INTERACTIONS BETWEEN FATIGUE CRACK GROWTH RATE AND KINETICS OF MAGNESIUM CALCIUM DEPOSITS FORMATION AT CRACK TIP OF MILD STEEL CATHODICALLY POLARIZED IN SEA WATER

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ABSTRACT

Important ways for corrosion protection are used to increase fatigue lifetime and decrease corrosion rate : one of them is cathodic polarization. Nevertheless, high cathodic current may promote hydrogen embrittlement. On the other hand higher cathodic current density or potential enhances also local pH at metal surface immersed in sea water. Under these conditions, mineral deposits essentially composed of $CaCo_3$ and $Mg(OH)_2$ are formed. These deposits may hinder crack closure and hence crack growth rate is decreased.

KEYWORDS

Fatigue crack growth rate, sea water, magnesium - calcium deposits, cathodic polarization potential, mild steel.

INTRODUCTION

Fatigue - corrosion is a complex process which depends on many parameters, mechanical and/or electrochemical. Paris - Erdogan relationship [$da/dN = C(\Delta K)^m$] is not valid and we have to apply other models such as superposition (Wei and Landes, 1969) or competition (Austen and Mc Intyre, 1979). Crack growth rate depends then on metal-environment couples, K_{IC}, $\Delta K/K_{ISCC}$ ratio, R and frequency.

"OFF - SHORE" plants subjected to sea swell effect and corrosion actions due to sea water are usually protected by cathodic polarization. Therefore interactions may occur between cyclic stresses and aggressive environment. Cathodic protection decreases the corrosion process, but on the other hand, hydrogen diffusion may embrittle steel structure in specific conditions such as cathodic current density or pH values. Under these conditions, initiation of fatigue-corrosion crack is observed and crack growth rate is enhanced. Steel cathodic protection in sea water at potential values $\geqslant$ -980 mV/SCE produces at its surface calco-magnesium deposits which reduce oxygen adsorption (HUMBLE, 1948) and cathodic current density (Compton and others, 1974), i.e. hydrogen diffusion (Marette and others, 1961). When cathodic current interrupts, the deposits decrease , for some time, corrosion rate (Heuze, 1961).

We have studied in this work kinetics of deposits formation and fatigue crack growth rate in synthetic sea water, without stirring, in function of cathodic potential value at pH$\simeq$8. Mechanical properties in tensile tests are performed on cathodically polarized mild steel to study potential and pH effects. Fatigue crack growth is measured on mild steel immersed in sea water and under different cathodic potential values, i.e. from the dissolution potential E_D to -1500 mV/SCE. At the beginning of fatigue test, pH is always equal to 8. After failure, fatigue cracked surfaces are analysed using E.D.S apparatus (Energy dispersive spectometry) coupled to S.E.M. to measure (Mg/Mg + Ca) ratio in function of the crack length, i.e in relation with applied ΔK.

EXPERIMENTAL

Kinetics of deposits formation and crack growth rate are measured on normalized mild steel E355 which has the following chemical composition (Table 1) :

Table 1 : Chemical composition of E355 steel

C%	S%	P%	Si%	Mn%	Ni%	Cr%	Mo%	Cu%	Sn%	N%	V%
0.160	0.023	0.019	0.300	1.36	0.048	0.029	0.009	0.445	0.010	0.007	0.011

Tensile tests are performed with and without previous hydrogen charging in sea water (ASTM D1141), on an Instron machine with deformation rate $3.10^{-4}s^{-1}$ at room temperature. Cylindrical specimens having a diameter of 8 mm and a gauge length of 50 mm are employed. A servohydraulic machine and S.E.N.T. specimens with 10 mm thickness are used to measure fatigue crack growth while cathodic polarization potential is applied in sea water. Fatigue tests are achieved under the following conditions : constant cyclic load, triangular wave form, R$\simeq$0.1 ($R = K_{min}/K_{max}$) and frequency equal to 1 Hz. All fatigue tests are achieved at room temperature. Fatigue crack growth is measured by optical microscope with 30 µm precision. Deposits formation kinetics are studied at room temperature by using samples of 3 cm^2 area. To prevent chloride formation in sea water, a special cell has been designed. This cell has two compartements separated by sintered glass sheet so that the pH value is maintained constant ($\simeq$ 8) during the longest test (80 hours) and specially at high applied potential (Philipponneau, 1982). Also, to prevent Mg^{++} and Ca^{++} concentration decrease with time, a greater cell of about 500 cm^3 of sea water for 1 cm^2 steel surface is employed. Two parameters are studied to evaluate deposits formation kinetics :

1- Cathodic polarization time (0 to 80 hours) at a constant current density 0.1 $mA.cm^{-2}$ ($\simeq$1050 mV/SCE).
2- Cathodic polarization potential (-900 to -1100 mv/SCE).

Chemical analysis of steel surface are achieved to quantify (Mg/Mg + Ca) ratio by using chemical dosimetry technics. Also, SEM and X-rays analysis are performed to identify deposits constitution.

RESULTS AND DISCUSSION

Kinetics of calcium carbonate $CaCo_3$ and magnesium hydroxide $Mg(OH)_2$ precipitation under a given cathodic polarization condition (i_d = 0.1 $mA.cm^{-2}$, E $\simeq$1050 mV/SCE) are shown in figure 1. (Mg/Mg + Ca) ratio decreases firstly up to 17 hours polarization time and then becomes constant between 17 to 80 hours. Magnesium hydroxide kinetics formation is faster than these of calcium carbonate. The first $CaCo_3$ crystals are detected after 3 to 6 hours of polarization time at 0.1 $mA.cm^{-2}$ current density, figure 2. After 17 hours polarization in sea water at room temperature and at different cathodic potential values, we have observed a deposits morphology modification with increasing applied potential (E = -965 to - 1150 mV/SCE), figure 3. This shows that $CaCo_3$ structure changes with cathodic potential, i.e. from vaterite at -965 mV/ECS to vaterite + aragonite at -1000 mV/SCE, only secondary aragonite between -1060 to -1100 mV/SCE. At -1150 mV/SCE and higher, those formations are not observed. In all cases we observe $Mg(OH)_2$, brucite, precipitation. Plotting now (Mg/Mg + Ca) ratio versus applied potential and after 17 hours cathodic polarization at room temperature, we notice that the relation is roughly linear, figure 4. In the following text we are going to use this relation in order to estimate the potential drop evolution at the fatigue crack tip.

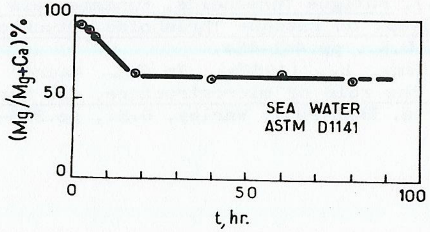


Fig. 1. (Mg/Mg + Ca) ratio versus time of cathodic polarization potential at -1050 mV/SCE.

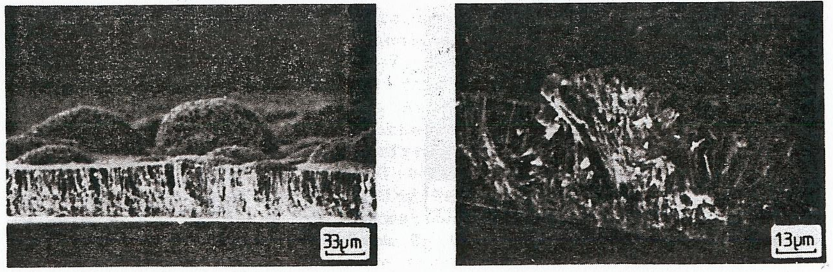
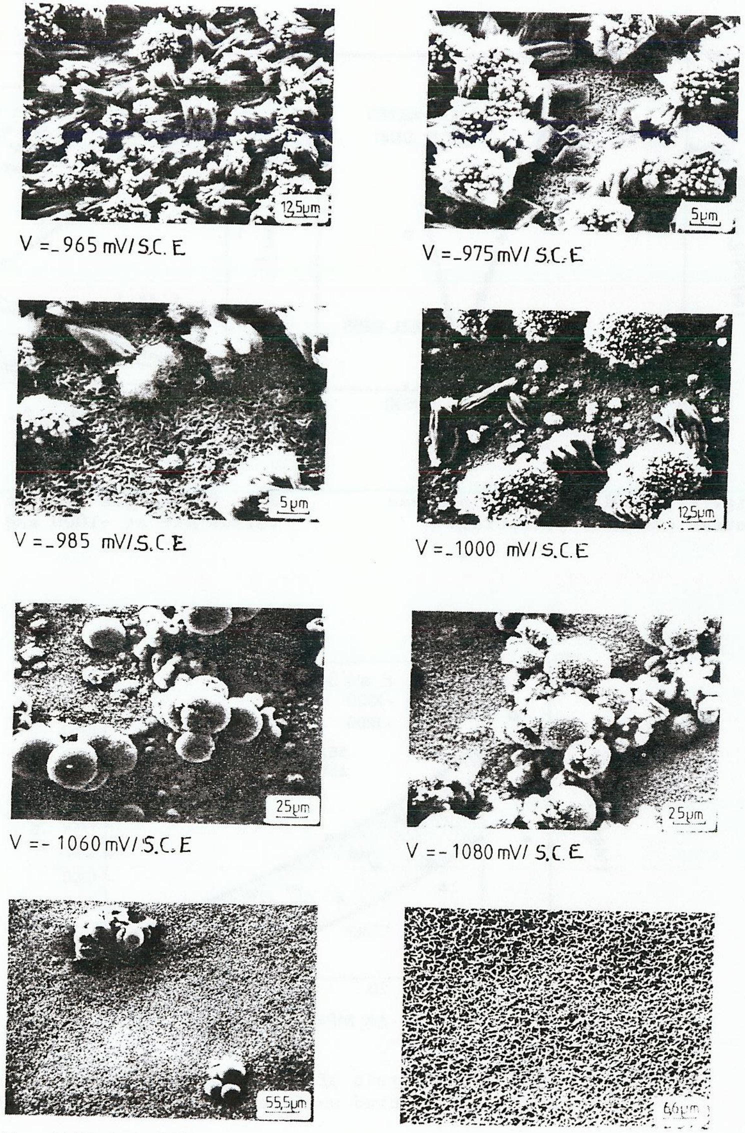


Fig. 2. Kinetics of $Mg(OH)_2$ and $CaCo_3$ formation on the metallic surface.



V =_965 mV/S.C.E

V =_975 mV/S.C.E

V =_985 mV/S.C.E

V =_1000 mV/S.C.E

V =- 1060 mV/S.C.E

V =- 1080 mV/S.C.E

V =- 1100 mV/S.C.E

V =- 1150 mV/S.C.E

Fig. 3. Evolution of magnesium calcium deposits constitution with cathodic potential polarization values.

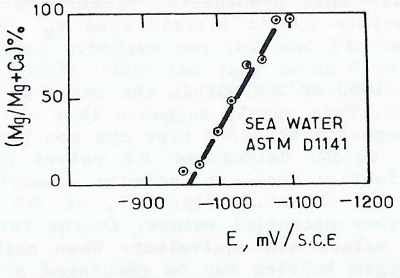


Fig. 4. (Mg/Mg + Ca) ratio versus cathodic potential after 17 hours of polarization

Mechanical properties σ_Y and σ_U of mild steel cathodically polarized during 24 hours in sea water at room temperature are not affected much by applied potential (-1200 or 1500 mV/SCE) or pH value. At pH = 4 or 8 and potential polarization equal to -1200 mV/SCE, mechanical properties are slightly increased by 10% in comparison with those obtained at -1500 mV/SCE and pH = 4 (Authors, 1983). Mechanical properties at -1200 mV/SCE, pH = 4 and 8 and those measured in air are equivalent.

Fatigue lifetime decreases approximatly linearly with increasing cathodic polarization potential. At corrosion potential E_D, loss is 50% w.r.t the value measured in air, while this loss at -1500 mV is about 87%. These results suggest that fatigue lifetime in sea water for mild steel is reduced by 4 to 5% for each 100 mV cathodic polarization potential in relation to E_D. Figure 5 shows an example of results obtained in air and in sea water at -1000 mV/SCE, pH $\simeq$ 8. In air, crack growth rate da/dN increases linearly with cyclic stress intensity coefficient ΔK, with $da/dN = 6x10^{-12} (\Delta K)^{2.9}$, [da/dN, m c^{-1} and ΔK, MPa$\sqrt{m}$]. Haagensen and others (1981) results give, on the same steel, but with specimens of thickness equal to 20 mm and 20 Hz frequency : $da/dN = 5.1x10^{-13}x(\Delta K)^{3.85}$ within ΔK range 7 to 30 MPa$\sqrt{m}$. On the other hand, Austen and others (1981) mentioned that Paris relationship may be writen as $da/dN = 5.32x10^{-11} (\Delta K)^{2.53}$. With hydrogenation in sea water, the curve da/dN = f (ΔK) has a "pseudo-plateau" beginning at $\Delta K_p \simeq$ 31 MPa$\sqrt{m}$. ΔK_{ISCC}, i.e $K_{ISCC}/(1-R)$, is estimated to be equal to 28 MPa$\sqrt{m}$. It seems then, following the competition model, (Austen and McIntyre, 1979) that at $\Delta K \gtrsim$ 28 MPa$\sqrt{m}$, we are in presence of a fatigue-stress corrosion process and at $\Delta K \leqslant$ 28 MPa$\sqrt{m}$, true fatigue corrosion process is active. Plotting da/dN versus ΔK for all cathodic polarization values (E_D to -1500 mV/SCE), we observe, figures 6 and 7, that crack growth rate at "pseudo-plateau", $(da/dN)_p$, decreases firstly with increasing applied cathodic potential up to -1200 mV/SCE. At E $>$ -1200 mV/SCE, $(da/dN)_p$ is an increasing function of E. Maahn and others (1981) and Morgan and others (1981) results show, in vigorously stirring water at 20°C, that da/dN increases within potential range -800 to -1100 mV/SCE. It seems that stirring is an important factor governing fatigue crack growth. Stirring may damage or hinder calco-magnesium formation at crack tip. Under our conditions, aggressivity reduction from E_D to -1200 mV/SCE is then due to calco-magnesium deposits which has more than 120 µm thickness at crack tips, figure 2. Deposits thickness raises with increasing cathodic applied potential and polarization time, (Philipponneau, 1982). This increasing thickness at crack tip hinders crack closure, and reduces ΔK and da/dN values. Therefore, we can expect that da/dN is continuously reduced with potential values higher than -1200 mV/SCE. This is not the case in our results and one may suspect that adherence quality could vary with applied potential. To verify this hypothesis, Vickers hardness measurements were performed to appreciate cyclic plastic size r_y" (Bathias, 1978) at crack tips in function of ΔK and for two cathodic potential values, -1000 and -1200 mV/SCE. Figure 8 shows that for -1200 mV/SCE, r_y" is much higher than that measured for -1000 mV/SCE within the range 15 to 30 MPa√m and decreases with increasing ΔK. This result suggests that at -1200 mV/SCE, adherence and thickness of deposits at crack tips are too high to hinder crack closure and hence to reduce da/dN. Calculated ΔK values for E ≤ -1200 mV/SCE are higher than the effective ones. At cathodic potential equal to -1500 mV/SCE, the pseudo-plateau is observed, figure 6, at ΔK values lower than that obtained for the other potential values. In the former condition, calculated and effective ΔK values are equivalent. When cathodic potential exceeds -1200 mV/SCE, hydrogen bubbles may be generated at crack tips (Attaya and other, 1975) and the deposits is then destroyed.

It has been shown that pH value required to achieve precipitation of $CaCo_3$ and $Mg(OH)_2$ on the metallic surface are respectively 8.35 and 9.54 (Philipponneau, 1982). All our fatigue tests start at pH = 8 but after failure, pH is equal to 4. pH evolution during the test may affect crack growth rate and also calco- magnesium composition. Deposits analyses are performed on sample polarized at -1200 mV/SCE for two pH values 4 and 8 and the results show that (Mg/Mg+ Ca) ratio is the same and about 1. It seems that, under these conditions, the pH value at the crack tip is always higher than 8. Deposits thickness is not yet measured at pH = 4. After fatigue failure in sea water, deposits composition on ruptured surfaces is analysed by using X-rays (E.D.S) coupled with S.E.M. ; (Mg/Mg+Ca)% evolution with ΔK, for two cathodic polarization potentials (-1000 and -1200mV/SCE) and in relation with figure 4 is shown in figure 10. We can observe that potential drop raises with increasing crack length or ΔK. The average drop is about 70 mV, i.e 3,5 mV/MPa√m, within ΔK range 15 to 35 MPa√m. This result is in good agreement with Maahn and others results (1981) in which potential drop is about 4 mV/MPa√m in ΔK range 10 to 30 MPa√m and at -1100 mV/SCE.

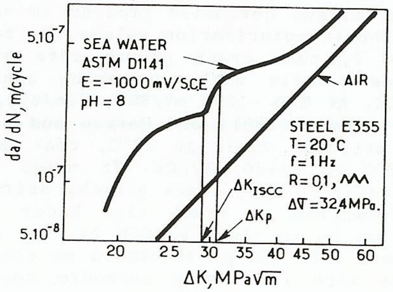


Fig. 5 : Fatigue crack growth rate versus ΔK.

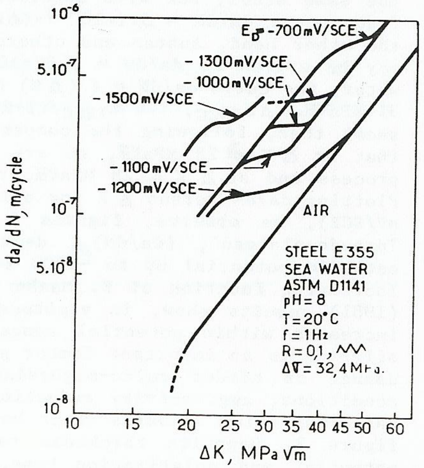


Fig. 6. Cathodic polarization potential effect on fatigue crack growth rate.

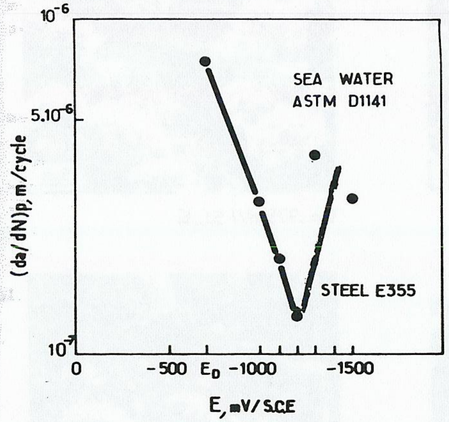


Fig. 7. da/dN at pseudo plateau versus cathodic potential.

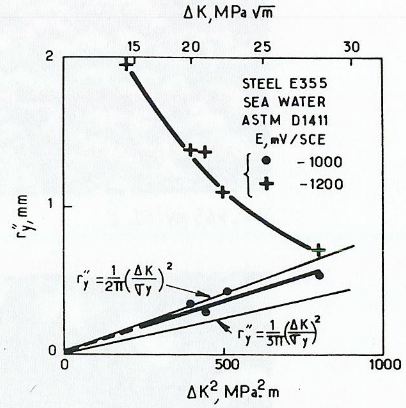


Fig. 8. Fatigue plastic zone r_y" versus ΔK^2 at -1000 and -1200 mV/SCE

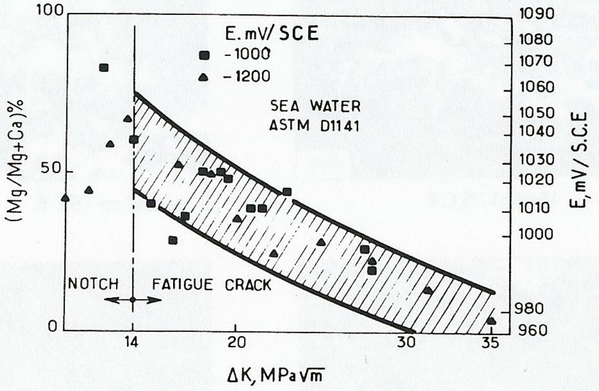


Fig. 9. Chemical analysis of calcomagnesium deposits versus ΔK on fatigue fractured surface after cathodic polarisation.

CONCLUSION

1- Magnesium hydroxide $Mg(OH)_2$ kinetics are faster than those of calcium carbonate $CaCO_3$ at cathodic polarization potential $\simeq$1050 mV/SCE and at room temperature.
2- (Mg/Mg+Ca) ratio is roughly a linear function of cathodic potential between -960 to -1100 mV and at pH values 4 and 8.
3- Cathodic potential values between -1200 to -1500 mV/SCE and pH values between 4 and 8 do not modify the mechanical properties of mild steel.
4- Without sea water stirring, and in potential range from E_D to -1500 mV/SCE, a "pseudo-plateau" has been observed in da/dN = f(ΔK) curves. (da/dN) at "pseudo-plateau" has a minimum value at about -1200 mV/SCE. This is due to high thickness and good adherence deposits at crack tip.
5- After fatigue failure in sea water, chemical analysis of deposits on the rupture surface shows that (Mg/Mg+Ca) ratio decreases with increasing ΔK values. In relation to point 2, this means that we could estimate the potential drop at the crack tip w.r.t crack length.

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