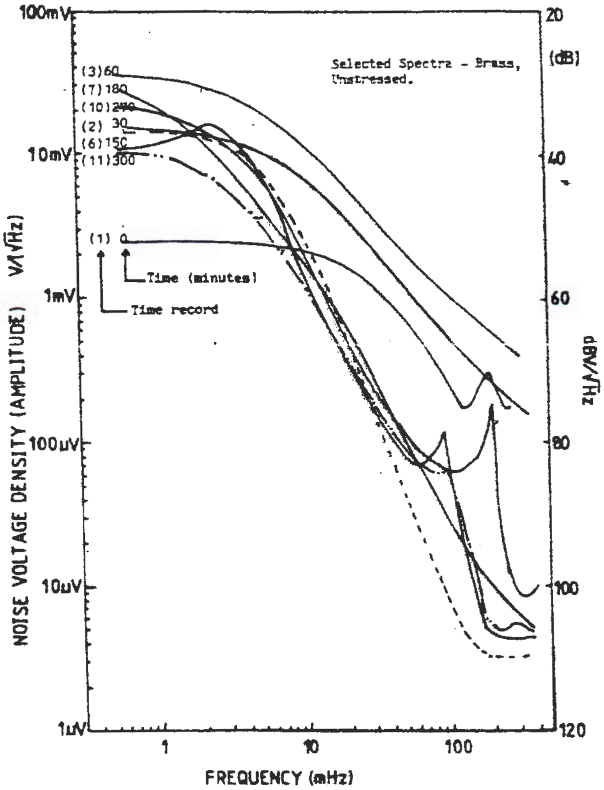

FIGURE 3 — Selected spectra—brass, unstressed.

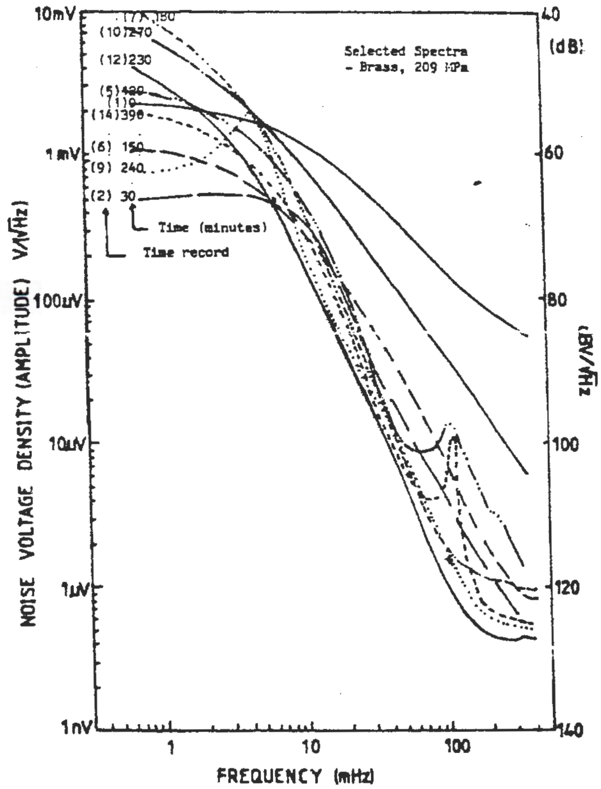

FIGURE 4 — Selected spectra—brass, stress 209 MPa.

Electrochemical Noise Measurements—Spectral Density Curves

Figure 3 gives the unstressed specimen's spectral curves. The curves tend to merge at higher frequencies of 10 and 100 mHz. Figure 4 shows the stressed specimen curves. In most cases, the times that a macroscopic crack was observed correspond to the highest noise amplitude at low frequency. For example, the highest noise amplitude occurred at time record 7 (180 min) at the lower frequency and at time record 10 (270 min from the start of the experiment) at higher frequencies. The crack first became discernible when these times were observed. For all specimens tested, the first time record is always observed to have one of the highest noise amplitudes at low frequency, and always the highest at the higher frequency ranges.

All of the spectra took the form of a low frequency plateau with a roll-off at increased frequency. The curves' noise voltage densities (amplitude) decreased with an increase of frequency. Some peaks were indicated in the spectra. The source of the electrochemical noise is assumed to be metal dissolution and repassivation transients resulting from the exposure of fresh metal surface, following the rupture of the passive film on the brass.

Standard Deviation (Spectrum) vs Time Curves

The standard deviation (spectrum)[5] vs time curves for the unstressed specimen (Figure 5) showed no particular trend. For the stressed specimen – 209 MPa (Figure 5), the highest peaks occurred at 180 and 270 min, respectively, from the start of the experiment and correspond to the times that

[5]The standard deviation (spectrum) is one of the results obtained from the computer analysis of the data from the time domain. It is essentially the average noise power within a spectrum and can be shown as the area under a particular spectral curve in the plot of noise voltage density (amplitude)/frequency.

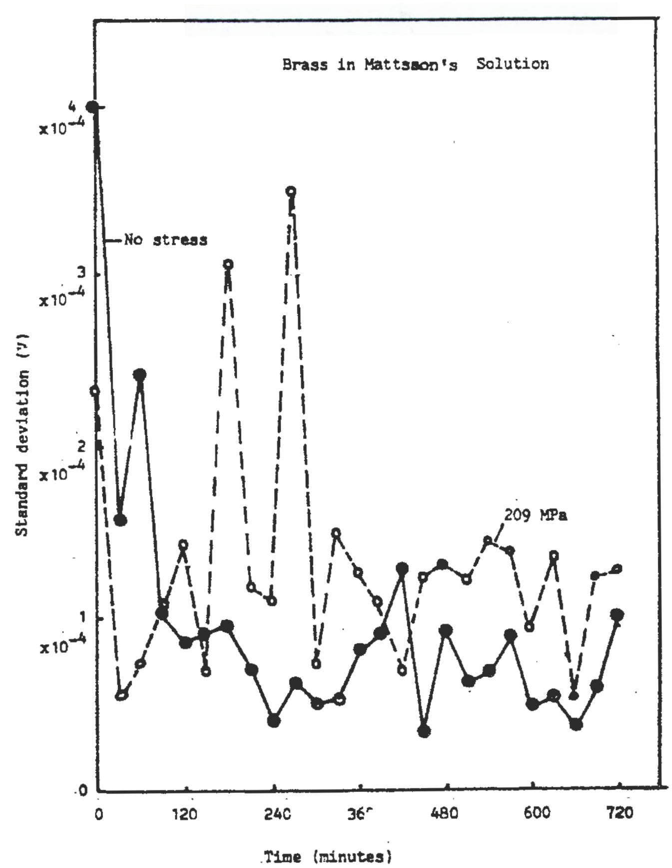

FIGURE 5 — Standard deviation vs time—brass, stress 209 MPa and unstressed.

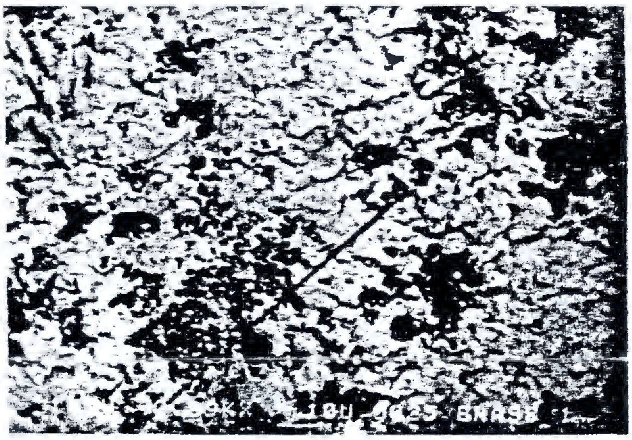

FIGURE 6 — Ruptured crack tarnish film of the brass specimen—20 min in solution. (Time record 2.)

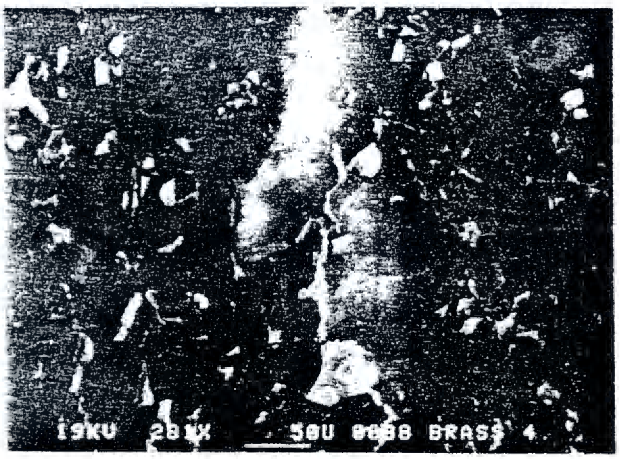

FIGURE 7 — Brass specimen observed cracks—240 min in solution. (Time record 8.)

macroscopic cracks were observed on the specimen's surface. This observation is also in agreement with the spectral density curves in which the curves that show the highest noise voltage density (amplitude) at the lower frequency range in the plot are given by the times of 180 min (time record 7) and 270 min (time record 10) respectively (however, this correlation is expected since the standard deviation (spectrum) bears a direct relationship with the spectral density curve as expressed in footnote (5)).

SEM Micrographs

Within 20 min, the rupture of the black tarnish film on the specimen's surface was observed in solution (Figure 6). The micrographs showed that pitting occurred on the specimen surface within 1 h of its immersion in the Mattsson's solution. A crack was observed on the specimen's surface as at 4 h (time record 8) of the specimen in solution, and the cracks apparently started from the pits (Figure 7). The micrographs also show that more than one crack was formed and all tended to originate from corrosion pits on the specimen surface (Figures 8 and 9).

Figure 10 shows the fractured surface of the alpha-brass specimen which indicates intergranular failure, a characteristic of SCC.

Discussion

Various mechanisms for the SCC of alpha-brass in ammoniacal cupric sulfate solution have been proposed. The main theories fall into three groups:

1. Those involving a continuous electrochemical dissolution[8] which proceeds rapidly along susceptible paths.

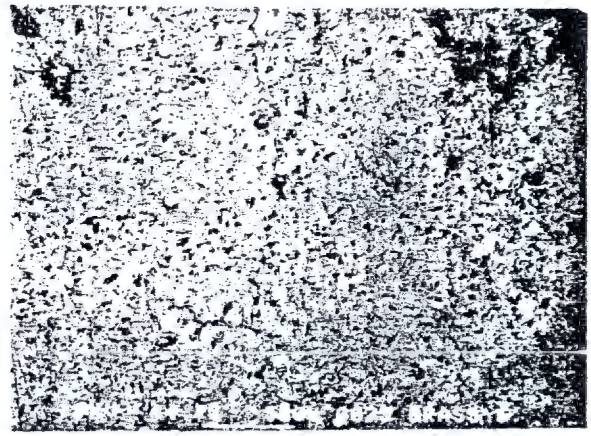

FIGURE 8 — Observed crack propagation and pits linkage; brass.

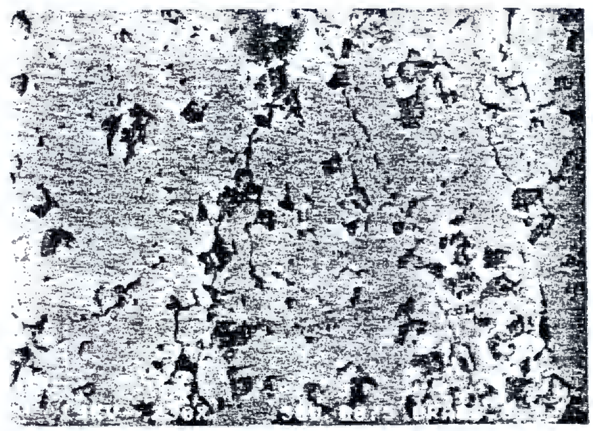

FIGURE 9 — Brass specimen, observed crack propagation and pits linkage at higher magnification.

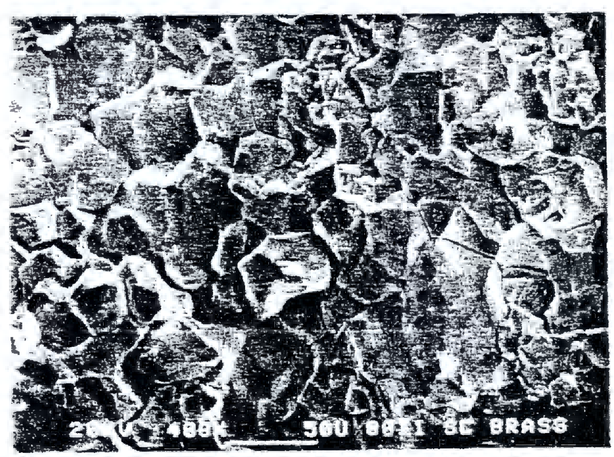

FIGURE 10 — Fractured surface of the alpha brass alloy specimen (showing intergranular failure).

2. Those in which the electrochemical stage alternates with a mechanical propagation of the crack through metal that is locally embrittled by chemical means or of dislocation pile-up.[9]

3. Those involving a film rupture mechanism.[10,11] The results obtained in this work may be related to one or more of the above mechanisms.

Generally, the corroding specimens follow a trend of high noise amplitude at the beginning as indicated, particularly by the curves of the spectral density and the standard deviation/time (Figures 4 and 5). This observation may be associated with the growth of black tarnish film. The high amplitude was followed immediately by a period of low noise amplitude or decrease of standard deviation with time, which may be associated with passivity. A change in electrochemical noise is further indicated by an increase of noise amplitude or rise of standard deviation which may be associated with film breakdown and the onset of pitting by specimen dissolution. Further low noise amplitude or low standard deviation were observed, which may correlate with repassivation by the black tarnished film, but the overall trend remains upward. A very high noise amplitude or standard deviation peak obtained for the stressed specimens (Figures 4 and 5) when the cracks first appeared constitutes one of the major differences between the unstressed and stressed specimens.

The unstressed alpha-brass specimen shows spectra, as denoted by the time record numbers, that are inversely proportional to the frequency. The noise amplitudes are very distinguishable only at the very low frequency and the noise spectral density tends to increase without limit as the frequency decreases. These characteristics indicate a low frequency noise and are typical of *1/f* or *flicker* noise.[12,13]

The highest noise amplitudes recorded for time record 1 to 3 (Figure 3) with roll-off slopes of −19, −18, and −19 decibel (db)/decade respectively, may be associated with the formation of the black tarnish film identified as Cu_2O[11,14]. The formation of Cu_2O is thought to result from the preferential dissolution of Zn atoms accompanied by the oxidation of the remaining enriched copper layers to Cu_2O; the oxidation to Cu_2O is believed[15] to involve solid state diffusion processes. In contrast, the formation of the black tarnish, Cu_2O, is also thought by Vermilyea to result from the dissolution of the whole alloy followed by precipitation of Cu_2O[16]. Whichever mechanism is correct, diffusion and dissolution of an electrode have been identified as sources of noise.[17] The diffusion fluxes of reaction species at the electrode/bulk solution interface may contribute to the noise generated at the interface. The randomness of the diffusion phenomenon of a corroding metal may be explained in terms of the collisions between ions of the diffusing species, and/or ions of the diffusing species with solvent molecules, under the influence of the concentration gradient. Also, complete alloy dissolution followed by precipitation of Cu_2O may cause the generation of noise resulting in high noise amplitudes. This behavior is possibly caused by surface inhomogeneity resulting from the metal dissolution, and the randomness of the precipitation reactions which might have contributed to the potential fluctuations. The highest noise amplitudes, as given above, seem to indicate the degree of corrosion process on the specimen.

The time records 4 to 6 have increasing noise amplitude with a single sharp peak at the higher frequencies of 100 mHz. This increasing noise amplitude may correspond to the occurrence of pitting;[7,18,19] however, the sharp peak is still difficult to explain. Though this has been associated with crevice attack,[18] it is subject to further verification. The roll-off slopes have changed substantially to −36, −38 and −40 db/decade respectively. The increased surface inhomogeneity, chemical reactivity and the randomness of diffusing fluxes possibly contributed to the increased potential fluctuations of the pitting processes and hence the increasing noise amplitude recorded.

A further increase in noise amplitude was recorded at time record 7 with a roll-off slope of −38 db/decade. This change in the noise behavior may be associated with further pitting.

The stressed specimen shows similar characteristics as unstressed specimens discussed above in respect to spectral density curves' shapes. The spectrum is inversely proportional to the frequency or some power or frequency. This is characteristic of low frequency noise as observed and hence *1/f* or *flicker* noise. The major change or difference when compared with the unstressed specimens is that the noise amplitudes are generally further apart from time records 2 and 3 for unstressed specimen. A possible explanation for this difference caused by the noise behavior changes may be that higher noise was generated from more corroding actions such as film rupture and crack growth by dissolution. Secondly, the formation of the black tarnish film, Cu_2O, appears faster as indicated by time record 2 (Figure 4), which has the lowest noise amplitude.

As with the unstressed specimen, the spectrum for time record 1 with a roll-off slope of −14 db/decade is presumably related to the formation of the Cu_2O film by solid state diffusion or dissolution-precipitation. The spectral density curve, time record 2 with a roll-off slope of −32 db/decade, may be associated with further partial and temporary passivation of the Cu_2O film because at this stage, the chemical reactivity or the anodic and cathodic processes would have been reduced from the tarnished film which probably caused a partially temporary passivation of the specimen's surface. The passivation could be partially temporary since the tarnished film is porous and not strongly adherent. The assumed reduction in anodic and cathodic processes, chemical reactivity and diffusion processes could have caused less potential fluctuations and hence reduced noise amplitude.

Increased noise amplitudes as indicated by the time records 3, 4 and 5 of the spectral density curves with roll-off slopes of −39, −39 and −50 db/decade respectively, were obtained (Figure 4). These increasing noise amplitudes which give sharper slopes than time records 1 and 2 presented above, may relate to a process of film-breakdown and probably with the onset of pitting. The roll-off slopes here can be compared with similar corrosion process in the unstressed specimen discussed above. A further decrease in noise amplitude at time record 8 with less steep roll-off slope of −26 db/decade indicates a change in noise behavior from the upward trend: this change may be associated with a repassivation process resulting from a probable reduction in the anodic processes, diffusion processes, and chemical reactions which could lead to a reduction in potential fluctuations. The spectral density curve at time record 9 gives a low noise amplitude at the low frequency but with a single sharp peak at ~5 mHz and at 100 mHz. As stated earlier,[18] it is difficult to characterize the single sharp peak with crevice corrosion in this work since crevice corrosion has been observed in association with pitting.

It seems very difficult to separate the roll-off slopes of the spectral density curves presumably associated with film rupture from that of pitting and/or crack growth by dissolution. However, the trend seems to be that the pitting corrosion processes could be indicated by the increasing negative or sharper roll-off slopes and higher noise amplitudes. The noise amplitude at time record 10 (270 min) with a roll-off slope of −25 db/decade was the observed time that the crack first appeared. Also, the noise amplitude at time record 7 (180 min) could indicate a crack since the observation of the specimen's surface showed that more than one crack occurred. The noise generated here could be associated with crack formation and growth. The highest noise amplitude and less sharp roll-off slope here might result from the bare metal created by crack, which in contact with the bulk solution gives a short but intense anodic reaction of metal dissolution, which results in noise. The peaks and deflections of the standard deviation (spectrum)/time curves, generally correspond with the spectral density curves and could be used, as indicated earlier in this section, to interpret and discuss the above results.

Combined with plastic replication processes, the problem of reproducing the results of the electrochemical noise measurements was created by the repeated withdrawal and immersion of the test electrode in and out of the test solution. This might result from the air film created by the oxygen of the air, the impurity created by acetone solvent and the plastic replicating material itself. These combined results might have affected the sensitivity of the readings taken and hence some irregularities. The observations of the formation of the black tarnish film oxide (Cu_2O), the occurrence of film break-down, pitting, and cracking through the pits linkage as given in the

micrographs and as related to the changes in the electrochemical noise behaviors appear consistent with film-rupture mechanism.

Conclusion

1. Electrochemical noise measurement technique can be used to monitor SCC processes of the alpha-brass alloy.

2. The source of the electrochemical noise is believed to be the repassivation transients resulting from the exposure of fresh metal surface following rupture of the passive film on the brass, and fresh surface exposed by the cracking.

3. Cracks in alpha-brass in Mattsson's solution are intergranular at pH 7.2, further confirming the results obtained by other various works.

4. Specimen cracking gave the highest noise amplitudes in most cases; the cracking failure is also indicated by the highest standard deviation peaks.

5. The initial high noise amplitudes and standard deviation observed in time record 1 for all the alpha-brass specimens may result from the growth process of the black tarnished film, Cu_2O.

6. All the noise amplitudes generally increase with decreasing frequency and the power spectral density is inversely proportional to some power of the frequency thus indicating *1/f* or *flicker* noise.

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