Harmonic analysis has been used in corrosion measurements for several decades. During this period the method has been refined and developed. Nevertheless, the technique has not been applied to properties determination in local scale yet. This paper is focused on local corrosion current measurements based on harmonic analysis. For this purpose, a non-linear nature of electrode processes is used and measured in local scale applying Harmonic Analysis Microscope (HAM).

At the beginning HA was limited to processes where both reactions were activation controlled or one of the reaction was under full-diffusion control. In that case, the harmonic analysis results are not questionable. However, the attempts of HA application to the systems with different controlling factors were made. Bosh et al. examined mild steel in 0.5 M Na2SO4, presenting mathematical model which applies to the reaction where anodic process is under activation control, but cathodic reaction is under mixed control. The obtained results were confirmed by Tafel extrapolation. For corrosion current calculation two extra parameters were required: diffusion coefficient and concentration profile of the oxidant. Jankowski also attempted to analyze more complex systems.

Nonetheless, it is worth to notice that all of these results are global harmonic response of total investigated object. Rarely is a sample homogenous, thus conventional electrochemical measurements present response over the entire electrode/electrolyte interface. No information on localized electrochemical reactions is provided in the process of response analysis, which causes data misinterpretation. Investigating the material in local scale, it is possible to detect active and passive sites and measure their impact on material global properties.

The local approach to corrosion measurements was presented in the work of Galica et al. The studies were performed on magnesium alloy to investigate contribution of particular phase into overall corrosion rate. Thanks to Local Electrochemical Impedance Spectroscopy, it was possible to determine differences in corrosion rate of particular phases. Nevertheless, the impedance measurements implement a set of frequencies. Thus, the application of HA to local measurements should decrease time required for parameters mapping due to single frequency perturbation.

This paper is focused on determination of local corrosion current based on harmonic analysis. For this purpose, a non-linear nature of electrode processes is used and measured in local scale applying Harmonic Analysis Microscope (HAM). The advantage of utilized approach base on receiving simultaneous information on corrosion current and both Tafel coefficients, during a single measurement. Therefore, HAM allows determination of local changes of corrosion process kinetics, particularly important when evaluating the role played by microstructure of an alloy.

**Experimental**

The electrochemical measurements were performed by means of Autolab PGSTAT30 potentiostat/galvanostat (Ecochemie, The Netherlands). The system was expanded with NI PXI-4461 and NI PXI-4462 (National Instruments, USA) measurement cards for AC signal generation and acquisition, respectively. The aforementioned cards were operating in NI PXI-1031 chassis and controlled by NI PXIe-8105 embedded controller.

The measurements were carried out in five-electrode system. The conventional part consists of platinum counter electrode (CE), silver/silver chloride reference electrode (RE) and the investigated metal acting as a working electrode (WE). Two additional electrodes act
The SEM analysis was carried out by means of S-3400N microscope (Hitachi, Japan) with a tungsten source. The microscope is coupled with energy dispersive spectroscopy (EDS) analyzer UltraDry (ThermoFisher Scientific, USA).

The measurements were performed on M58 duplex brass. With regards to EDS measurements, metal consists of 58.9% zinc and 41.1% copper (wt%). Prior to measurements, the investigated sample was grinded with abrasive paper with increasing grit sized up to 2000. After mechanical preparation, brass sample was subjected to etching solution to reveal the structure. The treatment lasted for 60 second in etching solution composed of 100 cm³ H₂O, 30 cm³ HCl and 5 cm³ FeCl₃. The efficiency of etching was determined by Scanning Electron Microscope.

The sample area subjected to electrochemical investigations was 2 cm². A solution of 0.1 M KCl was used as an electrolyte. The conductivity of solution was 12.3 mS cm⁻¹. The solution was aerated prior to each experiment. During the experiment, the sample was held at open circle potential (EₒCP = −0.19 V vs Ag|AgCl).

Results and Discussion

For the purpose of this work, the local corrosion rate was calculated on the basis of particular harmonic component. The measured drop of the voltage caused by perturbation signal between UME was subjected to Short-Time Fourier Transformation. The obtained spectrum was analyzed in order to describe values of the fundamental, the second and the third harmonic component. The amplitudes of particular harmonic were determined from the spectrum automatically by the authors’ original program. The amplitudes of harmonic potential were calculated to local current according to Equation 1 with respect to Ohm’s law:¹⁷

\[ i(\omega)_{loc} = \frac{\Delta V(\omega)_{probe} \cdot \kappa}{d} \]  

where \( i(\omega)_{loc} \) is a value of local current, \( \Delta V(\omega)_{probe} \) is a drop of voltage measured between UME, \( \kappa \) is conductivity of the solution and \( d \) is distance between UMEs. As a result, the set of parameters was obtained, including fundamental, second and third harmonic current values with specific coordinates.

As the anodic and cathodic charge transfer reaction is non-linear, the form of faradaic current is a distorted sinusoid.¹ Later, the faradaic current consists of fundamental harmonic component with frequency of \( \omega \) and higher harmonics with frequencies of \( k \omega \) (\( k = 2, 3, \ldots \)). Using the Fourier series, it is possible to describe faradaic current as follows:

\[
\begin{align*}
    i_F &= i_{corr} \left\{ \left[ I_0 \left( \frac{U_0}{\beta_0} \right) + 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1} \left( \frac{U_0}{\beta_0} \right) \sin (2k+1) \omega t \right]ight. \\
    &\quad + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k} \left( \frac{U_0}{\beta_0} \right) \cos 2k \omega t \right\} e^{\frac{\beta_0}{\beta_1}} \\
    &\quad - \left[ I_0 \left( \frac{U_0}{\beta_1} \right) - 2 \sum_{k=0}^{\infty} (-1)^k I_{2k+1} \left( \frac{U_0}{\beta_1} \right) \sin (2k+1) \omega t \right]ight. \\
    &\quad \left. + 2 \sum_{k=1}^{\infty} (-1)^k I_{2k} \left( \frac{U_0}{\beta_1} \right) \cos 2k \omega t \right\} e^{-\frac{\beta_0}{\beta_1}}
\end{align*}
\]

where \( I_n (n = 0, 1, 2, \ldots) \) are modified Bessel functions of the first kind.

The equation presented above allows to determine the value of current for each of the first three harmonic components. For the purpose of mathematical model simplification, the assumption that amplitude \( U_0 \) is limited to the extent that the Bessel function could be approximated with Taylor polynomials is applied. In such case, the equations describing particular harmonic components could be presented as
The magnitude of amplitude of individual harmonic components depends on properties of the investigated system and resistance of the environment. For this reason, a perturbation amplitude has to be chosen with respect to achieve steady-state conditions and sufficient resolution. Low frequency (below 0.1 Hz) is usually applied in case of harmonic analysis. However, the lower the frequency, the longer the acquisition time. In scanning mode of such low frequency, the time required to obtain at least three waveforms for harmonic analysis at a single measuring point would be a great disadvantage. During this time, the condition of the investigated system could change and two consecutive points would be described by different conditions. The frequency was selected according to Sathiyanarayanan’s work based on the knowledge about polarization resistance $R_p$ and double layer capacitance $C_{dl}$. For the measurements to be reliable, $R_p$ should be greater than $(\sigma C_{dl})^{-1}$. This condition is fulfilled, when the frequency is lower than 5.5 Hz. On the other hand, equation proposed by Jankowski was used to verify the level of relative error during fundamental harmonic current measurement. Therefore, we can calculate that this error is less than 0.1%. Summarizing, the upper limit of frequency depends on properties of particular system and assumed relative error. Thus, the frequency should be selected individually for specific investigated system.

The obtained maps of the particular harmonic are presented on Fig. 2. Each successive signal is characterized by a lower magnitude, in accordance with the theory. Furthermore, the high level of correlation can be distinguished between the second and the third harmonic map, as expected. Simultaneously, fundamental harmonic response is quite the opposite.

Equations 6–8 describe relationship between individual harmonic components from specific parameters of system. Corrosion current may be calculated on the basis of the first three harmonic components separated from the signal, which require solving Eqs. 3–5.

The local current map, calculated with Equation 6, is presented on Fig. 3b. Two main areas can be distinguished, characterized by differences in corrosion current values. Created local current path should be associated with brass structure presented on Fig. 3a. Phases size and distribution can be observed. The structure of investigated duplex brass consists of two phases: $\alpha$- and $\beta$-phase, the primary difference is zinc contribution. In $\beta$-phase contribution of zinc is higher than $\alpha$-phase. If the brass is exposed to corrosive environment, different structure leads to formation of galvanic microcells, where $\beta$-phase acts as an anode and $\alpha$-phase as a cathode.

It is important to state that both presented images do not represent the same region of sample surface. However, similar pattern could be distinguished between both figures. Higher corrosion current represents areas of $\beta$-phase, while lower values should be associated with $\alpha$-phase.
According to Equations 7–8, calculation of both $\beta$ coefficients is possible based on HA measurements. The spatial distribution of particular parameters is presented on Figs. 4a and 4b. Both coefficients are higher in areas where corrosion current increases according to Fig. 3b. Nonetheless, it is worth to notice that $\beta_c$ is locally characterized by high values. Such behavior would imply that the dynamics of the cathodic reaction (oxygen depolarization, in neutral pH) is locally diversified. There are few possible reasons for such behavior, such as difference in local oxygen demand or locally altered adsorption of oxygen to the active sites. Moreover, the changes in $\beta_c$ Tafel slope lead to different corrosion currents. When the slope is rising, the current increases as well.

It should be noted that according to Equations 7–8 calculated Tafel coefficients depend on perturbation amplitude $U_0$, as was also discussed by Gabrielli et al.\textsuperscript{27} It was concluded that high correlation between obtained results was visible for perturbation amplitudes no greater than 30 mV. Higher values of $U_0$ should not be considered due to limitation resulting from application of Besell function.\textsuperscript{1,27}

In order to determine the type of control, series of Tafel plot were made. Polarization curves, as shown in Fig. 4c, are characterized by activation control of cathodic and anodic process. Average values of $i_{corr}$ and both $\beta$ coefficients resulting from Tafel’s plot with their standard deviation have been presented on Fig. 4d. Furthermore, the average values of the same parameters based on harmonic measurements were added for comparison. The results of both experiments are correspondent.

In order to compare changes of corrosion current with material structure, an additional measurement was made. The main objective of the measurement was one to one correlation of SEM image and corrosion current changes. For the purpose of measurement, sample surface was significantly limited through coverage by insulator. Series of line scans were performed in the limited area. Subsequently, the relevant areas were photographed with SEM in order to compare the results. The obtained corrosion current dependency from the distance was presented on Fig. 5b. Presumably, the corrosion current increased when the probe was located above $\beta$-phase, while decreasing over $\alpha$-phase. For comparison, Fig. 5a presents a white line to mark the place.
of measurement. What is worth to mention is that with respect to diffusion field, the line scan may have been performed a few micrometers below or above the marked line.

Conclusions

The application of harmonic response in local scale was presented. Using appropriate measuring setup and mathematical approach, it is possible to calculate corrosion current and both Tafel coefficients in microscale. In case of harmonic response analysis in scanning mode choice of appropriate frequency is crucial for reasonable time of experiment, and therefore, reliable results.

It is crucial to emphasize that presented values with HAM technique were obtained by equation which consists of certain approximation described in this work. Nevertheless, applying of harmonic analysis in local scale allowed to reveal differences in corrosion current of particular phases.

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