Methodology for determination of corrosion current density evolutions. Case of AISI 1020 steel in high content chloride ion solutions.

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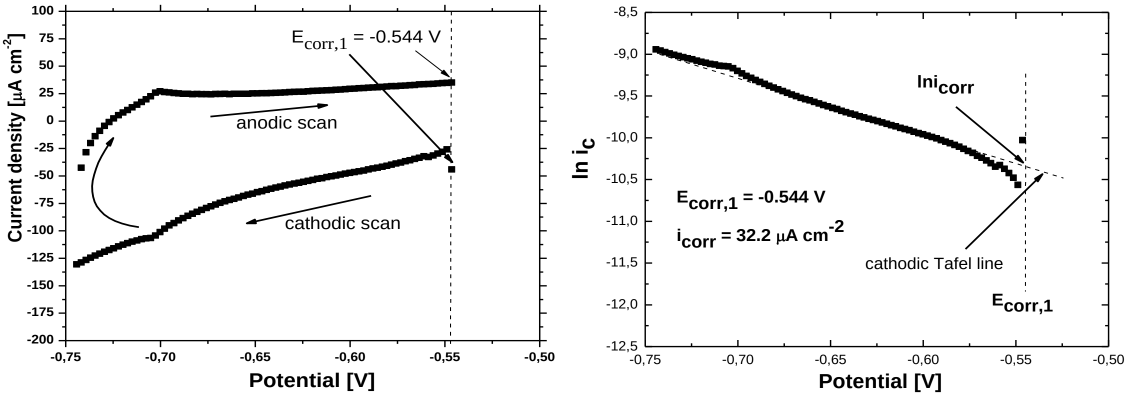
Introduction

In general, in several published corrosion works [1, 2], the corrosion current densities are not followed against the immersion time. This makes that the results can not constitute a real description of the corrosion problem. On the other side, there are small number of papers dealing with the problem of how to determine the corrosion current density after important periods of immersion [3]. The present paper is an effort to show one way to follow the evolution of the corrosion current density with immersion time for the case of a normal steel (AISI 1020) in solution containing important amounts of NaCl. The AISI 1020 in NaCl solutions will have pitting attack and then, several determination methodologies of corrosion current densities can be compromised. Nevertheless, if after sometimes high amount of corrosion products are present on the corroded surface (even when they are downward), they can perhaps permit to apply some classical ways for the determination of the corrosion current densities. The present paper is a study to see if for large immersion times, but with the formation of corrosion products, one of these classical methods is applicable in the case of the analyzed system.

Experimental

The working electrode was a bare AISI 1020 steel included in an epoxy resin, with an exposed area of 1.34 cm^2. The solutions were NaCl 1.0 mol L^{-1} or 3.0 mol L^{-1} or 5.0 mol L^{-1}, always plus NaNO$_3$ 0.3 mol L^{-1}, oxygenated. The reference electrode was Hg/HgO/NaOH 0.1 mol L^{-1}. The working electrode was always initially polished with 600 emery paper before each experiment. Experiments were done by electrode immersion with its surface pointed downward into the selected solution. Free corrosion potential, E_{fc}, was followed vs time (t).



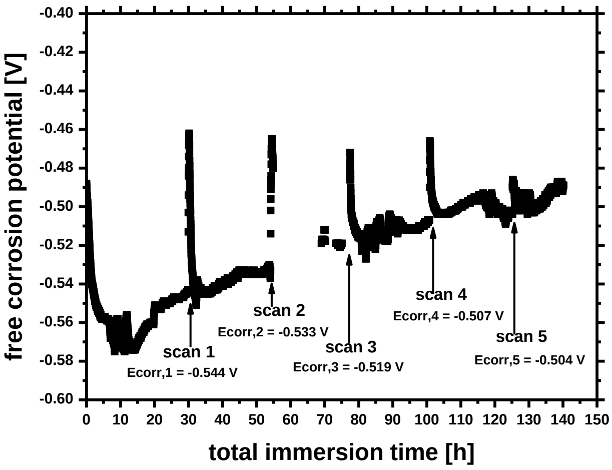
(a) **(b)**

Figure 1. (a) Typical cathodic/anodic voltammetric sweeps for $E_{corr,1}$ (see Figure 2). Voltage sweep interval 200 mV. Scan rate 1 mV.s^{-1}. Solution: NaCl 1.0 mol L^{-1}+NaNO$_3$ 0.3 mol L^{-1}. (b) ln|i_c| versus potential from the cathodic scan of Figure 1a.

Each 24 hours cathodic/anodic voltammetric sweeps at 1 mVs^{-1} were made in a voltage interval of 200 mV, beginning at the E_{fc} of the moment ($E_{corr,i}$, i = 1, 2, …) and returning to it. Then, the same sequence was followed. The corrosion current densities were determined from the cathodic Tafel representation of the corresponding cathodic sweep by extrapolation to the $E_{corr,i}$ ($i = 1, 2, \ldots$). All this procedure can be seen for $E_{corr,1}$ (from Figure 2) in Figure 1.

Results and Discussion

In Figure 2, it is plotted a typical behavior of E_{fc} vs t for one of the three studied solutions. It is seen the evolution of E_{fc} in each time interval (about one day in time and interrupted by the voltammetries). The E_{fc} in each interval shifts first cathodically and then anodically. It is evident that each voltammetric experiments affect the electrode. At the same time the fact that the general evolution of E_{fc} with time, for the different intervals, following a continuous curve, shows that the voltammetric perturbation is auto-eliminated. This general behavior is like if, at the beginning of each interval, a pitting process becomes active, making that the E_{fc} becomes more cathodic. Pitting initiation or activation is characterized by a cathodic potential evolution. After that, in each time interval, the E_{fc} evolves in the anodic direction. This must imply a film formation in the surface regions without pitting. The E_{fc} anodic evolution will make that the total anodic current increases and, consequently, the total cathodic current must increase too. The anodic one would be formed by the pitting contributions plus the external film formation contribution. The total cathodic current will be done by the oxygen and/or hydrogen evolution at the external surface of the samples, out of the pitting. This analysis would be valid for the three studied chloride concentrations because they present the same behaviors. All these must mean the increase of the measured corrosion current densities, fact which will be shown. The pitting presence is proved in Figure 3 where a surface micrograph, representative of one of the studied cases, is shown. The figure shows some pitting with diameters of about 40 μm together with the formed surface film.



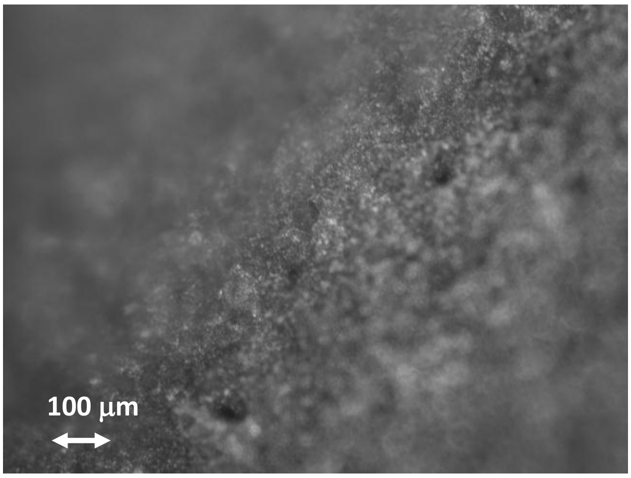


Figure 2. Free corrosion potential versus total immersion time. NaCl 1.0 mol L^{-1}, $NaNO_3$ 0.3 mol L^{-1} solution. Arrows points out the moments for each voltammetry (unregistered) at each $E_{corr,i}$.

Figure 3. Typical pitting micrograph for the same solution of Figure 1. Pitting diameter 40 μm.

In Figure 4, the corrosion current densities (determined through the cathodic Tafel extrapolation) versus the immersion times for the three studied solution have been plotted. They point out to the evolution of the total cathodic and, consequently, anodic currents. Figure 4 shows: a) that the corrosion results seems to be consistent because they give perfectly determined patterns (1.0 and 3.0 mol L^{-1} increase linearly with time, 5.0 mol L^{-1} remains constant); b) the total corrosion currents are greater for the 5.0 mol L^{-1} than for 3.0 and 1.0 mol L^{-1}. At the same time, the 5.0 mol L^{-1} gives a constant value, when 3.0 and 1.0 mol L^{-1} increase with the immersion time (the first one with a higher slope than the second). Nevertheless, these data do not agree with the observed precipitation at the bottom of the experimental vessels. The precipitation is maximum for 1.0 mol L^{-1}, and decreases for 5.0 and 3.0 mol L^{-1}. This is showing that there are two causes of the precipitate: the pitting action and the dissolution of the external film, possibly influenced by the solution concentrations.

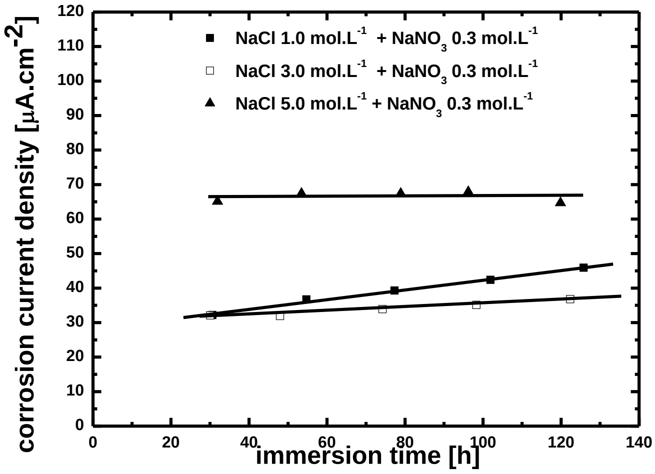


Figure 4. Determined corrosion current density for the different corrosion potential $E_{corr,i}$. $i_{corr,i}$ (i = 1, 2, 3, 4 and 5) versus immersion (corrosion) times. Solutions: NaCl 1.0 mol L^{-1} + NaNO$_3$ 0.3 mol L^{-1} (■); NaCl 3.0 mol L^{-1} + NaNO$_3$ 0.3 mol L^{-1} (□); NaCl 5.0 mol L^{-1} + NaNO$_3$ 0.3 mol L^{-1} (▲). Determination of $i_{corr,i}$ through figures like Figure 1b.

Conclusions

Nevertheless the complications of the analyzed system, the obtained results, meanly that of Figure 4, seem to show that the extrapolation of Tafel curves to the corrosion potential can be used to follow the corrosion current density with time for extended periods of immersion, even in the presence of pitting, when there is external film formation.

References

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