Corrosion evaluation of multi-pass welded nickel–aluminum bronze alloy in 3.5% sodium chloride solution: A restorative application of gas tungsten arc welding process

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In this research, the corrosion behavior of a gas tungsten arc welded nickel–aluminum bronze (NAB) alloy is investigated by DC and AC electrochemical techniques in 3.5% sodium chloride solution. Regarding the electrochemical impedance spectroscopy and potentiodynamic results, uniform corrosion resistance of instantly immersed weld and base samples are almost analogous and increased (more in weld region) during the immersion times. Moreover, zero resistant ammeter results demonstrated that the few nanampere galvanic currents are attributed to microstructural and morphological differences between these two regions. Therefore, the welding procedure could not deteriorate the general corrosion resistance of the restored damaged NAB parts operating in marine environments.

1. Introduction

Nickel–aluminum bronze (NAB) alloys containing 9–12% (wt.%) aluminum with additions of up to 6% (wt.%) of iron and nickel, represent one of the most important groups of commercial aluminum bronzes. As the major alloying element, aluminum content would result in higher strength and improve the corrosion resistance (by formation of an oxide/hydroxide film) and castings/hot working properties. On the other side, nickel also improves corrosion resistance, strength and stabilises the microstructure while iron refines grains and increases the alloy tensile strength [1,2]. Both cast and wrought aluminum bronze compounds offer a good combination of mechanical properties and corrosion resistance. Consequently, aluminum bronzes have been widely used for decades in a variety of marine or saline environments including valves, fittings, ship propellers, pump castings, pump shafts, valve stems and heat exchanger water boxes [2–4]. However, these alloys can suffer from localized corrosion (e.g. pitting, crevice, etc.) especially in flow conditions [5]. NAB alloys are metallurgical complex alloys with several intermetallic phases such as α, β, K1, K1ii, K1iii and K1iv, in which small variations in composition can result in development of markedly different microstructures. This can also lead to extensive changes of alloy corrosion resistance in seawater. The microstructures that can result in an optimum corrosion resistance can be obtained by controlling the composition and the heat treatment procedure [1]. Wharton et al. used five types of NAB alloys (as-cast and wrought) with different compositions and heat treatment (annealing) backgrounds and compared their corrosion behaviors through various electrochemical techniques [1]. They reported that the cast annealed samples represented higher corrosion current densities in compared to wrought samples in seawater [1]. However, NABs are the most corrosion resistant types of copper-based alloys to flow-induced corrosion [5,6]. Their resistance has been attributed to a thin protective layer, containing aluminum and copper oxides [7,8]. Due to the presence of stable intermetallic compounds in NAB and the α/β phase boundary that is near the solidus line, it is very difficult to homogenize these alloys at their solid state and thus, a welding approach can be performed for this aim [9]. Indeed, this is a crucial matter whenever an inevitable industrial assembling process such as welding operation is carried out.

Alternatively, some defects and cracks can be induced by cavitation, de-alloying, stress corrosion cracking, pitting and erosion–corrosion mechanisms in some parts of NAB alloys (e.g. impellers), after long exposure times to seawater [10–14]. For instance, Alfanti et al. reported that for a couple of copper alloys in 1 M NaCl solution (pH = 6), the samples experienced a general dissolution mechanism at higher overpotentials and did not suffer from localized corrosion while at more alkaline pH conditions, they revealed a type of passivity (and passivity breakdown) behavior in
samples were ground up to 1200 SiC abrasive paper, polished using wire. For corrosion and microstructural investigations, the electrical connection was made between the sample and a cop-mounted using a self-cure epoxy resin in cylindrical molds after to examine the corrosion properties, the samples were cold imaged by quantometry method as 0.203 cm² in cross section were extracted from the base weldments were cooled in air. Identical, in surface area, specimens selected for plotting. Representative data that was closest to the reported average values were tests was repeated for at least three times. Finally, the most repre-
sentative corrosion potential. The EIS results were analyzed and the
equivalent circuits parameters were extracted by using the EIS
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3. Results and discussion
3.1. Microstructure characterization

Fig. 2 shows the microstructures and morphologies of the base and weld regions provided by OM. The image with lower magnification clearly reveals the sharp interface between these two regions (base and weld); see Fig. 2a. Base metal can be observed at the left

potentiodynamic results [2]. Also, Ni et al. showed that the NAB samples had finer and more homogenous microstructure (after performing a friction stir process) in comparison with the unprocessed alloy and that resulted in better corrosion resistance [15]. Furthermore, the namely materials can suffer surface damage under conditions of extreme flow velocity or fluid disturbance [5]. Since replacement of these parts with exactly the same material is very expensive, welding operation could be an economical method for restoration of NAB parts. Meanwhile, this method may lead to severe corrosion attacks due to occurrence of galvanic couples between weld and base alloy zones. However, there have been few studies committed to corrosion investigation of welded NAB alloys. For example, Ni et al. have employed the friction stir processing as a technique to modify the microstructure of the NAB alloys and have investigated the general corrosion properties of the surface processed NAB alloy [15]. Xiao-ya et al. also studied the cavitation behavior of NAB welds and showed that this type of corrosion initiates at the phase boundaries [16].

The aim of this research is devoted to assess the general and galvanic corrosion behavior of multi-pass gas tungsten arc (GTA) welded nickel–aluminum bronze (C95800) plates by DC and AC electrochemical techniques in aerated 3.5% (wt.%) sodium chloride solution. On the basis of ZRA measurement, a clear picture of the mechanism responsible for galvanic corrosion between the base and weld regions is presented. Finally, it will be inferred from the results whether this specified operation can be employed on the restored NAB alloys.

2. Materials and methods

Two as-cast NAB (C95800) plates were used as welding materials. The chemical composition (in wt.%) of the alloy was determined by quantometery method as 9.14% Al, 4.75% Ni, 3.1% Fe, 0.75% Mn and Cu as balance. U-shape groove of alloy plates with 10 mm in thickness and 100 mm in both length and width were joined using a multi-pass GTA welding process. Argon gas, as shielding gas, was continuously purged during the four welding passes. The filler metal was ERCuNiAl that was chosen due to AWS A5.7 standard in the proposed nominal composition range (in wt.%) of 8.5–9.5% Al, 4–5.5% Ni, 3–5% Fe, 0.6–3.5% Mn, 0.1% Zn, 0.1% Si, 0.02% Pb, 0.5% of other elements and Cu as balance. The mean values of AC welding current and voltage were 220 A and 22 V, respectively. After completion of the welding operations, the weldments were cooled in air. Identical, in surface area, specimens with ca 0.203 cm² in cross section were extracted from the base and weld zones; see Fig. 1. Due to excessive conductivity of copper alloys and thus narrowness of the heat affected zone (HAZ), it was impossible to extract an individual sample from this zone. In order to examine the corrosion properties, the samples were cold mounted using a self-cure epoxy resin in cylindrical molds after an electrical connection was made between the sample and a copper wire. For corrosion and microstructural investigations, the samples were ground up to 1200 SiC abrasive paper, polished using 1 μm diamond paste, degreased by ethanol, washed by distilled
side of the figure and in the right side, weld zone with smaller grain size is clearly apparent. A narrow transition zone with about 200 µm width, so called HAZ, could be observed as well. The microstructure of the NAB alloy in base region is shown in Fig. 2b. This region contains α phase as matrix (light color), which is a FCC copper-rich solid solution, β' or retained β (darkest regions), also called as martensitic phase and several intermetallic phases such as $\kappa_{\text{I}}$, $\kappa_{\text{II}}$, $\kappa_{\text{III}}$ and $\kappa_{\text{IV}}$ [15]. Where, $\kappa_{\text{I}}$ and $\kappa_{\text{II}}$ appear as large dendritic structures adjacent to $\alpha$ phase. Also, $\kappa_{\text{II}}$ is an iron-rich phase (based on Fe$_3$Al) which has the same dendritic structure, but its size is noticeably smaller than $\kappa_{\text{I}}$. Moreover, $\kappa_{\text{III}}$ is a nickel-rich phase (NiAl) and appears as a laminar eutectoid structure that coexists with $\alpha$ phase. Finally, $\kappa_{\text{IV}}$ is an iron-rich phase, mostly appears as fine round particles embedded in matrix [1,16,18]. As can be seen, due to rapid solidification during welding operation, microstructural changes including significant grain refining and phase fraction modification in weld region occur; see Fig. 2c. Microstructural image processing (MIP) cleared that the volume phase fraction of $\beta'$ increases from 3% (±0.5%) in base metal to about 14% (±0.5%) in weld zone. Also, the phase fraction of $\alpha$ decreases from 73% (±0.5%) in base metal to about 62% (±0.5%) in weld zone and almost no change in the fraction of $\kappa$ phase (including all types of $\kappa$ phases) is identified; see Fig. 2d and e. This indicates that the cooling rate in welding operation is quite high that there is not enough time for decomposition of $\beta$ to $\alpha$ (as can be achieved at equilibrium cooling rates in base metal). Due to decomposition of $\beta$ to $\beta'$ instead of $\beta$ to $\alpha$, the volume fraction of $\beta'$ phase increases after the welding procedure. Fig. 3 shows an OM image of the HAZ zone representing some of its constituent phases. Where, $\alpha$ Widmanstatten forms from $\beta$ phase (in the alloy equilibrium diagram) at a moderate to low cooling rate [19]. In this zone, the cooling rate is considered to be higher than the base metal (in casting condition) and lower than the weld zone, therefore, $\beta$ phase could not decompose to $\alpha$ and consequently it decomposes to $\alpha$ Widmanstatten. Other constituent phases such as $\beta'$, $\kappa_{\text{III}}$, $\kappa_{\text{IV}}$ and $\alpha$, are also evident in this figure.

3.2. Potentiodynamic polarization tests

Fig. 4a represents the PDP curves and Table 1 shows the extracted parameters of these results. For more clarity, higher
Concerning Fig. 4, at low positive overpotentials, active dissolution parameters from potentiodynamic curves is represented in Fig. 4b. This is shown in the inserted figure. Moreover, a schematic illustration magnification of polarization curves at potentials around their parameters from potentiodynamic curves.

As can be seen in Fig. 4 and Table 1, there are no noticeable differences in anodic curves (including anodic Tafel slopes and limiting current densities) of 0 and 72 h immersed specimens. On the other side, the cathodic reaction is significantly polarized during 72 h of immersion. It is evident that after 72 h of immersion, there is a deviation from the anodic Tafel slope (or a small step in anodic branch) at around 100 mV (vs. SCE) overpotential with respect to the sample $E_{\text{corr}}$. This can be attributed to the unreduced part of the oxide layer (after cathodic polarization), which forms after longer exposure times [20]. However, by further increasing the overpotential, this film destroys and almost all the anodic branches depict the same behavior. In other words, the cathodic surface activity plays a major role in decrease of $i_{\text{corr}}$.

After 72 h, the corrosion current density of the weld sample (7 $\mu$A/cm$^2$) has a smaller value comparing with the base sample (9 $\mu$A/cm$^2$). This slight difference is associated to the more homogenized morphology and finer microstructure of the weld sample. Hence, the protective layer formed on this sample may be more homogeneous than the base sample. Ni et al. also reported that the finer microstructure of NAB alloys (after friction stir processing) resulted in a better corrosion resistance of the alloy [15].

By time elapsing, the air-formed copper oxides is believed to be gradually replaced by chloride containing complexes, whereas the nickel alloying element is assumed to be almost soluble and the aluminum alloying element is proposed to be in oxide/hydroxide state [1]. It is reported that in neutral chloride solutions, the main initial corrosion product of copper (after removal of air-formed oxides) is cuprous chloride, CuCl, which forms from the following reaction steps [21]:

$$\text{Cu} \rightarrow \text{Cu}^+ + e^- \quad (1)$$

$$\text{Cu}^+ + \text{Cl}^- \rightarrow \text{CuCl} \quad (2)$$

It was also proposed that the cuprous chloride reacts to produce cuprous oxide (cuprite) which is the main constituent of thick corrosion product layers [21]. The cuprous oxide generally oxidizes over longer exposure times to cupric hydroxide (Cu(OH)$_2$) and atacamite (Cu$_2$(OH)$_3$Cl) in chloride containing solution according to the following reactions [22–24]:

$$\text{Cu}_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{Cu(OH)}_2 + 2\text{H}^+ + 2e^- \quad (3)$$

$$\text{Cu}_2\text{O} + 2\text{H}_2\text{O} + \text{Cl}^- \rightarrow \text{Cu}_2\text{Cl}(\text{OH})_2 + \text{H}^+ + 2e^- \quad (4)$$

If the chemical nature of scale formation is considered only as a function of oxygen supply, the sequence (from left to right) of the formed layers at longer immersion times is CuCl/CuCl$_2$/Cu(OH)$_2$–CuO/CuCl/Cu(OH)$_2$Cl [21]. It can be concluded that at higher chloride concentrations, copper chloride complexes form via the following reactions [23,25,26]:

$$\text{Cu}^{\text{Cl}}_2^- \rightarrow \text{CuCl}_2^2^- \rightarrow \text{CuCl}_2^4^- \rightarrow \text{CuCl}_2^6^- \quad (5)$$

In copper alloys, it is well established [1,6,15,27] that the major corrosion process of the NAB alloys is the anodic dissolution of copper to form the cuprous dichloride anion simplified as:

$$\text{Cu} + 2\text{Cl}^- \rightarrow \text{CuCl}_2^- + e^- \quad (6)$$
The method of cuprous oxide formation (or in the inverse condition air-formed oxide dissolution) in presence of chloride ions is usually taken as a precipitation reaction rather than a direct electrochemical or chemical formation from the base metal or cuprous chloride as following [24,28,29]:

\[
2\text{CuCl}_2^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 4\text{Cl}^- \tag{7}
\]

or alternatively, the CuCl produced by precipitation of dissolved Cu(I) in a chloride media may lead to further Cu$_2$O formation and growth [29]:

\[
2\text{CuCl} + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{Cl}^- \tag{8}
\]

On the other hand, the stability of Cu$_2$O or its redissolution is inversely dependent on the concentration of chloride ions [21].

The apparent Tafel region of copper and copper alloys is limited by a peak current at around 10 mV (vs. SCE), which is associated to the CuCl formation [32,5]. It starts when the activity of CuCl$_2$ in the outer Helmholtz plane exceeds the solubility equilibrium due to the following reaction [20,25,30]:

\[
\text{CuCl} + \text{Cl}^- \rightarrow \text{CuCl}_2^- \tag{9}
\]

At higher overpotentials (after the current density peak), a subsequent film dissolution is observed giving a limiting current density, above that any increase in current density is due to the formation of Cu(II) species [7,23]. The cathodic reaction in base and weld samples in an aerated solution is mainly oxygen reduction reaction [31–34]:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \tag{10}
\]

By initially immersing the specimens in solution, the only film, which could be present at the surface, is the air-formed oxide layer. While by time elapsing, porous corrosion products constituted of chloride and oxide containing complexes, form and act as a barrier on the surface [7,35–37]. By formation of this layer, the diffusion rate of cathodic reaction species is restricted and consequently the cathodic current densities are decreased. This is due to the interaction between reaction species and the corrosion products in porosities.

By considering the cathodic branches of polarization curves (see Fig. 4 and Table 1), it seems that the cathodic reaction is under diffusion limited control condition. Indeed, it is found that the cathodic characteristics of polarization curves are strongly dependent on the immersion time prior to polarization [1,6]. It has been reported that at initial immersion times, reduction of CuCl influences the oxygen reduction reaction while at higher immersion times; the former reaction is mainly affected by reduction of the formed Cu$_2$O species [6,7]. Moreover, it was proposed by some authors that during the cathodic polarization of copper, an underlying layer of cuprous species will be initially reduced followed by immediate reduction of overlying cupric species at higher overpotentials [6,7]. This will complicate the overall oxygen reduction mechanism. The substrate, temperature, surface and electrolyte conditions can all affect the reduction mechanisms. Therefore, the oxygen reduction reaction can be taken place under charge transfer/kinetic, mass-transfer or even mixed mass and charge transfer control [6].

In summary, the corrosion rates at corrosion potentials are quite low due to low rate of reduction reactions (predominately-dissolved oxygen). Since the corrosion behavior of this alloy in under cathodic control, the corrosion potential does not increase with time but rather decreases with time because of more polarization of the cathodic reaction [6]. That is the reason for employing these types of alloys in marine environments (considering the sharp increase in anodic current densities at anodic overpotentials). In this study, in both base and weld specimens, their corrosion potentials (at initial immersion times) are decreased about 50 mV after 72 h of immersion. More details on surface layer characterization will be discussed later by EIS results in the next section.

### 3.3. Electrochemical impedance spectroscopy results

In order to characterize the uniform corrosion behavior of the two distinct regions and also to authenticate the PDP results, the EIS technique was employed on each sample. Figs. 5–7 show Nyquist and Bode plots of the base and weld samples at their $E_{corr}$ and at ±100 mV overpotentials (with respect to their $E_{corr}$) after 0 and 72 h of immersion. The solid lines in these figures show simulated curves which are obtained by EIS spectrum analyzer while, the symbol ones represent the real experimental data. According to the EIS results, two possible types of equivalent circuits could be proposed for the surface reactions response. This is most likely due to complex reactions that can occur on the surface in presence of Cl- ions, particularly since Cu, Al and Ni elements are present in the alloy matrix [24,31,38–47], Fig. 8a and b show the proposed equivalent circuits for extraction of EIS data considering a porous corrosion product film. Moreover, based on the extracted C vs. n values from the EIS results, the schematic images depict the base and weld samples (maintained at their $E_{corr}$ and $E_{corr} ± 100$ mV) surface evolution (variations in surface roughness, film thickness) during 72 h of immersion in aerated 3.5% NaCl solution; see Fig. 8c–e.

The obtained Nyquist and Bode curves at $E_{corr}$ in Fig. 5 consist of a double-loop Randle-like semicircle in two parts; a high frequency impedance arc (related to charge transfer resistance) and a low frequency impedance arc (related to protective surface layer or film resistance). The equivalent circuits generally contain $R_c$ (Ω cm$^2$) as the solution resistance, $R_f$ (Ω cm$^2$) as the charge transfer resistance (also known as polarization resistance) at the alloy/electrolyte interface, $CPE_{ct}$ (μF/cm$^2$) as the non-ideal capacitance of charge transfer, $R_f$ (Ω cm$^2$) as the surface film resistance, $CPE_f$ (μF/cm$^2$) as the non-ideal capacitance of surface film and W (Ω s$^{1/2}$) as the Warburg element. The constant phase element, $CPE_f$ (μF/cm$^2$), is expressed in the form of $P(i\omega)^n$ in which $P$ (μF/cm$^2$) is related to the capacitance, $n$ is a parameter related to surface roughness, and $\omega$ (rad/s) is the angular frequency [48,49]. Applying CPE (a leaking capacitance) instead of pure capacitance improves EIS data fitting of the experimental results. In order to evaluate the corrosion product layer, the CPE values should be correlated to the capacitance (C) values. One of the most acceptable equations for calculation of capacitance from CPE values is the following [49]:

\[
C = \sqrt[n]{P(R_c)^{1-n}} \tag{11}
\]
Moreover, it is well known that the capacitance is inversely proportional to the surface film thickness according to following equation [42,49]:

$$C = \frac{\varepsilon_0 \varepsilon S}{d} \quad (12)$$

where $d$ (cm) is the thickness of the surface film (e.g., double layer thickness), $S$ ($cm^2$) is the surface of the electrode (or the active surface area), $\varepsilon_0$ ($\mu F/cm$) is the permittivity of air and $\varepsilon$ is the local dielectric constant. While $\varepsilon_0$, $\varepsilon$, and $S$ are assumed to be constant in all experiments, variations in $C$ values are an indication of surface layer thickening/thinning process ($C$ is inversely correlated to $d$). Extracted and calculated values obtained from equivalent circuits (as described in Figs. 5–7) are listed in Tables 2 and 3.

In Fig. 5, the recorded corrosion potentials of the base sample at 0 and 72 h were $-243$ and $-265$ mV (vs. SCE), respectively, while for the weld sample they were $-255$ and $-296$ mV (vs. SCE), respectively. It is obvious that the general difference observed between the base and weld samples at 0 h curves is insignificant. From Table 2, in both regions and at $E_{corr}$, the surface film resistance ($R_f$) is around five times higher than the charge transfer resistance ($R_{ct}$) which is in agreement with literature [22,39,41,47]. This means that the formed surface layer on the C95800 alloys can play a considerable role on their corrosion resistance. This layer is aluminum-rich adjacent to the base metal and richer in copper in the outer regions, see Fig. 8 [1,4,15,27].

Moreover, since $n_f$ values of the weld region at 0 h (0.72) is higher than the base (0.60), it gives a more uniform surface layer with slightly higher thickness (comparing the capacitance values of 0.015 F/cm$^2$ and 0.020 F/cm$^2$ for the weld and base samples, respectively). This can be attributed to more homogenized micro-structure of the weld region, see Figs. 2 and 8.

Comparing the results of Fig. 5 and Tables 2 and 3, it is obvious that the semicircles diameters and thus, the values of $R_{ct}$ and $R_f$ (particularly surface film resistance) are enhanced by increasing in the exposure time from 0 to 72 h. By comparing the curves, it can be inferred that at longer immersion times, only one semicircle appears. This is due to formation of double layer in surface layer porosities (typically at the bottom of diffusion paths). While the double layer can be formed at various sites (e.g., upon a dense surface layer or in diffusion paths), the elicited charge transfer parameters cannot be scientifically analyzed. Also, it is noticeable that the values of $C_f$ for both samples are diminished, revealing that the layers thicknesses are increased in accordance; see Fig. 8. This means that by increasing in immersion time, the protective surface film, which acts as a corrosion barrier, grows and hence, slows down the general surface dissolution reactions. Moreover, the value of surface film resistance ($R_f$) in the weld sample is greater.
than that for the base sample i.e., 10,000 and 6500 Ω cm², respectively. This result is suitable in agreement with \( i_{\text{corr}} \) results obtained from PDP measurements. Furthermore, by comparing the \( C_f \) and \( n_f \) values of the two regions (see Table 3) it can be deduced that the higher \( n_f \) value of the weld is related to its lower roughness (more homogenized microstructure) while its thickness is also lower; see Fig. 8. Indeed, it can be concluded that the corrosion product layer formed on the weld sample is denser in compared to the base. In addition, due to the \( n_f \) values of base and weld, it should be mentioned that the surface layers follow the Warburg behavior. This can be related to surface layer porosities that act as diffusion-controlling submicron paths or even the nature of the anodic controlling reactions [39,41].

In order to investigate the effect of anodic and cathodic polarizations on the film stability behavior, ±100 mV overpotentials were applied to the samples. Prior to apply these overpotentials, \( E_{\text{corr}} \) values of the electrodes (base and weld samples at various immersion times) were recorded against the reference electrode. In Figs. 6 and 7, (in both polarized conditions) the recorded \( E_{\text{corr}} \) values of the base sample at 0 and 72 h were around −240 and −270 mV (vs. SCE), respectively, while for the weld sample they were about −264 and −305 mV (vs. SCE), respectively.

At 0 h immersion, applying a 100 mV anodic overpotential leads to a remarkable decrease in \( R_f \) and \( R_t \) values (also an increase in \( C_f \) values) and appearance of a Warburg element (in comparison with \( E_{\text{corr}} \) results); as can be observed in Fig. 6. This indicates that at this potential, the thin surface layer, to a greater extent, is uniformly dissolved and thus, the exposed bare surface does not exhibit a complete barrier characteristic. The Warburg element is believed to be related to the anodic mixed controlled reactions, e.g. dissolution reactions of copper to copper complexes such as CuCl₂⁻ [2,39]. In summary, both regions revealed almost similar behaviors at 100 mV anodic potentials after initial immersion. This may be due to the active dissolution of surface constituents.

After 72 h of immersion, by applying a 100 mV anodic overpotential, the \( C_f \) and \( n_f \) values of both samples decreased (i.e. a considerable decrease in their surface layer thickness and homogeneity) while the \( R_f \) values increased comparing with 0 h results. This can be attributed to the formation of a more resistant and a thicker surface layer (smaller \( C_f \) values) with higher density of porosities (smaller \( n_f \) values) that affects the diffusion of the reaction species through them; see Fig. 8 (submicron paths). In other words, since at this potential the anodic curve is under mixed (diffusion and activation) control [2], and the values of \( n_f \) for both samples decreased, it can be stated that the surface layer has lost its uniformity and acts as a diffusion layer, in which the anodic reactions occur in porosities present at this layer. Comparing the 72 h results at the 100 mV anodic overpotential and at \( E_{\text{corr}} \) (Figs. 5 and 6 and Table 3), it can be observed that \( R_f \) values decreased regarding to higher kinetics of dissolution at this overpotential. Furthermore, while the \( C_f \) values are increased during the anodic polarization, the \( n_f \) values has not varied considerably. This in accordance with previous descriptions can be attributed to higher anodic dissolution rates.

Contrarily, considering Fig. 7 and Table 2, applying a 100 mV cathodic potential (at 0 h immersion) leads to a noticeable increase in the \( R_f \) values, particularly about four times higher than \( R_f \) values recorded at \( E_{\text{corr}} \). On the other hand, it can be seen that the \( C_f \) and \( n_f \) values of both samples are decreased (compared to \( E_{\text{corr}} \) results) as a result of the cathodic polarization, hence, a layer with higher thickness and roughness is formed on the surface; see Fig. 8. While the surface consists of a thin layer of corrosion products at instant immersion times, this phenomenon can be attributed to a non-uniform copper redeposition (formation of copper-deposited islands) during the cathodic polarization.

After 72 h of immersion, \( R_f \), \( C_f \) and \( n_f \) values of both specimens are increased in compared to \( E_{\text{corr}} \) results (Figs. 5 and 7 and Table 3). This reveals that during the cathodic polarization, the corrosion product layer partially dissolves (an increase in \( C_f \) value and a decrease in the layer thickness) and the reduced copper, redeposits in porosities and results in an increase in the surface homogeneity (an increase in \( n_f \) values). Moreover, by copper redeposition, the open porosities are blocked and thus the rates of reactions (the diffusion of reaction species) are slowed down (an increase in \( R_f \) values).

From Fig. 7 and Tables 2 and 3, it can be clearly observed that the \( R_f \) values are increased by increasing in immersion time (from 0 to 72 h). On the other side, while the \( C_f \) values are diminished after 72 h, \( n_f \) values are almost unchanged. This fact in accordance with previous results is an indication for the thickening process of the surface layer by time elapsing; see Fig. 8. Moreover, it can be deduced that the surface homogeneity in compared to 0 h results is most likely remained unaffected. This is due to the copper redeposition process during the cathodic polarization at both immersion times. Since the surface layer is the main reason for the corrosion resistance in C95800 alloys, it is found that the exposure time, has a great effect on the cathodic reaction(s) (comparing with anodic reactions) and in this manner, it results in a decrease in the corrosion current densities.
Fig. 8. (a and b) show the proposed equivalent circuits for extraction of EIS data considering a porous corrosion product film. (c–e) are schematic images depicting the surface layer evolution (based on extracted $C_{\text{an}}$ values from EIS results) of the base and weld samples during 72 h immersion in aerated 3.5% NaCl solution. (c) For samples at their $E_{\text{corr}}$, (d) for samples at their $E_{\text{corr}} + 100$ mV and (e) for samples at their $E_{\text{corr}} - 100$ mV. The brownish layer is assumed to be the product film and the white spots are the porosities.

Table 2

Extracted EIS parameters (at $E_{\text{corr}}$ and $E_{\text{corr}} \pm 100$ mV) of the base and weld specimens after initial immersion in aerated 3.5% sodium chloride solution. The represented data are the average of at least three experimental results; errors shown in the brackets are standard deviations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential (mV/SCE)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_i$ (Ω cm$^2$)</th>
<th>$A_{\text{an}}$ ($\Omega \cdot \text{s}^{1/2}$)</th>
<th>$n_{\text{an}}$</th>
<th>$n_f$</th>
<th>$p_s$ (μF/cm$^2$)</th>
<th>$p_f$ (μF/cm$^2$)</th>
<th>$C_{\text{ct}}$ (μF/cm$^2$)</th>
<th>$C_f$ (μF/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>$E_{\text{corr}}$</td>
<td>4 (±1)</td>
<td>830 (±20)</td>
<td>9500 (±150)</td>
<td>–</td>
<td>0.80</td>
<td>300 (±10)</td>
<td>400 (±20)</td>
<td>230 (±10)</td>
<td>1500 (±100)</td>
</tr>
<tr>
<td></td>
<td>±100</td>
<td>4.7 (±1)</td>
<td>650 (±10)</td>
<td>3500 (±200)</td>
<td>–</td>
<td>0.68</td>
<td>500 (±30)</td>
<td>3400 (±250)</td>
<td>360 (±30)</td>
<td>20,000 (±450)</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{corr}}$</td>
<td>4 (±0.5)</td>
<td>20 (±2)</td>
<td>8 (±1)</td>
<td>5.7</td>
<td>0.73</td>
<td>20,000 (±400)</td>
<td>48,000 (±250)</td>
<td>570 (±45)</td>
<td>40,000 (±600)</td>
</tr>
<tr>
<td>Weld</td>
<td>$E_{\text{corr}}$</td>
<td>4 (±1)</td>
<td>1350 (±80)</td>
<td>12,000 (±300)</td>
<td>–</td>
<td>0.80</td>
<td>400 (±50)</td>
<td>100 (±15)</td>
<td>380 (±40)</td>
<td>1700 (±50)</td>
</tr>
<tr>
<td></td>
<td>±100</td>
<td>4 (±1)</td>
<td>610 (±30)</td>
<td>3300 (±100)</td>
<td>–</td>
<td>0.75</td>
<td>500 (±40)</td>
<td>5200 (±100)</td>
<td>380 (±30)</td>
<td>15,000 (±400)</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{corr}}$</td>
<td>4.1 (±1)</td>
<td>19 (±3)</td>
<td>9 (±2)</td>
<td>5.8</td>
<td>0.57</td>
<td>6600 (±200)</td>
<td>72,000 (±400)</td>
<td>1500 (±100)</td>
<td>60,000 (±1400)</td>
</tr>
</tbody>
</table>
To sum up, the EIS in conjunction with DC results discloses that the uniform corrosion resistance of the alloy in aerated 3.5% sodium chloride solution in heat affected (weld) and unaffected (base) regions is improved by increasing in immersion time. In addition, it can be observed that the better homogeneity of the weld region results in a slightly better corrosion resistance of this zone almost at all polarization conditions.

3.4. Zero resistance ammeter results

The galvanic current and potential measured by ZRA method for the galvanic couples of base/weld are presented in Fig. 9. Due to higher corrosion potential of the base sample in compared to the weld sample, $E_{\text{corr}}$ values in Table 1, base metal acts as the cathode and weld zone acts as the anode in the galvanic cell. During the first 900 s of immersion, the mean value of galvanic current ($I_{\text{couple}}$) is 0.75 nA. By time elapsing, the mean values of $I_{\text{couple}}$ increases to about 0.93 nA after 24 h, then it decreases to around 0.06 nA in 48 h, and finally reaches to 2.95 nA after 72 h of exposure time. Considering the couple potentials ($E_{\text{couple}}$) presented in Fig. 9b, it can be seen that the mean values of the $E_{\text{couple}}$ are $-248, -234, -281$ and $-260$ mV (vs. SCE) for 0, 24, 48 and 72 h of immersion, respectively. While the $I_{\text{couple}}$ values are of few nanoamperes magnitudes, it seems that there is not such a considerable electrochemical difference between the base and weld zones during the whole immersion times; see Fig. 9. This means that the welding procedure could not result in the formation of a destructive galvanic couple between these two zones.

Taking into account the welding operation, induced microstructural and morphological changes in weld zone comparing with base sample are as follows: a decrease in $\alpha$ phase, an increasing in $\beta_0$ phase and almost no changes in $\gamma$ phase volume fractions. Although, the character of the phases may be altered because of the welding procedure, see Fig. 2. To differentiate the microstructural and morphological modifications, an additional superscript ($\alpha_w, \beta_0_w$ and $\gamma_w$ shown in Fig. 10) was used for individual phases in the weld region. The difference between volume fractions of the constituent phases most likely plays the major role in anodic and cathodic behaviors of these zones. To better identify the corrosion behavior of the constituent phases, phase fraction calculations were performed for both regions. For this couple, the anode (weld sample) is composed of 62 vol.% $\alpha_w$, 24 vol.% $\beta_0_w$ and 14 vol.% $\gamma_w$ (all with ±0.5% deviation), while the cathode (base sample) is composed of 73 vol.% $\alpha$, 24 vol.% $\gamma$ and 3 vol.% $\beta_0$ (all with ±0.5% deviation); see Fig. 2d and e. For this couple, according to the same volume fractions of $\gamma$ and $\kappa_w$ in both regions, it could also be assumed that these phases do not act as corrosion rate determining factors.

### Table 3

Extracted EIS parameters (at $E_{\text{corr}}$ and $E_{\text{corr}} \pm 100$ mV) of the base and weld specimens after 72 h immersion in aerated 3.5% sodium chloride solution. The represented data are the average of at least three experimental results; errors shown in the brackets are standard deviations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential (mV/SCE)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$R_f$ (X cm$^2$)</th>
<th>$n$</th>
<th>$j$</th>
<th>$p_{fr}$ (µF/cm$^2$)</th>
<th>$p_{fr}$ (µF/cm$^2$)</th>
<th>$C_{fr}$ (µF/cm$^2$)</th>
<th>$C_{fr}$ (µF/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>$E_{\text{corr}}$</td>
<td>4.5 (±0.5)</td>
<td>500 (±50)</td>
<td>12,500 (±100)</td>
<td>0.85 (±0.03)</td>
<td>0.54 (±0.01)</td>
<td>200 (±20)</td>
<td>380 (±30)</td>
<td>100 (±10)</td>
<td>1100 (±15)</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{corr}} \pm 100$</td>
<td>5.5 (±0.5)</td>
<td>1300 (±100)</td>
<td>6500 (±100)</td>
<td>0.83 (±0.03)</td>
<td>0.36 (±0.01)</td>
<td>300 (±10)</td>
<td>300 (±20)</td>
<td>220 (±10)</td>
<td>1000 (±25)</td>
</tr>
<tr>
<td>Weld</td>
<td>$E_{\text{corr}}$</td>
<td>6 (±1)</td>
<td>4400 (±200)</td>
<td>17,500 (±400)</td>
<td>0.87 (±0.02)</td>
<td>0.62 (±0.03)</td>
<td>300 (±30)</td>
<td>500 (±30)</td>
<td>310 (±25)</td>
<td>1400 (±30)</td>
</tr>
<tr>
<td></td>
<td>$E_{\text{corr}} \pm 100$</td>
<td>5.5 (±1)</td>
<td>1100 (±50)</td>
<td>10,000 (±200)</td>
<td>0.78 (±0.01)</td>
<td>0.56 (±0.02)</td>
<td>400 (±20)</td>
<td>1400 (±40)</td>
<td>320 (±10)</td>
<td>1100 (±20)</td>
</tr>
</tbody>
</table>

Fig. 9. Galvanic measurements between base and weld samples after 0, 24, 48 and 72 h of immersion in aerated 3.5% sodium chloride solution; (a) couple current (nA); and (b) couple potential (mV vs. SCE).

Fig. 10. Descriptive galvanic model representing the anodic and cathodic currents on each of the base and weld surface constituent phases. The arrow length is assumed to be an indication of current magnitudes.
phases in the proposed galvanic couple. In other words, it is assumed that the \( \kappa \) phase reveals anodic behavior on the anode \( (\kappa_{an}) \) and cathodic behavior on the cathode \( (\kappa) \). Due to higher volume fractions of \( \beta_{an} \) phase in the weld sample; this can be accounted as the most important cause of the anodic behavior in this sample. In contrast, the volume fraction of \( \alpha \) phase in base sample is higher than the weld \( (\alpha_{an}) \) and therefore, it can be responsible for the cathodic behavior of the base specimen. Additionally, it was reported that the corrosion resistance of \( \alpha \) phase is superior to \( \beta \) phase \cite{13} and hence, it can be assumed that \( \beta \) (also \( \beta_{an} \) in weld) phase behaves anodic at both the anode (weld) and the cathode (base) with similar anodic current densities, \( i_p \). Moreover, \( \alpha \) (also \( \alpha_{an} \) in weld) phase in these samples plays mainly a cathodic behavior (oxygen reduction reaction takes place on its surface) with similar cathodic current densities, \( i_c \) \cite{50}.

To better understand the origin of overall current \( i_{\text{couple}} \) measured in ZRA method, a schematic illustration of the galvanic couple is presented in Fig. 10. Such an approach has been previously employed to express the effect of Cu-rich phases on galvanic corrosion of aluminium–copper model alloys \cite{50}. In Fig. 10, the length of the current vectors is a criterion of their magnitude. To elucidate the proposed model at galvanic potential, sum of the anodic and cathodic currents should be equal according to the following equation:

\[
\sum i_a = \sum i_c \tag{13}
\]

where \( \sum i_a \) is sum of anodic currents and \( \sum i_c \) is sum of cathodic currents generated/consumed from the individual phases, which are present in each of the base and the weld samples. To simplify the galvanic model, the anodic and the cathodic currents with lower values (small current magnitudes illustrated by vectors in Fig. 10) are assumed to be negligible. In other words, although \( \alpha \left(\alpha_{an}\right) \) demonstrates a cathodic behavior in both samples, its elicited anodic currents in base and weld samples are insignificant. Also, it is assumed that the \( \kappa \) phase in base sample acts as a cathode while it \( (\kappa_{an}) \) inversely acts as an anode in weld sample, thus, the net current induced by \( \kappa \) phase is zero. In summary, the following relation is the expanded form of Eq. (13):

\[
\bar{T}_{\text{weld}} + \bar{T}_\text{base} = \bar{T}_{\text{weld}} + \bar{T}_\text{base} = \bar{T}_{\beta_{an}} + \bar{T}_{\alpha_{an}} + \bar{T}_{\beta} + \bar{T}_{\alpha} \tag{14}
\]

The overall current measured by ZRA method, \( i_{\text{couple}} \), is exactly the net current associated with the anode that flows toward cathode and that can be expressed as:

\[
i_{\text{couple}} = \bar{T}_{\text{weld}} - \bar{T}_\text{weld} = \bar{T}_{\beta_{an}} + \bar{T}_{\alpha_{an}} - \bar{T}_{\beta} - \bar{T}_{\alpha} \tag{15}
\]

or, if it is assumed that the galvanic current is the net current associated with the cathode that flows toward anode, then, it can be written as:

\[
i_{\text{couple}} = \bar{T}_\text{base} - \bar{T}_\text{base} = \bar{T}_{\beta} + \bar{T}_{\alpha_{an}} - \bar{T}_{\beta_{an}} - \bar{T}_{\alpha} \tag{16}
\]

In summary, the proposed model clearly explains the origin of the galvanic current measured by ZRA method, which is also in agreement with potentiodynamic results. From microstructural point of view, the proportions of \( \beta \) and \( \alpha \) were different in the base and weld samples, so the anodic current densities caused by \( \beta \), as well as cathodic current densities caused by \( \alpha \), of the base and weld samples were not similar. Moreover, the results indicated that the couple current is about few nanoamperes and hence, the gas tungsten arc welding procedure can be employed as a restorative and almost an invulnerable method for NAB joints.

4. Conclusions

In this research, corrosion of GTA welded nickel–aluminum bronze (C95800) is investigated by DC and AC electrochemical tests along with microscopic examinations. The microstructural and morphological modifications occurred during the welding operations in weld zone include a decrease in \( \alpha \) phase, an increase in \( \beta \) phase and almost no changes in \( \kappa \) phase volume fractions. In addition, due to the higher volume fraction of \( \beta \) (the anodic phase) in the weld sample, it reveals anodic behavior. While, because of higher volume fraction of \( \alpha \) (the cathodic phase) in base it behaves cathodic. Based on PDP and EIS results, the uniform corrosion resistance of instantly immersed weld and base regions are almost analogous and improved during immersion. At longer exposure times, the corrosion product layer grows and by slowing down the diffusion of reaction species through its porosities resulting in the alloy general corrosion resistance enhancement. Moreover, due to the better homogeneity of weld region, its surface layer discloses somewhat a better barrier characteristic after 72 h. On the other hand, since the major consequence of partial difference between volume fractions of the constituent phases is generation of a galvanic couple, ZRA results demonstrated that the couple current is only about a few nanoamperes. Therefore, it can be concluded that the general corrosion resistance of the restored damaged NAB parts could not be deteriorated in marine environments.

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References


