and to establish dependencies between them [30-35]. These chemometrics methods are very convenient, because they provide a possibility for the successful systematization of a large amount of data of different origins, as well as recognize and elimination of unnecessary information.

The Cluster Analysis belongs to a convenient method which can sort data into groups (clusters) based on their likeness [35]. Hierarchical cluster analysis compares the distances between objects, and puts those closest to each other in the variable spaces in the same cluster. There are many methods of determining the distance between two objects or clusters: (Single linkage, Complete linkage, Average linkage, Ward's method, etc.). A dendrogram was obtained as a result of the cluster analysis. The similarity between two objects is presented on the vertical axis in the dendrogram. Non-hierarchical cluster analysis forms a cluster in the opposite way to a hierarchical cluster analysis.

Principal Component Analysis is one of the most commonly used multivariate methods in investigations that contains a lot of heterogeneous data, or data collected in different ways, as it enables the elimination of redundant data and to obtain lower-dimensional data by recognising the basic components without major information loss [35-37]. The Principal component analysis is based on extraction of the important information from original data and representation it as a set of new variables called Principal Components (PCs). The Principal Components are linear combinations of the original variables. In the presence of an appropriate correlation, there is a significant reduction in the number of variables (PCs) necessary to describe the analyzed system in relation to the original variables.

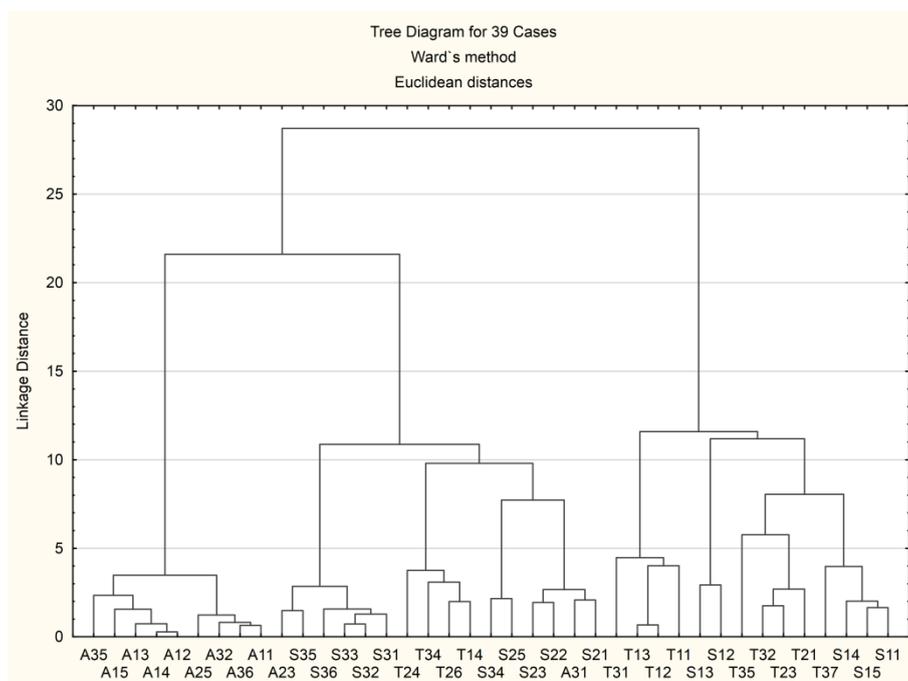


Figure 8. Dendrogram of the CuAlNi SMA in the studied environments

In this manuscript, during the CA and the PCA analysis the data matrix was formed the following way: the results of the elemental (EDS) analysis represented variables (columns) and used measuring points on the alloy surface (spectrums) were rows.

The matrix data standardisation was applied before calculation, with the aim of ensuring the equal significance of all analyzed data. Euclidean distance was applied in the Custer Analysis as a measure of the dissimilarity between data and the Ward’s linkage method was used for clusters formation.

The dendrogram of the influence of various environments on the corrosion behaviour of the tested alloy as a result of CA is shown in Fig. 8.

From Fig. 8 the grouping of the analysed corrosion environments is noticeable, based on corrosion action into two well separated clusters. The first cluster describes the corrosion behaviour of the tested CuAlNi SMAs in the atmosphere and seawater dominantly (except only a few points in the tide zones), within which the data for the seawater are separated from those for the atmosphere (two sub-clusters). On the other hand, the second cluster generally groups CuAlNi SMA behaviour at the tide zones (only a few points in the seawater). These divisions of the analysed corrosion environments indicate a clear difference in the corrosion behaviour of this CuAlNi SMA in the marine atmosphere and by the tide zones, and similarity between alloy behaviour in the seawater and in the atmosphere.

This kind of grouping of the analysed environments also confirms that the cluster analysis has the ability to recognise the effect of the corrosion medium on the rate of CuAlNi SMA degradation.

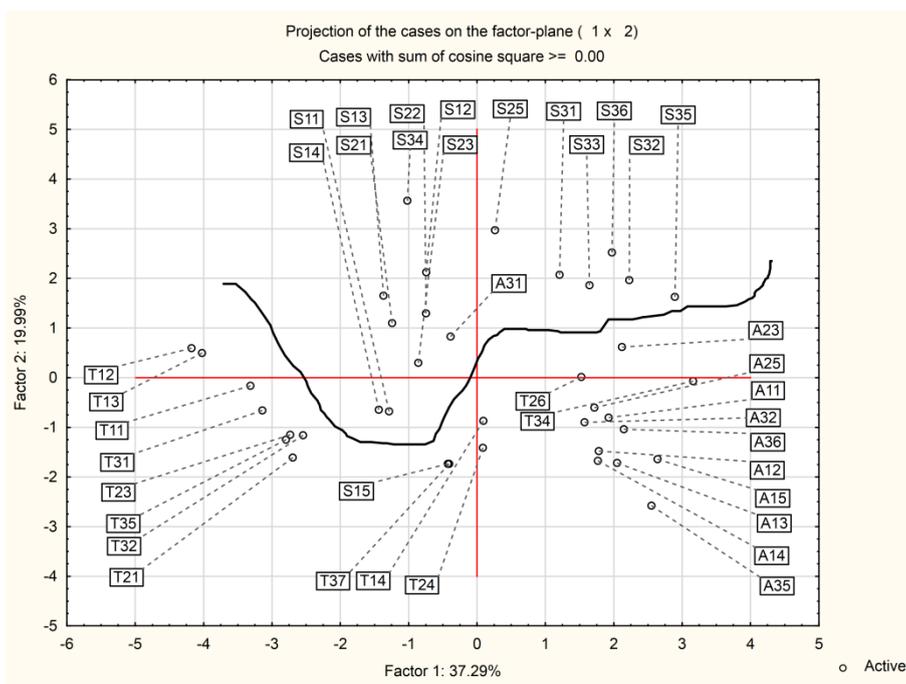


Figure 9. The distribution of the tested corrosion environments as a result of PCA (PC1 vs PC2)

The dendrogram (Fig. 8) also shows that the best agreement (shortest vertical lines) was obtained between the data related to corrosion of the CuAlNi SMA in the marine atmosphere, and the largest difference was observed in the case of the tide zones. This can be interpreted by the corrosion of CuAlNi

SMA in the marine atmosphere air in the most uniform way (individual measurements were most similar to each other), while corrosion by the tide zones produced the most heterogeneous surface. This behaviour is justified, given that the external conditions (temperature, humidity) change most during the tide zones. On the other hand, the withdrawal and arrival of water during the tide can wash away corrosive products from some parts of the surface, causing greater damage and heterogeneity of the surface [27].

PCA also allows grouping the investigated corrosion areas. The distribution of analysed corrosion environments which was described by the first two PCs for the analysed CuAlNi SMA (score plot) is shown in Fig. 9. From Fig. 9 it is noticeable that the first two PCs achieve the distribution of the investigated corrosion media in a very similar way as cluster analysis.

Fig. 9 shows that PCA separated the CuAlNi SMA corrosion behaviour dominantly depending on the environment to which it was exposed, and there is a clear separation of effects in the atmosphere, in the seawater and by the tide zones, with some exceptions. The corrosion of CuAlNi SMA in the atmosphere was described with positive PC1 and negative PC2 values, by the tide zones with negative PC1 and also with negative PC2, while the behaviour of CuAlNi SMA in the seawater was characterised dominantly with positive PC2 values. Since PC1 (37.29%) carries almost twice the percentage of the original variables relative to PC2 (19.99%) it can be said that, based on the PCA analysis, a larger difference was registered between the effects of the marine atmosphere air in relation to the tide zones on the corrosion of the tested CuAlNi SMA, while the seawater effect was distributed between these two localities.

On the other hand, although PC2 values carry less information than PC1, they describe the corrosion behaviour of CuAlNi SMA in the same way in both atmosphere and tide zones with negative values, and in the seawater with positive, which is a sign that the PCA also recognised small similarities between the behaviour of this alloy in the atmosphere and by the tide zones.

3.4. Correlation of the obtained results after 6 months of exposure of CuAlNi SMAs in different marine environments

The results of the elemental analysis (Figs. 4-7) obtained during EDS were compared, in order to obtain more detailed information on how the coastal environments influence the corrosion of the CuAlNi SMAs.

Fig.10 shows the total metals` amount (copper, aluminium and nickel) in the function of total anions` content (oxide and chloride).

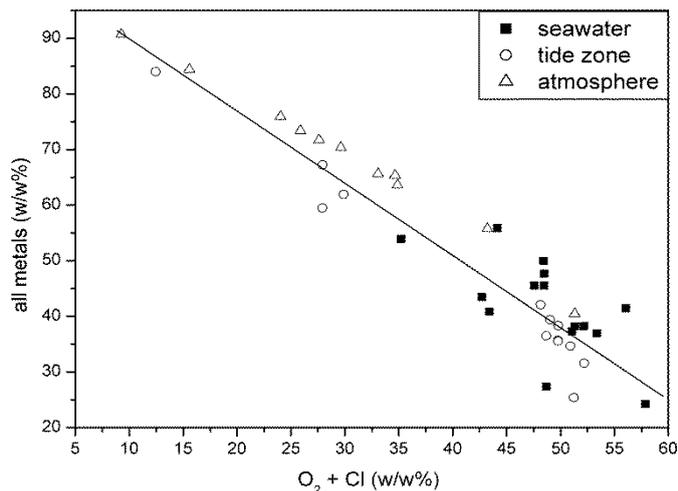


Figure 10. Change in the total metal amount in the function of oxygen and chloride content

As can be seen from Fig. 10, a comparison of the total content of metals and anions resulted in a linear dependence, (Equation 1), which indicated that the degradation of metals within this alloy happened mostly as oxides and chlorides` formation.

$$\text{All metals (w/w\%)} = 104.602 - 1.310 \text{ O}_2 + \text{Cl}(\%) \quad (R = -0.948 \quad \text{sd} = 5.639 \quad N = 39 \quad P < 0.0001) \quad (1)$$

If we observe the behaviour of individual metals in the function of these anions, we can see the following:

The amount of copper was decreasing proportionally as the oxygen content increased in all of the tested localities. Linear correlation was found (Equation 2):

$$\text{Cu (w/w\%)} = 90.030 - 1.404 \text{ O}_2 \text{ (w/w\%)} \quad (R = -0.962 \quad \text{sd} = 4.748 \quad N = 39 \quad P < 0.0001) \quad (2)$$

The existence of linear dependence may indicate that the copper corrosion in this alloy is reflected mainly in the formation of an equivalent amount of copper oxide in all localities.

Comparing the change in the amount of aluminium and nickel in the function of the oxygen content, a complex distribution was obtained within any correlations.

In order to check whether the data obtained by applying the selected multivariate method can also give a quantitative description of changes in the amount of metals and anions during the corrosion processes of this alloy, the obtained PC1 values are compared with the oxygen content and the content of each metal in this alloy after corrosion (Figs.4 and 6). Equations 3 and 4 show the change of the percent of copper and oxygen obtained by EDS analysis in the function of the PC1 values.

$$\text{O}_2 \text{ (w/w\%)} = 34.677 - 4.834 \text{ PC1} \quad (R = -0.885 \quad \text{sd} = 5.576 \quad N = 37 \quad P < 0.0001) \quad (3)$$

$$\text{Cu (w/w\%)} = 41.326 + 7.235 \text{ PC1} \quad (R = -0.907 \quad \text{sd} = 7.331 \quad N = 37 \quad P < 0.0001) \quad (4)$$

Equations 3 and 4 point out that the values of oxygen and copper content were changed linearly in the function of the PC1. The rise in oxygen content followed an almost identical trend of decreasing copper content in this alloy. This kind of behaviour confirms that the copper corrosion in this alloy is reflected mainly in the formation of an equivalent amount of copper oxide.

The existence of these linear quantitative dependencies confirm that PC1 well describes the copper dissolution, and, on the other hand, that copper dissolution/oxide formation had the greatest influence on the degradation of CuAlNi SMA in all of the tested environments.

The dependence between PC1 value and aluminium and nickel content was not obtained.

Fig.11 shows dependence between the aluminium content during corrosion and the chloride amount in each of the tested marine environments.

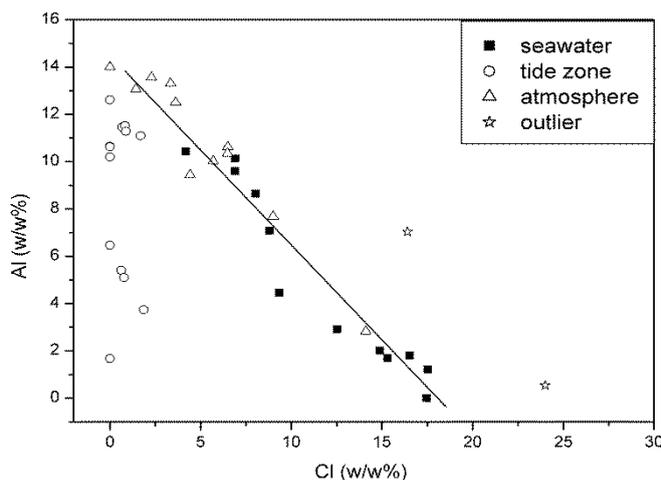


Figure 11. Change in the aluminium amount in the function of chloride content

As is evident from Fig.11, the correlation between the aluminium and chloride content by the tide zones was very different from the other two localities. By the tide zones the chloride content was negligibly small (0-1.8%), while, in the other two localities, a linear change can be observed in the aluminium content compared to the chloride content (with some outliers). This behaviour can be interpreted in a way that aluminium, during the corrosion, formed predominantly $AlCl_3$ in all environments, but the tide probably washed it off the surface.

Comparing the change in the amount of nickel in the function of the chloride content, complex distribution was obtained within any correlations. If we observe the results obtained using multivariate analysis, we can see that the score plot obtained by PCA (Fig. 9) indicated that PC2 also participated in describing CuAlNi SMA corrosion in all of the tested environments. For this reason, the values obtained for PC2 were compared with the chloride content and the sum of aluminium and nickel content in this alloy after corrosion. Equation 5 shows the linear dependence between the chloride and PC2 values, while Equation 6 describes the correlation between the sum of aluminium and nickel content after corrosion and the PC2 value (except in the tide zones).

$$Cl (w/w\%) = 10.278 - 4.302 PC2 \quad (R = -0.937 \quad sd = 2.540 \quad N=10 \quad P < 0.0001) \quad (5)$$

$$Al+Ni (w/w\%) = 10.495 - 4.075 PC2 \quad (R = -0.938 \quad sd = 2.276 \quad N=12 \quad P < 0.0001) \quad (6)$$

The linear relationship between PC2 and content of chloride indicate the fact that in addition to oxide formation (copper oxide), chloride formation also had an influence (less than oxide) on the corrosion process of this alloy (except in the tide zones).

The existence of a very similar linear dependence between PC2 and the sum of the aluminium and nickel content (Equation 6) indicates that aluminium and nickel during the corrosion formed predominantly chloride, and, on the other hand PCA analysis can recognise it.

With the intention of noticing the difference in chloride formation between aluminium and nickel, their content was correlated with the results obtained by PCA. Unfortunately, no dependence was obtained that would indicate noticeable difference in the corrosion behaviour of these two metals under the given conditions.

All the obtained results indicate that the used chemometric methods (CA and PCA) are sufficiently sensitive tools for detecting the influence of various environments on the corrosion behaviour of the tested CuAlNi SMAs. Using the above methods we have opportunity that on the basis of a large number of very heterogeneous data still come to a conclusion about effects that have the greatest influence on the corrosion of the tested alloy under given conditions. One of the specific highlights of this research was that, contrary to the usual laboratory experiments that are performed under controlled conditions and in an accelerated manner [38], here, it is the case of experiments performed in real coastal environments for a prolonged period.

4. CONCLUSIONS

Based on the obtained results, the following conclusions can be drawn:

- The results obtained by EDS were correlated with applying linear regression analysis and CA and PCA multivariate methods in order to identify the impact of different coastal environments on the corrosion behaviour of CuAlNi SMA.
- The correlation between the most important degradation products of CuAlNi SMA was determined under all the tested coastal conditions.
- The obtained results suggested that corrosion of the CuAlNi SMA within each tested locality leaves behind a quite heterogeneous surface.
- An average point of view showed that within of 6 months the least metal is lost in the marine atmosphere, while about the same amount of metal dissolution was registered by the tide zones and in the seawater.
- During the corrosion process, the copper formed predominantly oxide, unlike aluminium and nickel, in which corrosion mainly takes place in the direction of chloride formation.
- The obtained results indicate that the used multivariate methods with combination of EDS analysis can be used successfully for identification of corrosion behaviour, because the methods had high enough sensitivity. Finally, the applied multivariate methods can be used for recognition of the corrosion process by similar materials in various environments.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from

1. The Bilateral Projects Slovenia – Montenegro and Serbia – Montenegro (BI-ME/18-20-024)
2. The EUREKA Program PROCHA-SMA E! 13080 funded by the Ministry of Science of the Republic of Montenegro.
3. The Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2020-14/200125).
4. The University of Rijeka, Project uniri-technic-18-200 “Failure analysis of materials in a marine environment”.

References

1. G. Koch, Trends in Oil and Gas Corrosion Research and Technologies: Production and Transmission Woodhead Publishing, (2017), Cambridge, England.
2. <https://www.g2mtlabs.com/corrosion/cost-of-corrosion/>
3. X. Yang, L. Zhang, S. Zhang, K. Zhou, M. Li, Q. He, J. Wang, S. Wu, H. Yang, *Int. J. Electrochem. Sci.*, 16 (2021) 151015.
4. S. Syed, *Corros. Sci.*, 50 (2008) 1779.
5. G. Fajardo, P. Valdez, J. Pacheco, *Constr. Build. Mater.*, 23 (2009) 768.
6. J.G. Liu, Z.L. Li, Y.T. Li, B.R. Hou, *Int. J. Electrochem. Sci.*, 9 (2014) 6699.
7. H.C. Vasconcelos, B.M. Fernández-Pérez, J. Morales, R.M. Souto, S. González, V. Cano, J.J. Santana, *Int. J. Electrochem. Sci.*, 9 (2014) 6514.
8. S. Sathish, U. S. Mallik, T. N. Raju, *JMMCE*, 2 (2014) 71.
9. T. N. Raju, Sampath, *Trans. Indian Inst. Met.*, 64 1(2011) 165.
10. K. Otsuka and C.M Wayman, Shape Memory Materials, University Press, (1998), Cambridge, England.
11. T.W. Duerig, K.N. Melton, D. Stoeckel, C.M. Wayman, Engineering aspects of Shape Memory Alloys, Butterworth-Heinemann, (1990) London, England.
12. J. Van Humbeeck, *Adv. Eng. Mater.*, 3(2001) 837.
13. H. Wu, T. Wang, X. Liu, N. Lin, X. Liu, Z. He, Z. Wang, *Int. J. Electrochem. Sci.*, 12 (2017) 2376.
14. M. A. Amin, N. El-Bagoury, H. Shokry, *Int. J. Electrochem. Sci.*, 8 (2013) 2791.
15. D. Mantovani, *JOM*, 52 (2000) 36.
16. J. Ryhänen, M. Kallioinen, J. Tuukkanen, J. Junila, E. Niemelä, P. Sandvik, et al., *Biomed. Mater. Res.* 41 (1998) 481.
17. D.E. Hodgson, M.H. Wu, R.J. Biermann, Shape memory alloys. ASM Handbook, ASM International, (1990) Geauga County, Ohio, United States.
18. J. MohdJani, M. Leary, A. Subic, M. A. Gibson, *Mater. Des.*, 56 (2014) 1078.
19. M. Guerioune, Y. Amiour, W. Bounour, O. Guellati, A. Benaldjia, A. Amara, N.E. Chakri, M. Ali-Rachedi, D. Vrel, *Int. J. Self Propag. High Temp. Synth.* 17 (1) (2008) 41.
20. V. Recarte, J.I. Pérez-Landazábal, M.L. Nó, J. San Juan, *Mater. Sci. Eng.*, 370 (2004) 488.
21. Š. Ivošević, R. Rudolf, *Sci. J. Pol. Nav. Acad.*, 218 (3) 25.
22. Š. Ivošević, P. Majerić, M. Vukićević, R. Rudolf, *J. Mar. Trans. Sci.*, 3 (2020) 265.
23. Š. Ivošević, R. Rudolf, D. Kovač, “The overview of the varied influences of the seawater and atmosphere to corrosive processes“*1st International Conference of Maritime Science & Technology*, Dubrovnik, Croatia, 2019, 182.
24. L. Weng, L. Du, H. Wu, *Int. J. Electrochem. Sci.*, 13 (2018) 5888.

25. Y. Feng, Z. Bai, Q. Yao, D. Zhang, J. Song, C. Dong, J. Wu, K. Xiao, *Int. J. Electrochem. Sci.*, 14 (2019) 11300.
26. S. Zou, X. Li, C. Dong, H. Li, K. Xiao, *Acta Metall. Sin.*, 48 (2012) 687.
27. J. Wu, K. Pang, D. Peng, J. Wu, Y. Bao, X. Li, *Int. J. Electrochem. Sci.*, 12 (2017) 1216.
28. P. Yi, K. Xiao, K. Ding, G. Li, C. Dong, X. Li, *Trans. Nonferrous Met. Soc. China*, 26 (2016) 1146.
29. S. Feliu, M. Morcillo and S. F. Jr, *Corros. Sci.*, 34 (1993) 415.
30. Gy. Vastag, S. Apostolov, N. Perišić-Janjić, B. Matijević, *Anal. Chim. Acta*, 767 (2013) 44.
31. B. Teofilović N. Grujić-Letić, S. Goločorbin-Kon, S. Stojanović, Gy. Vastag, S. Gadžurić, *Ind. Crops Prod.*, 100 (2017) 176.
32. S. Kovačević, S. Podunavac-Kuzmanović, N. Zec, S. Papović, A. Tot, S. Dožić, M. Vraneš, Gy. Vastag, S. Gadžurić, *J. Mol. Liq.*, 214 (2016) 276.
33. Gy. Vastag, S. Apostolov, B. Matijević, F. Assaleh, *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.*, 1084 (2018) 141.
34. Š. Ivošević, G. Vastag, P. Majerič, D. Kovač, R. Rudolf, *The Handbook of Environmental Chemistry*, Springer, (2020) Berlin, Germany.
35. J. N. Miller, J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, 5th ed. Pearson Education Limited, (2004) Edinburgh Gate Harlow, England.
36. P. Guccione, M. Lopresti, M. Milanesio, R. Caliandro, *Crystals* 11 (2021) 12.
37. I.T. Jolliffe, *Principal Components Analysis*, 2nd ed. Springer, (2002) Berlin, Germany
38. G. Vizin, G. Vukelić, *Mater. Sci.-Medzg*, 26 (2020) 337.

© 2021 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).