Instances of Chaotic Behaviors in Several Types of Localized Corrosion Processes

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It has been extensively shown in the last decade that potential and current fluctuations in the curse of pitting corrosion exhibit all the features of low dimensional chaos. Such a behavior was first observed in pitting corrosion of aluminium alloys whereas pitting of stainless steels rather exhibit stochastic characteristics, in the form of randomly distributed pitting transients. Recently, crevice corrosion of stainless steels was found to produce complex periodic signals in its propagation phase. Last, applied stress was shown to play a major role on the characteristics of the potential oscillations in the corrosion of Copper base alloys in galvanostatic conditions. It is intented in this paper to recall some of the more striking findings in these fields, in order to help for further modeling of the occurrence of chaos in localized corrosion processes, whatever the type of localized corrosion under condideration.

Pitting Corrosion [1,2]

Recent works however suggest that fine structure of current and potential fluctuations inside the individual transients also present chaotic features. Then, chaos was felt to be the signature of propagating pits, or of the propagation stage in case of metastable pits.
The composition of the corrosive (chloride containing) electrolyte plays of course a major role in the occurrence of chaos. One of the more striking effect is the effect of pH. It has been shown that aluminium alloys pitting (in NaCl +NO_3Na electrolytes) shows randomly distributed single pitting transients at neutral pH, periodic behavior close to the depassivation pH (~4) and chaotic behaviors in acidic media, the transition to chaos occurring mainly through the period doubling cascade mechanism.
From another hand, chaotic behavior of Aluminium alloys is favoured by the presence of tartrate ions in the electrolyte, which are known as antirepassivationg agents. In the case of stainless steels, even at neutral pH, Chaos is promoted by the addition of thiosulfates ions in chloride containing solutions. Thiosulfates are also antirepassivating agents for stainless steels, suggesting that even in propagating localized corrosion, Chaos is the signature of the active passive transition.

Crevice Corrosion [3]
The occurrence of periodic oscillations in crevice propagation suggest that corrosion operates on the verge of the active passive transition, the potential in the crevice being controlled both by the ohmic drop and the electrochmiccal coupling with the cathodic zone outside the crevice.

Stress corrosion cracking [4]
The potential fluctuations obtained galvanostatically in the α brass /1M $NaNO_2$ system can be analysed as a function of an applied mechanical stress. This study was motivated by the observation that when coupling in this system SCC testing and galvanostatic measurements, the oscillatory behavior is strongly affected. It is clearly shown in this study that the oscillatory system pass throw periodic oscillations accelerated by the mechanical stress, then by an intermittency behavior (see figure) before completely disappearing when a sudden failure occurs. Last, a strong effect of the solution pH was evidenced

Concluding remarks

From these results it can be concluded that the well known chemical, the less known electrochemical and the rather new effect of mechanical parameters in synergy with chemical/electrochemical factors are responsible for current or current fluctuations. Recent attempts to model chaotic behavior in corrosion processes [2].suggest to consider that critical variations of these parameters produce bifurcations between different dynamic behaviors at the active passive limit, possibly leading to chaos either trough doubling period or intermittency mechanisms. Comparison of the different types of bifurcations occurring in several types of localized corrosion processes is felt to be of interest in this purpose

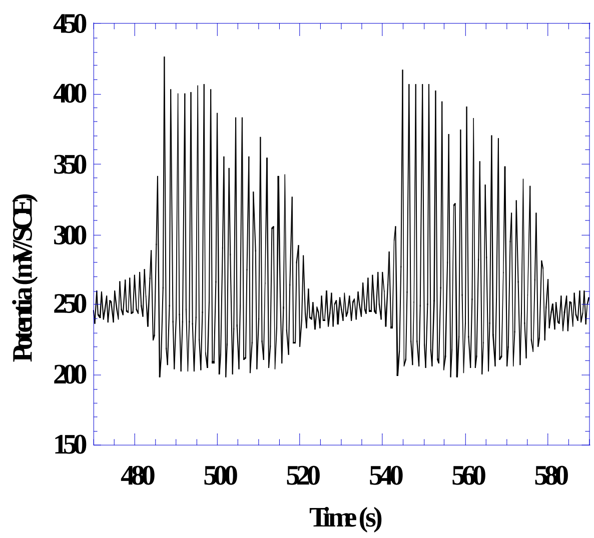

Figure : Intermittencies potential oscillations observed in α–brass/1M $NaNO_2$ system when tested galvanostatically under a mechanical stress.

References

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