The Corrosion Behavior of an Ag43Cu37Zn20 Alloy in the Natural Seawaters

Stevan P. Dimitrijević[1], Mirjana Rajčić-Vujasinović[2], Željko Kamberović[3],
Silvana B. Dimitrijević[4,*], Vesna Grekulović[2], Biserka Trumić[4] and Aleksandra Ivanović[4]

[1]*Innovation Center Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*
[2]*Technical Faculty in Bor, University of Belgrade, VJ 12, 19210 Bor, Serbia*
[3]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*
[4]*Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia*

We investigated the effects of natural seawater on the corrosion of an Ag43Cu37Zn20 alloy. The alloy was a commercial brazing filler alloy of composition (BS1845:1984 Ag5) and belongs to the class of Cd-free silver brazing alloys. The Ag-Cu-Zn system is corrosion resistant in chloride solutions has not been widely examined. In this study, the corrosion behavior of the alloy has been investigated using the open circuit potential measurements, Tafel plots and anodic potentiodynamic curves. By comparing different samples of marine water indicates that salinity is the primary influence on corrosion behavior near the open circuit potential. At higher anodic potentials, the impact of mineral composition becomes significant.   [doi:10.2320/matertrans.M2015284]

1. Introduction

Ag brazing alloys are used for joining most ferrous and nonferrous metals. Cd bearing alloys are known for the low melting point, excellent flow characteristics and high joint strength. However, due to Cd toxicity, the use of these filler alloys is restricted and alternatives with similar characteristics are developed.[1]

Despite the widespread use of this type of alloy, their corrosion resistance in chloride solutions is not thoroughly investigated. The initial studies were performed by the Japanese researchers during 70s and 80s of the last century.[2,3] The main aspects of the studies were a type of corrosion at the brazed joints and it was found that electrochemical galvanic action between the coexisting phases is responsible for the corrosion of filler metal and interface. The results suggest that the Ag-Cu-Zn corrosion resistance in chloride solutions is mainly affected by behavior of the Cu-rich phase in the alloy. Unfortunately, there were no new studies on this subject for decades. In a recent published study[4] the basic information about electrochemical behavior of several Ag-based soldering alloys in physiological solutions considering the dental use is given.

Investigated alloy is two phase fcc system. It consists of the Ag-rich and Cu-rich α-phases regardless the solidification regime as shown in isopleth at 20 (mass%) Zn of the Ag-Cu-Zn ternary phase diagram.[5] These two phases have a composition similar to the binary systems Ag-Zn and Cu-Zn, with low content of Cu and Ag, respectively. Corrosion behavior of both is important for the research of ternary alloys.

Detailed mechanism of corrosion processes in chloride media is explained only for the unalloyed copper.[6] For the pure Cu-Zn binary system in chloride media, the majority of publications have been focused on the dealloying process.[7,8] Brass corrosion in the natural and synthetic seawater is much less investigated.[9–11] Multi-component alloys, based on the Cu-Zn system, investigated with components that hinder a dezincation have different corrosion processes in chloride solutions.[12,13]

Composition of seawater may vary depending on the location. This can significantly influence the corrosion behavior of metals and alloys. Coastal location and season could influence the salinity of seawater, but generally the salinity of water from the Adriatic, Aegean and Ionian Seas are higher than the standard seawater.[14,15] The IAPSO standard seawater has $35.000 \pm 0.010\,\text{g/kg}$ TDS.[16] The Black Sea has much lower salinity. It is about half of the standard seawater due to a fact that it is very young sea (ca. 9000 years) connected with the global ocean only through the Bosphorus strait.[17]

Although synthetic and natural seawater have nearly same composition, the corrosion of brass in natural seawater was much higher than in artificial seawater.[9,10] Corrosion properties of the Ag-Cu-Zn alloys in seawater have not been reported. In the present paper, a comparative study is performed on the corrosion behavior of the Ag43-Cu37-Zn20 alloy in four different natural seawaters under same experimental conditions, with the aim to provide real corrosion parameters for marine application.

2. Experimental Procedure

Ag, Cu and Zn (purity of minimum 99.99%) for electrode were produced by the recycling process.[18] The alloy for electrode was prepared by two consecutive steps of the ingot metallurgy method, machined into cylinders with 7.14 mm diameter and homogenization annealing at 600°C for 24 h in nitrogen atmosphere. The chemical composition (mass%) of the alloy was 43.51 Ag, 37.69 Cu, 18.80 Zn, and trace amounts (less than 20 ppm total) of Pb, Sn, Fe, Ni, as confirmed by ICP-OES analysis (meet requirements of BS1845:1984 Ag5 standard).

In this study, the samples of water from four seas that surround the Balkan Peninsula were used. The samples of seawater have been taken from coastal tourist areas in July

*Corresponding author, E-mail: silvana.dimitrijevic@irmbor.co.rs

Table 1 Geographical location of the seawater sampling sites.

Location (Country, nearest town)	Latitude	Longitude
Adriatic Sea, Croatia, Opatija	45° 19′ 56″ North	14° 18′ 14″ East
Aegean Sea, Greece, Possidi	39° 24′ 25″ North	20° 14′ 20″ East
Ionian Sea, Greece, Syvota	39° 57′ 47″ North	23° 22′ 52″ East
Black Sea, Bulgaria, Sozopol	42° 24′ 47″ North	27° 42′ 07″ East

Table 2 Composition of the seawater used for investigation the corrosion behavior of the Ag43Cu37Zn20 alloy.

Element	Adriatic Sea	Aegean Sea	Ionian Sea	Black Sea	Standard seawater
Cl (g/kg)	21.33	20.87	20.55	10.14	19.38
Na (g/kg)	11.86	11.62	11.45	5.63	10.76
K (mg/kg)	441.7	424.84	416.71	195.03	399
Ca (mg/kg)	446.7	431.98	430.38	211.55	412
Mg (mg/kg)	1369.3	1380.5	1353.4	640.0	1296
S (mg/kg)	957.2	964.2	955.3	454.9	905
Sr (mg/kg)	6.75	6.57	6.36	3.35	8
Salinity, mass%	38.692	38.168	37.627	18.631	35.000 ± 10
pH	8.120	8.135	8.010	8.276	8.05*

*for batch P64.[17]

2014. Sampling sites and their coordinates are given in Table 1. The coordinates are determined by the publicly available Google Maps service. The composition and the pH of sea water are given in Table 2.

Before chemical analysis and electrochemical measurements, the seawater samples were filtered through 8 μm pore size filter paper and 0.2 μm pore size membrane.

SpectroBlue (Spectro) ICP-OES spectrometer was used in order to determine the content elements in seawaters. Shimadzu AX200 Analytical Balance was used for gravimetric determination of seawater salinity. The pH measurements were performed with a WTW pH meter Model 3110.

Electrochemical measurements were conducted in a thermostatic conventional three-electrode cylindrical glass cell. The working electrode was the cylindrical alloy electrode embedded in PTFE with active surface of $0.40\,cm^2$, whose potential was controlled against the saturated calomel reference electrode (SCE). Platinum sheet ($2.0\,cm^2$) served as a counter electrode. Before all measurements, the sample was ground through a series of grit SiC papers and then polished using 0.3 μm alumina paste. The electrode was thoroughly washed with deionized water and degreased with acetone. The electrolyte volume used in the experiments was $100\,cm^3$. Experiments were carried out at temperature of 25 ± 1°C.

System used to run the electrochemical experiments is fully developed at the University of Belgrade, Technical Faculty in Bor.[19]

The working electrode was immersed in the seawater and allowed to stabilize for 30 min. Following a stabilization at open circuit potential (OCP), the measurements of Tafel plots were performed. For the Tafel plots, a sweep from −200 to +200 mV versus OCP at a sweep rate of 0.1667 mV·s^{-1} was used. The anodic polarization curves were recorded starting from OCP up to +1000 mV using a scan rate of 1 mV·s^{-1}.

3. Results and Discussions

Composition of investigated seawaters, compared to the standard seawater are given in Table 2. Composition of the standard seawater is calculated from the chlorine concentration and ratios of ions in relation to it from literature.[20,21]

Chemical analyses of seawater samples confirmed that the salinity of each sample was in the literature range.

After determination of the filtered seawater composition, the electrochemical measurements are performed. The open circuit potentials for the Ag43Cu37Zn20 alloy in the different filtered natural seawater are shown in Fig. 1.

The OCP is inversely proportional to the salinity of seawater. Salinity is of the primary influence and it can be
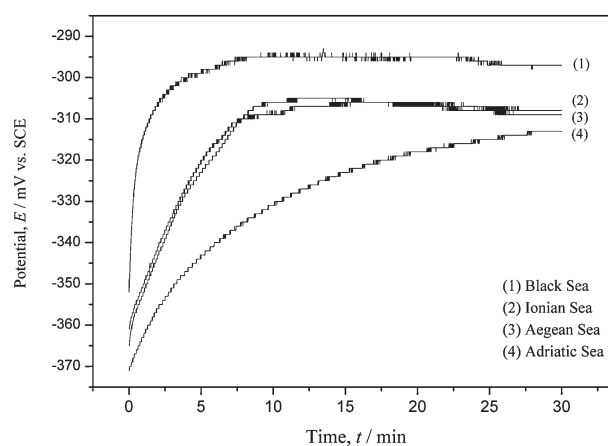

Fig. 1 Open circuit potential vs. time for the Ag43Cu37Zn20 alloy during 30 min in the samples of natural seawater from different regions at 25°C.

noticed from similarities of curves for the waters of the Aegean and Ionian seas, which are almost identical. Comparison of these samples shows that pH and mineral composition has low influence on the value of the OCP.

OCP in Black Sea water, with minimum salinity, has the most positive value. The OCP in this seawater is the fastest established and is the most stable. Figure 1 shows that OCP dependence on time in the Adriatic Sea water is the most different from the others. In this case, the value of the OCP is the most negative and the slowest established. This behavior indicates the influence of mineral composition, because the salinity is not sufficiently higher than in the Aegean and Ionian Sea.

During the OCP evolution in chloride solutions, there is adsorption of hydroxyl and chloride ions. At the pH of seawater there is an equilibrium of adsorbed species $Cu(OH)_{ADS}$ and $Cu(Cl)_{ADS}$. Although Cl$^-$ is present at higher concentration than OH$^-$, the adsorption of latter is faster than of chlorides.[22] In natural seawater, a great number of different ions affect the characteristics of the OCP dependence on the time by competition of different adsorbed species which causes the disturbance of stable equilibrium.

Corrosion parameters were obtained by potentiodynamic method at a slow scan rate. Figure 2 shows the results recorded in the water of the Adriatic Sea.
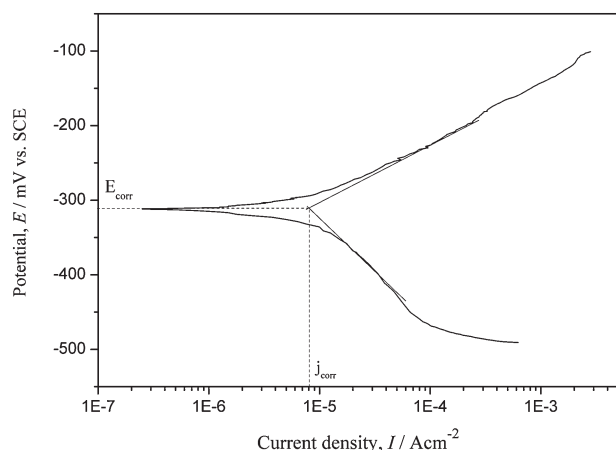
Fig. 2 Anodic and cathodic polarization curves in the apparent Tafel region at a scan rate of 0.1667 mV/s for the Ag43Cu37Zn20 alloy in filtered natural seawater from the Adriatic Sea.

Table 3 Corrosion parameters obtained from polarization curves by Tafel extrapolation for the Ag43Cu37Zn20 alloy in different natural seawaters.

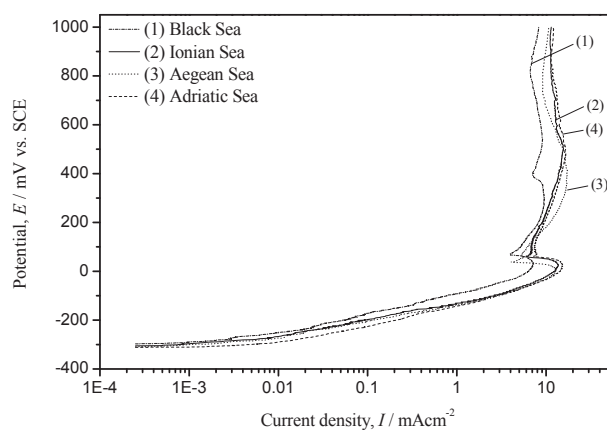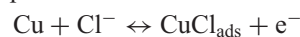| Parameter	Seawater (geographic area, sea name)			
	Adriatic	Aegean	Ionian	Black
E_{corr}, mV vs. SCE	−313	−309	−307	−297
I_{corr}, µA/cm^2	8.13	7.41	7.24	4.57
Anodic Tafel slope, mV/dec	66	68	71	75
Cathodic Tafel slope, mV/dec	−151	−155	−158	−167

Fig. 3 Anodic polarization curves for the Ag43Cu37Zn20 alloy in natural filtered seawaters at scan speed 1 mV/s.

Table 4 Current density values in a full range of potential for the Ag43Cu37Zn20 alloy in filtered natural seawaters and pH at beginning and end of the experiment.

Parameter	Adriatic Sea	Aegean Sea	Ionian Sea	Black Sea
I, mA/cm^2 for anodic peak	15.0	12.9	13.6	7.2
I, mA/cm^2 for minimum after anodic peak	7.3	4.1	6.1	4.0
Maximal value of I at polarization curve mA/cm^2	16.7	17.1	15.6	9.4
pH at beginning of the experiment	8.120	8.135	8.010	8.276
pH at end of the experiment	8.099	8.102	7.963	8.308

Similar curves were obtained for all other seawaters and results from the Tafel extrapolation are shown in Table 3. They suggest that increasing salinity of sea water reduces both Tafel slopes. Higher salinity increases the corrosion current.

The values of corrosion current are slightly less than the obtained for brass in synthetic seawater in other studies, 8.98 µA/cm^2.[23] This indicates that the Cu-rich phase primarily affects the value of j$_{corr}$ and that corrosion resistance of the alloy in the seawater depends on behavior of this metallurgical phase.

Table 3 shows that the parameter values close to the OCP and in apparently Tafel region depend primarily on salinity, while the influence of pH and total mineral compositions are of less importance. However, the impact of both parameters exists as indicated by the results of the water from Adriatic Sea. Higher corrosion current is not only the result of salinity which is not significantly greater than for other two seas (Table 2).

Anodic polarization curves at a scan rate of 1 mV/s for the alloy in four different seawaters, from the OCP till +1.0 V, are shown in Fig. 3.

The first part of polarization curves in Fig. 3 is characterized by a pronounced current density peak followed by the corresponding minimum immediately after it. Subsequent short region of limiting current density is also characteristic for all curves. The region of higher anodic potentials has a broad current wave consisting of two parts in the case of the Black Sea water. Generally, this behavior is very similar to the behavior of pure copper during anodic polarization in near neutral solution of NaCl.[24]

At the pH of natural sea water (Table 2) at a concentration lower than 10^{-5} mol/dm^3, zinc appears in a stable hydrated form of $Zn(OH)^+$ ion. At higher concentrations of soluble ion, zinc oxide is formed. As shown in Table 4, the pH of sea water during anodic polarization does not change significantly which contributes to a wider area of potential where zinc is stable as soluble. Probably for this reason, zinc does not affect significantly shape of polarization curves.

Therefore, it can be assumed that the identical mechanism for peak appearance and minimum on polarization curves like for NaCl solution which involve consecutive reactions mechanism that produces CuCl surface film:[24]

$$Cu + Cl^- \leftrightarrow CuCl_{ads} + e^-$$
$$CuCl_{ads} + Cl^- \leftrightarrow CuCl_2{}^-$$
$$CuCl_2{}^- \leftrightarrow CuCl_{film} + Cl^-$$

Current density of anodic peak at polarization curves increases as the salinity of seawater rises. The impact of the overall mineral composition is observed on polarization curve of the Aegean Sea, which is significantly different compared to the other two sea waters with similar salinity. The pH of sea water of the Aegean Sea is close to the value of the Adriatic Sea water, which indicates that the influence of this parameter on polarization behavior of the alloy, in a wide area of anodic potential, is lower than the mineral-composition and salinity of seawater.

Table 4 shows that buffering properties of seawaters are sufficient that pH at the end of polarization measurements

remains basically unchanged. Except for the seawater from the Black Sea, for all other seawaters pH value at the end of the measurement is lower than at the beginning. This indicates that prevailing pH dependent reactions during anodic polarization are those which consume hydroxyl ion, for example, formation of copper oxides:

$$2Cu + 2OH^- \leftrightarrow Cu_2O + H_2O + 2e^-$$

$$Cu_2O + 2OH^- \leftrightarrow 2CuO + H_2O + 2e^-$$

Chemical reactions dependable on pH can take place simultaneously:

$$2CuCl_2^- + 2OH^- \leftrightarrow Cu_2O + H_2O + 4Cl^-$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)^+ + OH^- \leftrightarrow ZnO + H_2O$$
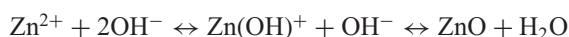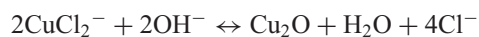
4. Conclusion

The effect of chemical composition and other properties of four different samples of seawater on the corrosion behavior of the Ag43Cu37Zn20 alloy were investigated. Salinity of seawater was found to have the most important influence on corrosion parameters. Mineral composition has influence at high anodic potentials. pH of investigated samples has the lowest impact. The alloy has similar corrosion behavior in the waters of the Adriatic, Ionian and Aegean Sea. In the Black Sea water, which salinity is much lower, the investigated alloy has significantly different corrosion parameters. Investigated alloy in all marine waters did not exhibit the passivation behavior in the whole range of measured potentials.

Acknowledgments

REFERENCES

1) T. Watanabe, A. Yanagisawa and T. Sasaki: Sci. Technol. Weld. Join. **16** (2011) 502–508.
2) I. Kawakatsu: Weld. J. **52** (1973) 233–239.
3) T. Takemoto and I. Okamoto: Quart. J. Jpn. Weld. Soc. **2** (1984) 300–308.
4) A. Ntasi, Y. Al Jabbari, W. D. Mueller, G. Eliades and S. Zinelis: Angle Orthod. **84** (2014) 508–515.
5) Y. A. Chang, D. Golberg and J. P. Neumann: J. Phys. Chem. Ref. Data **6** (1977) 621–673.
6) G. Kear, B. D. Barker and F. C. Walsh: Corros. Sci. **46** (2004) 109–135.
7) T. M. H. Saber and A. A. El Warraky: Desalination **93** (1993) 473–486.
8) J. Morales, P. Esparza and S. Gonzalez: Langmuir **12** (1996) 500–507.
9) C. S. Santos, M. H. Mendonça and I. T. E. Fonseca: J. Appl. Electrochem. **36** (2006) 1353–1359.
10) M. C. Bastos, L. F. A. Proença, M. M. M. Netoa and I. T. E. Fonseca: J. Solid State Electrochem. **12** (2008) 121–131.
11) X. Joseph Raj and N. Rajendran: J. Mater. Eng. Perform. **21** (2012) 1363–1373.
12) A. Drach, I. Tsukrov, J. DeCew, J. Aufrecht, A. Grohbauer and U. Hofmann: Corros. Sci. **76** (2013) 453–464.
13) W. A. Badawy, M. M. El-Rabieib and H. Nady: Electrochim. Acta **120** (2014) 39–45.
14) D. Velaoras, D. Kassis, L. Perivoliotis, P. Pagonis, A. Hondronasios and K. Nittis: Medit. Mar. Sci. **14** No. 3 (Special Issue) (2013) 5–18.
15) M. Marini and E. Frapiccini: Chemosphere **90** (2013) 1839–1846.
16) A. Poisson, T. Dauphinee, C. K. Ross and F. Culkin: Oceanol. Acta **1** (1978) 425–433.
17) I. Dobrevsky, V. Mavrova and B. Bonev: Desalination **41** (1982) 209–214.
18) S. P. Dimitrijević, Z. Anđić, Ž. Kamberović, S. B. Dimitrijević and N. Vuković: Bulg. Chem. Commun. **46** (2014) 814–824.
19) Z. Stević and M. Rajčić-Vujasinović: Chem. Ind. **61** (2007) 1–6.
20) F. Culkin and R. A. Cox: Deep-Sea Res. **13** (1966) 789–804.
21) J. P. Riley and M. Tongudai: Chem. Geol. **2** (1967) 263–269.
22) F. King, M. J. Quinn and C. D. Litke: J. Electroanal. Chem. **385** (1995) 45–55.
23) R. Ravichandran and N. Rajendran: Appl. Surf. Sci. **241** (2005) 449–458.
24) H. P. Lee and K. Nobe: J. Electrochem. Soc. **133** (1986) 2035–2043.