

Effect of NaCl addition on the voltage noise characteristics during oxidation of iron in NaNO₃-NaNO₂ melt

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Effect of NaCl addition on the oxidation of iron in NaNO₃-NaNO₂ melt at 250°C has been studied by electrochemical voltage noise analysis and harmonic current measurements. The voltage fluctuations, electrochemical noise power and oxidation rate were tend to decrease with immersion time in the NaNO₃-NaNO₂ melt due to the growth of compact oxide film. This trend was maintained even after the addition of 2% NaCl. However, a rapid increase of voltage fluctuations, noise power and oxidation rate were observed after the addition of 3% NaCl due to breakdown of the compactness of oxide film. The compact nature of oxide film and their breakdown has also been confirmed by recording power spectral density plots in particular melt system.

Among the various electrochemical monitoring techniques, electrochemical noise analysis is highly advantageous since it is a non perturbative method. Noise is a general term used to explain the fluctuating behaviour of a signal with time. In case of electrochemical corrosion this phenomenon is stochastic, random in time and is the result of series of transients associated with the film breakdown or general corrosion^{1,2}. Using noise method, studies related to monitoring of various corrosion events like pit initiation and their propagation, active-passive transition have been carried out in aqueous system³⁻⁵. In fused salt system this technique was introduced for the first time for the evaluation of hot corrosion of nickel based alloys in sulphates and sulphate-chloride melt⁶. It was reported that voltage fluctuations (electrochemical potential noise) at rest potential were similar to those in aqueous system. Recently, a correlation has been established between electrochemical voltage noise and oxidation rate of iron with temperature in fused NaNO₃-NaNO₂ and NaNO₃-KNO₃ melts^{7,8}. Moreover, the effect of addition of chloride ion in NaNO₃-NaNO₂ melt on the voltage noise behaviour and oxidation rate of iron has not been carried out. The present investigation is an attempt to understand the oxidation behaviour of iron in NaNO₃-NaNO₂ melt in the presence and absence of chloride ion by using electrochemical noise analysis.

Experimental Procedure

Analytical grades NaNO₃-NaNO₂ were dried in vacuum oven at 150°C upto 12 h to remove moisture content. Then their equimolar mixture (40 g) was kept in the inner Pyrex glass tube of the electrochemical cell and dried again in melt condition at 250°C till the disappearance of the characteristic water wave^{9,10}. The melt was deaired by bubbling of dry oxygen free Argon gas. The details of drying of salt melt and its deairation are available elsewhere^{7,11}. The electrochemical set-up employed in the present investigation, is shown in Fig. 1. Two identical rectangular iron electrodes (Armco iron) were used for electrochemical noise measurements. The gap between exposed area (0.16 cm²) of the specimen and glass wall was filled by MgO based high temperature ceramic adhesive (Ceramabond 571). The exposed metal surface of the specimens polished upto mirror finish by various grades of emery paper followed by cleaning with trichloroethylene. The temperature of the melt was maintained at 250±2°C by using a variable transformer.

The voltage fluctuations, autocorrelation function of the voltage vs time data and power spectral density (PSD) plots were recorded with signal processor (1200 solartron, UK) in the band width of 20mHz-1Hz. For measuring the corrosion (oxidation) rate at a particular time, harmonic current method was employed¹². In this method,

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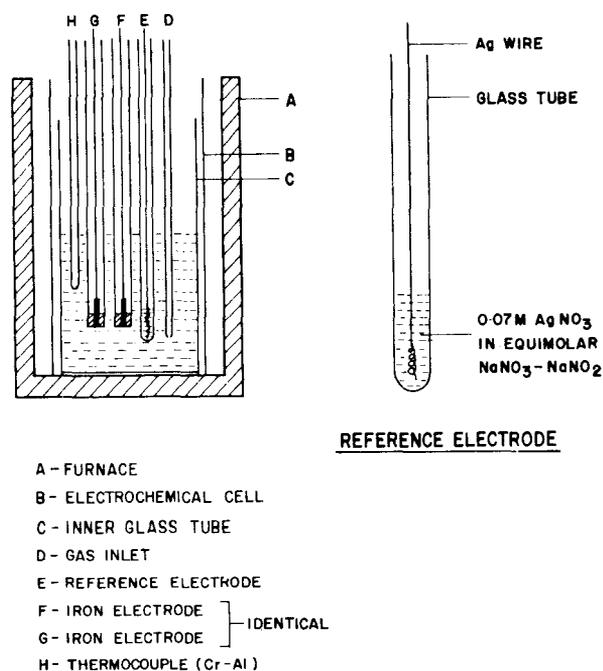


Fig. 1—Electrochemical set-up employed for noise analysis in NaNO₃-NaNO₂ melt

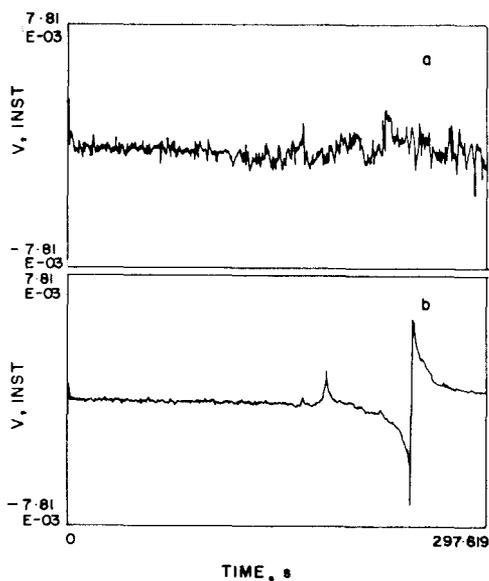


Fig. 2—Instantaneous voltage fluctuations with time after 0.5 h of immersion at 250°C. (a) NaNO₃-NaNO₂ melt, (b) 3% NaCl in NaNO₃-NaNO₂ melt

alternating voltage of 10 mV at 30 mHz was applied from sine wave generator (Model 142, Wavetek, USA) to the cell through the potentiostat (Model 173 PAR, USA) which was set at the corrosior potential. The harmonic current components were measured in the signal processor. The corrosion current was calculated from harmonic current values as per given relation^{7,12}.

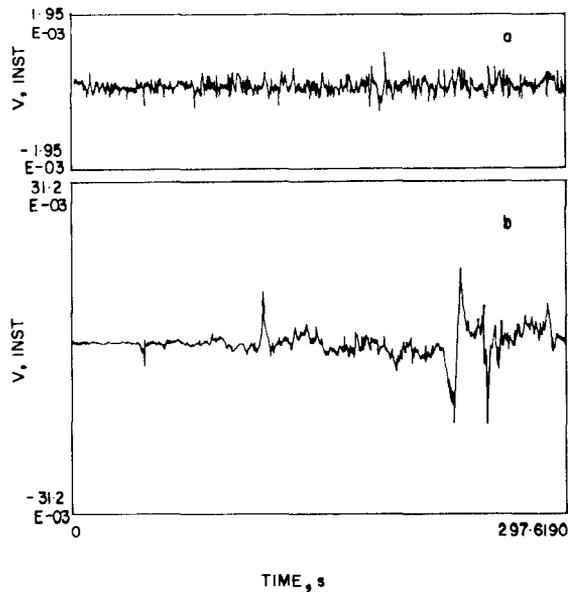


Fig. 3—Instantaneous voltage fluctuation of iron with time after 2.5 h of immersion at 250°C. (a) NaNO₃-NaNO₂ melt, (b) 3% NaCl in NaNO₃-NaNO₂ melt

$$i_{\text{corr}} = \frac{i_1^2}{\sqrt{48\sqrt{2i_1i_3} - i_2^2}}$$

where i_1 , i_2 and i_3 are the fundamental, second and third harmonic current components. The corrosion potential was measured with respect to Ag/AgNO₃ (0.07 AgNO₃ in equimolar NaNO₃-NaNO₂) reference electrode^{7,11}.

Results and Discussion

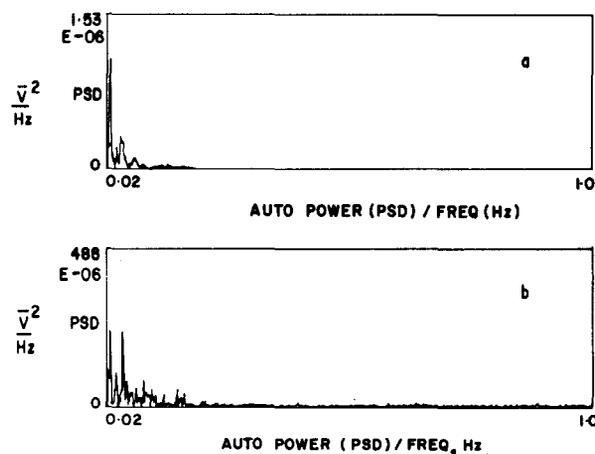
Voltage fluctuation vs time behaviour—The voltage fluctuation with time for iron in NaNO₃-NaNO₂ melt at 250°C after 0.5 and 2.5 h of immersion in presence and absence of 3% NaCl are shown in Figs 2 and 3. The voltage fluctuations in NaNO₃-NaNO₂ melt was nearly in uniform amplitude while it has become non uniform with potential splikes after the addition of 3% NaCl. The mean values of the amplitude of the voltage fluctuation after 0.5 h were found approximately ± 1.5 mV in NaNO₃-NaNO₂ melt while ± 5 mV in presence of 3% NaCl in the melt (Figs 2a & b). After 2.5 h of immersion, it decreased further to ± 0.2 mV in NaNO₃-NaNO₂ melt (Fig. 3a) while it has increased to ± 15 mV in presence of 3% NaCl in the melt (Fig. 3b). There are no notable changes of voltage fluctuations were observed even addition of upto 2% NaCl in the melt. It has been reported⁶ that the magnitude of the corrosion potential fluctuations or transient is dependent on the corrosion process and an increase in this value can be related to either localized

Table 1—Variations of noise power and corrosion current with time in presence of 3% NaCl in NaNO₃-NaNO₂ melt at 25°C

	Time, h	Without NaCl	With NaCl
Noise power, V ²	0	18000×10 ⁻⁹	31000×10 ⁻⁹
	0.5	661×10 ⁻⁹	13600×10 ⁻⁹
	1.0	47×10 ⁻⁹	3200×10 ⁻⁹
	1.5	42×10 ⁻⁹	1100×10 ⁻⁹
Corrosion current, μA	0	23	40
	0.5	13	33
	1.0	10	25
	1.5	9	21

corrosion or to an increase in corrosion rate. Present observation suggests that the initiation of some kind of discontinuities in the oxide film which generate a significant and abrupt voltage fluctuation in the presence of 3% NaCl in the melt. Generation of low amplitude noise in NaNO₃-NaNO₂ melt alone and in presence of upto 2% NaCl attributes the formation of compact type of oxide film. Decrease of this value with time is due to the increase in compactness of oxide layer. This result the decrease of diffusion of metal ions into the scale through the metal/melt interfaces. In the presence of 3% NaCl an increased value of voltage fluctuation indicates the enhanced rate of diffusion of metal ions into the scale.

Electrochemical noise and oxidation rate—To know the oxidation kinetics in terms of degree of voltage noise and oxidation rate, a detailed electrochemical voltage noise power (V²) and corrosion current were measured upto 1.5 h of exposure in the absence and presence of 3% NaCl in NaNO₃-NaNO₂ melt. The corresponding values are summarised in (Table 1). From the results, one may find the generation of higher noise and the flow of more corrosion current in the initial stage of oxidation and their apparent decrease with time in both melts. An increase of around two to three orders of magnitude of higher noise power and nearly 2 to 3 times more corrosion (oxidation) rate were noted in presence of 3% NaCl in the melt (Table 1). A slight increase of voltage noise and corrosion rates was also noticed after the addition of 1 and 2% NaCl in the melt. It may, therefore, be suggested that addition of high concentration of chlorides ion in the melt is quite effective in increasing of oxidation of iron. Addition of 7.5% NaCl in NaNO₃ melt was found to initiate the cracking of the scale¹³. It has also been reported⁶ that addition of even 1% of NaCl in sulphates melt

Fig. 4—PSD plots of iron after 0.5 h of immersion at 250°C. (a) NaNO₃-NaNO₂ melt, (b) 3% NaCl in NaNO₃-NaNO₂ melt

increases the generation of voltage noise significantly⁶. In the present investigation, generation of quite high noise during the initial stage of oxidation in both the systems (Table 1) suggest the randomness of the oxidation process in the beginning. Since the generation of voltage or current noise is mainly related to the random motion of the electron or ion within the systems¹⁻³. The apparent decrease of noise power and corrosion current with time is attributed to the decrease of oxidation rate due to the increase of compactness of the oxide film.

Power spectral density plot—In order to confirm the existence of compact oxide film formed on iron in NaNO₃-NaNO₂ melt, the power spectral density (PSD) plots were recorded at various time intervals. PSD plot is one of the frequency domain representation of a time domain signal, the PSD values at a particular frequency is proportional to the square of the amplitude at that frequency. Figs 4a & b show the corresponding PSD plots of iron in absence and presence of 3% NaCl in NaNO₃-NaNO₂ melt after 0.5 h of immersion. The observation of low frequency noise in both melts confirm the randomness of the oxidation process in the beginning which is within good agreement of observation of high voltage fluctuations and oxidation rate in the initial stage of exposure as discussed earlier. The extent of randomness was quite high in 3% NaCl containing melt because of the occurrence of higher degree of power spectral density (Fig. 4). It is interesting to note that PSD plot found to be nearly a white noise even after one hour of exposure in NaNO₃-NaNO₂ melt alone and became completely white noise with proportionate

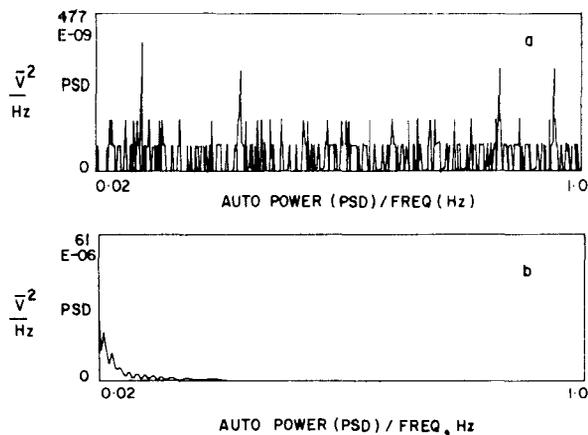


Fig. 5—PSD plots of iron after 2.5 h of immersion at 250°C. (a) NaNO_3 - NaNO_2 melt, (b) 3% NaCl in NaNO_3 - NaNO_2 melt

decrease of noise after 2.5 h (Fig. 5a). This clearly indicates the formation of a compact oxide film in NaNO_3 - NaNO_2 melt alone. In case of 3% NaCl containing melt the low frequency noise with fairly higher noise amplitude is observed (Fig. 6b).

The generation of white noise during the passive film formation and low frequency flicker type noise during breakdown of passive film has been reported in aqueous systems^{14,15}. It may be inferred that oxide film formed in NaNO_3 - NaNO_2 melt is of a compact type similar to that of passive film formed in aqueous system. However, oxide film formed in presence of 3% NaCl probably developed discontinuities into the oxide layer. This may lead breakdown of compactness of oxide film. This may be the main reason for the occurrence of quite higher voltage fluctuation, noise power and oxidation rate in presence of 3% NaCl in the melt.

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