Current Status and Future Trends on Environmental Strength of Metals*

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This paper deals with the current topics of environmental strength of metallic materials and its methodology from the theoretical and practical viewpoints, including cyclic stress corrosion cracking (cyclic SCC), dynamic SCC, corrosion-product-induced wedge effects, and the mechanical factors controlling crack initiation. Low-frequency variation (stress ratio being near zero) causes cyclic SCC even in materials insensitive to static SCC under a sustained load. Also, the dependence of the waveform on cyclic SCC is opposite that on corrosion fatigue (CF). Small, high-frequency vibratory stresses cause dynamic SCC, with a lower threshold than that of static SCC, K_{ISCC} ; the effects of the vibratory stress range, stress cycle frequency, solution temperature, and crack length on dynamic SCC are discussed. The corrosion-product-induced wedge effects (crack closure) have great potential in influencing CF crack growth, and the mechanisms are discussed. In the case of crack initiation at the bottom of a corrosion pit, the stress intensity factor, calculated on the assumption of a pit being a sharp crack, dominates its crack initiation. The image processing technique, including three-dimensional analyses and the region segmentation according to fracture surface morphology, provide us with powerful tools to investigate the environmental strength of materials.

Key Words: Strength of Materials, Environmental Strength, Stress Corrosion Cracking, Cyclic SCC, Dynamic SCC, Corrosion Fatigue, Corrosion-product-induced Wedge Effects, Image Processing, Metallic Materials.

1. Introduction

Continuous progress in science and technology creates a further increasing demand for structural materials, including high-strength, corrosion-resistant, and also light-weight materials. The introduction and utilization of these materials are widely spreading over various and severe service environments. In order to ensure the integrity of machines and structures for a long period, one must verify the environmental strength of the materials, which shall help the optimization and development of highly environment-resistant materials as well as the development of a reliable design basis for the application of materials. Moreover, the development of advanced technology such as aerospace industries is dependent on the development of advanced materials, though the

research on environmental strength of these materials has just come into consideration.

It was mid-1970s that the technical term "environmental strength" was widely accepted. Since then, the importance of environmental effects on material strength has been widely understood, and many investigations in this field have been reported. However, the environmental strength of materials results from time-dependent phenomena and also is affected by metallurgical, electrochemical, and mechanical factors. Thus, the environmental effects on material strength have not been comprehensively understood, and further systematic investigations are still required. In this review, the current topics of environmental strength, which have been recently made clear, and methodology will be summarized from the theoretical and practical viewpoints.

2. Stress Corrosion Cracking Under Dynamic Loading Conditions

Stress corrosion cracking (SCC) has been considered a different phenomenon from corrosion fatigue

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(CF), though it is very difficult to determine which is dominant in case histories of machines and structures in an aggressive environment. Moreover, one must note that SCC cannot be clearly distinguished from corrosion fatigue from a viewpoint of mechanisms. Especially in high-strength materials sensitive to an environment, fracture modes dominated by SCC are often observed even under dynamic loads.

2.1 Cyclic SCC

When materials, sensitive to static SCC under a sustained load, are subjected to dynamic loads such as a low-frequency variation (stress ratio $R = K_{\min}/K_{\max}$ being near zero), the crack growth is highly accelerated compared to fatigue in an inert environment because of cyclic SCC⁽¹⁾⁻⁽⁵⁾; crack growth rates suddenly increase above a threshold value for cyclic SCC, K_{FSCC} . The growth rates have been reported to be strongly dependent on the stress cycle frequency and the stress waveform. Threshold values, K_{FSCC} , were considered to be equal to a static SCC threshold, K_{ISCC} ⁽⁶⁾. However, recent results⁽¹⁾⁻⁽⁵⁾ prove K_{FSCC} values considerably decrease from K_{ISCC} . Especially, we must note that cyclic stress corrosion (SC) crack growth occurs even in a material/environment system insensitive to static SCC under a sustained load.

Figure 1⁽⁷⁾ shows the acceleration ratio, R_{acc} , the ratio of $(da/dN)_{\text{FSCC}}$ in a 3.5% NaCl solution to $(da/dN)_{\text{air}}$ in dry air, which is plotted against effective

Fig. 1 An acceleration ratio R_{acc} as a function of effective stress intensity factor range, ΔK_{eff} , of a HT80 steel immersed in a 3.5% NaCl solution at 298 K.

stress intensity factor range, $\Delta K_{\text{eff}} = K_{\max} - K_{\text{op}}$. Here, K_{op} is the crack opening stress intensity factor. The material tested was a high tensile strength HT80 steel ($\sigma_B = 820$ MPa) immersed in a 3.5% NaCl solution at 298 K. A cathodic polarization of -1.2 V vs. SCE was also applied to the specimens. At the free corrosion potential, R_{acc} in the whole range of ΔK_{eff} examined had values between about two and four, whereas under the cathodic overprotection, R_{acc} had a maximum at a certain ΔK_{eff} value, which increased with decreasing frequency. Especially under a high mean stress of $R = 0.8$, one must note that a great increase in crack growth occurred; R_{acc} at $\Delta K_{\text{eff}} = 20 - 25$ MPa·m^{1/2} was 10–19 at $f = 0.1$ Hz, and 40–90 at $f = 0.01$ Hz. Here, time-dependent hydrogen embrittlement became dominant over the crack growth kinetics under the dynamic loads. One should note that low-frequency varying loads cause cyclic SCC even in a material insensitive to static SCC under a sustained load.

In the case of cyclic SCC, the influence of waveform on cyclic SC crack growth is different from that on corrosion fatigue. Figure 2⁽⁸⁾ shows K_{FSCC} values as a function of the stress intensity factor rate, $\dot{K} = |\partial K / \partial t|$, of various waveforms. The material tested was a high-strength commercially available aluminum alloy, ZK141 ($\sigma_B = 420$ MPa), which belongs to the 7XXX series of aluminum alloys. The stress waveforms used here were as follows: positive sawtooth waves at $f = 0.1$ Hz and 0.01 Hz, positive pulse wave, negative pulse wave, negative sawtooth wave, triangular wave at $f = 0.1$ Hz, and sinusoidal wave at $f = 30$ Hz. The superimposed waves were used, where secondary sinusoidal loads at $f = 30$ Hz were superimposed at the period of the maximum load of the negative pulse wave at $f = 0.1$ Hz, i.e., a primary wave. Short vertical lines are added to the plots in the case of unloading. It is quite clear that K_{FSCC} increased with

Fig. 2 Threshold value for cyclic SCC, K_{FSCC} , as a function of stress intensity factor rate, $\dot{K}$, of a ZK141 aluminum alloy immersed in a 3.5% NaCl solution at $R = 0.1$.

decreasing $\dot{K}$. In this material/environment system, repassivation rates were so fast that no influence of hold time at the maximum stress on K_{FSCC} was observed; the restoration of passive films predominated at lower $\dot{K}$, i.e., positive sawtooth waves, resulting in higher K_{FSCC} compared to that at higher $\dot{K}$, i.e., pulse waves. In the case of corrosion fatigue, crack growth rates have been reported to be increased with decreasing $\dot{K}$, i.e., longer rise time⁽⁹⁾. One should note that the dependence of cyclic SCC thresholds on $\dot{K}$ is opposite to that of corrosion fatigue.

Investigations on cyclic SCC hitherto conducted have mainly dealt with crack initiation and propagation under a uniaxial loading condition; SCC behavior under a multiaxial loading condition has been scarcely reported^{(10),(11)}. Figure 3⁽¹²⁾ shows the relationship between von-Mises-type maximum equivalent stress, $\sigma_{eq,max}$, and time to fracture t , of a 523K tempered 4135 steel ($\sigma_B=1770$ MPa) in a 3.5% NaCl solution at 298 K, which is sensitive to the hydrogen embrittlement (HE) type of SCC. Multiaxial cyclic loads, i.e., in-phase cyclic tension and torsion at a frequency of 0.1 Hz, were applied with a tensile stress ratio, R_σ , of zero and torsional stress ratio, R_τ , of zero.

Cyclic SCC life became longer with an increase in τ_{max}/σ_{max} , compared at a fixed value of an equivalent stress. Regardless of loading condition, a cyclic SC crack normal to maximum principal stress was initiated at the bottom of a corrosion pit and then propagated to a final fracture. Therefore, the cyclic SCC data shown in Fig. 3 were replotted against the maximum principal stress, $\sigma_{1,max}$, which is shown in Fig. 4⁽¹²⁾. A single curve was obtained between $\sigma_{1,max}$ and time to fracture regardless of τ_{max}/σ_{max} value, and low-frequency variation caused a considerable

decrease in cyclic SCC strength from those of static SCC and of fatigue in dry air.

In this type of SCC (HE), tensile stresses have been reported to dominate over SCC lives; this fairly well coincided with the results. In the case of the active path corrosion (APC) type of SCC, the existence of a tensile stress is considered not to be necessarily required, and shear stresses caused SC crack initiation⁽¹³⁾ and Mode II or Mode III SC crack propagation was reported^{(10),(14)}. In such cases, the dominating mechanical variables in multiaxial loading are considered to be more complicated compared to the HE type of SCC; further systematic investigations are required.

2.2 Dynamic SCC

2.2.1 Effects of vibratory stress range Even in the absence of low-frequency variation, the loading pattern such as a sustained load with small, high-frequency vibratory loads superimposed, is often observed in machines and structures. Endo et al. termed SCC under such loading patterns as "dynamic SCC"⁽¹⁵⁾, and differentiated it from static SCC under a sustained load.

Figure 5⁽¹⁶⁾ shows the relationship between maximum stress, σ_{max} , and time to crack initiation, t_i determined by an AE monitoring technique. The material/environment system used was a 673K tempered high-strength 4135 steel ($\sigma_B=1700$ MPa) in a 3.5% NaCl solution at 298 K. Small, high-frequency axial loads of $f=30$ Hz were applied to smooth round-bar specimens.

At the free corrosion potential, $E=E_c$, the 600 ks strength, σ_{DSCC} under the vibratory stress ranges smaller than 74 MPa, was equal to the static SCC strength, σ_{SCC} . At $\Delta\sigma \geq 83$ MPa, however, σ_{DSCC} became lower than σ_{SCC} ; the greater the superimposed vibratory

Fig. 3 Relation between von-Mises type maximum equivalent stress, $\sigma_{eq,max}$, and time to fracture, t , in multiaxial cyclic SCC tests of a 4135 high-strength steel immersed in a 3.5% NaCl solution at 298 K. (In-phase cyclic tension and torsion at $R=0$ and $f=0.1$ Hz)

Fig. 4 Relation between maximum principal stress, $\sigma_{1,max}$, and time to fracture, t , in multiaxial cyclic SCC tests of a 4135 high-strength steel in a 3.5% NaCl solution at 298 K. (In-phase cyclic tension and torsion at $R=0$ and $f=0.1$ Hz)

stress range was, the lower was the 600 ks strength.

Figures 6(a)⁽¹⁷⁾ and (b)⁽¹⁷⁾ show a bird's-eye view and a matching topography of a crack initiation site of dynamic SCC at $\sigma_{\max} < \sigma_{\text{SCC}}$, which were obtained by a three-dimensional computer image processing technique⁽¹⁸⁾⁻⁽²⁰⁾ that can evaluate surface topographies without human assistance. The technique used a pair of stereophotographs that were converted into 256 gray level (8-bit) digital images. Subsequently, the digital images were processed by a FACOM VP200 supercomputer (Fujitsu Co. Ltd.) at the Data Processing Center of Kyoto University. After suitable preprocessing including noise reduction, the corresponding points on the surfaces were searched by the mutual correlation coefficient technique, 20×40 -pixel window area being set on the standard surface, and the corresponding area was searched on the other oblique surface. Then, the height measured above a standard point could be computed.

The figures make it clear that an intergranular dynamic stress corrosion (SC) crack was initiated at a crack-like defect by stress-assisted dissolution preceded by a corrosion pit. On the other hand, a dynamic SC crack at $\sigma_{\max} > \sigma_{\text{SCC}}$ as well as a static SC crack was immediately initiated at the corrosion pit formed on the surface. At higher superimposed vibratory stress ranges of $\Delta\sigma \geq 83$ MPa, crack-like defects by stress-assisted dissolution were produced at the bottom of a corrosion pit, resulting in dynamic SC crack initiation and a fall of σ_{DSCC} from σ_{SCC} .

Small vibratory loads also affect SC crack growth behavior. Figure 7⁽¹⁵⁾ illustrates the relation between crack growth rates, da/dt , and the maximum stress intensity factor, $K_{\max}$, in sensitized ZK141 ($\sigma_B = 420$ MPa), which was the same as the material used in Fig. 2, and 7075 ($\sigma_B = 460$ MPa) alloys sensitive to an active path corrosion (APC) type of SCC. The corrosive environment was a 3.5% NaCl solution at 298 K,

Fig. 5 Effects of small, high-frequency vibratory stresses on time to SC crack initiation, t_i , of a 4135 high-strength steel in a 3.5% NaCl solution at 298 K and at $f = 30$ Hz.

and the dynamic loads were sinusoidal waves with a stress cycle frequency f of 30 Hz. The threshold stress intensity factor at $R = 0.98$ of dynamic SCC, K_{DSCC} , was almost equal to that of static SCC, K_{ISCC} at $R = 1.0$. At $R \leq 0.965$, however, K_{DSCC} was considerably lower than K_{ISCC} ; the smaller the stress ratios were, the lower the threshold values were. Similarly, crack growth rates of dynamic SCC involving $R = 0.98$ in Region II, where subcritical crack growth is observed, were higher than those of static SCC; the smaller the stress ratios were, the higher the crack growth rates were.

SC crack growth by an anodic dissolution mechanism is considered to be dominated by a process of damage (rupture) and restoration (repassivation) of passive films formed at crack tips, and the threshold condition of passive films not being damaged corresponds to the values of K_{ISCC} . For dynamic SCC, damage of the passive films was promoted by small,

(a) Bird's-eye view of dynamic SC crack initiation site at $\sigma_{\max} < \sigma_{\text{SCC}}$ of a 4135 high-strength steel in a 3.5% NaCl solution. (Crack-like defects by stress-assisted dissolution, $\sigma_{\max} = 686$ MPa, $\Delta\sigma = 98$ MPa)

(b) Matching topography of Fig. 6(a).

Fig. 6

high-frequency vibratory stresses superimposed on a sustained stress, which resulted in an enhancement of da/dt and a fall of K_{DSCC} .

Figure 8^{(15),(21)} shows the endurance limit diagram, where the ordinate is an amplitude of stress intensity factor, $\Delta K/2$, and the abscissa a mean stress intensity factor, K_{mean} , taken from a growth rate of 3.0×10^{-10} m/s. The small diagram shown in the figure is a usual endurance limit diagram, where both scales of an ordinate and an abscissa are equalized. It is clear that K_{DSCC} at $R=0.98$ hardly decreased from K_{ISCC} . This is due to the fact that the superimposed small vibratory stresses were lower than the fatigue strength of the passive films. In this case, the threshold stress intensity factor range against dynamic SC crack growth, ΔK_{DSCC} was approximated at $0.7 \text{ MPa} \cdot \text{m}^{1/2}$. At $0.95 \leq R < 0.98$, ΔK_{DSCC} values were unchanged and were almost equal to $0.7 \text{ MPa} \cdot \text{m}^{1/2}$ corresponding to the fatigue strength of the films; the threshold condition of dynamic SC crack growth at $R \geq 0.95$ was solely determined by ΔK_{DSCC} , below which integrity of the passive films was kept. We must note that the value of ΔK_{DSCC} was smaller than the fatigue threshold value of $\Delta K_{th} = 1.19 \text{ MPa} \cdot \text{m}^{1/2}$ in dry air at $R=0.95$ ⁽²¹⁾. In the case of 7075 alloy, a fall of K_{DSCC} from K_{ISCC} was also observed at $\Delta K = 0.4 \text{ MPa} \cdot \text{m}^{1/2}$: see Fig. 8. The threshold values against the passive films, ΔK_{DSCC} , might not exist, or had a very small value if present.

Fig. 7 Effects of small, high-frequency vibratory stresses on SC crack growth rates of ZK141 and 7075 aluminum alloys immersed in a 3.5% NaCl solution at $f=30$ Hz.

At $R=0.90$ and 0.85 for ZK141 alloy, an allowable vibratory stress range increased; even if the vibratory stress range ΔK greater than ΔK_{DSCC} caused damage of the passive films, restoration of the films predominated owing to K_{max} being small. In this situation, SC crack growth was considered to be caused by dynamic SCC with cyclic SCC superimposed.

In the region of $K_{max} > K_{DSCC}$, da/dt of dynamic SCC inclusive of $R=0.98$ was much enhanced compared with that of static SCC, because the passive films were ruptured by an increased vibratory stress associated with an increase in K_{max} . Moreover, dynamic SCC failures were a mixed mode of intergranular and transgranular ones in contrast to the intergranular failures observed in static SCC. This implies that an alternating mechanism of intergranular dissolution and subsequent transgranular hydrogen embrittlement caused an enhancement of dynamic SC crack growth.

Similar degradations by superimposed small vibratory stresses were also observed in a sensitized austenitic stainless steel in oxygenated high-temperature water⁽³⁾ and in a high-strength steel sensitive to an HE type of SCC⁽⁵⁾. Here, dynamic SC crack growth was brought about even at $K_{max} \leq K_{ISCC}$ by the superimposed small high-frequency vibratory stresses, because they promoted damage of oxide films and an increase in hydrogen content.

2.2.2 Effects of stress cycle frequency The rupture of passive film or oxide film under dynamic loading conditions is considered to be strongly dependent on the competition between mechanical rupture and repassivation of films. These also relate to the vibratory stress range and the crack tip strain rate, i. e., to the stress cycle frequency. In this section, we will discuss the influences of the stress cycle frequency on dynamic SC crack growth behavior.

Figure 9⁽²²⁾ shows the frequency effects ranging

Fig. 8 Endurance limit diagram of ZK141 and 7075 aluminum alloys immersed in a 3.5% NaCl solution at $f=30$ Hz.

from 1 Hz to 120 Hz on dynamic SC crack growth rates. The material tested was a high-strength 300 M steel ($\sigma_B = 1\,310$ MPa). The corrosive environment was a 3.5% NaCl solution, and cathodic protection of 3 mA/cm² was applied. The K_{DSCC} values at $f \geq 30$ Hz were almost equal to each other and were smaller than the K_{ISCC} value. In this case, the oxide films were effectively ruptured, which enhanced hydrogen entry into the material, resulting in a decrease in K_{DSCC} from K_{ISCC} .

At lower frequencies of $f \leq 5$ Hz, however, the K_{DSCC} values were almost equal to K_{ISCC} ; the stress cycle frequency was so small that the oxide films were effectively repaired, resulting in no influence of vibratory stresses on the threshold values. In the case of a high-strength Al alloy sensitive to an APC type of SCC, similar effects of the stress cycle frequency on K_{DSCC} were observed, and was explained from the viewpoints of repassivation and rupture of films at the SC crack tip⁽²¹⁾.

The fracture surfaces of static SCC and dynamic SCC at $f = 1$ and 5 Hz, where the influence of small vibratory stresses was not observed, were a mixed mode of intergranular and brittle transgranular cracking. At higher stress cycle frequencies of $f \geq 30$ Hz, the fracture surfaces at $K_{max} < K_{ISCC}$ were also similar to that of static SCC, though the area fractions of brittle transgranular cracking of the former were more dominant than those of the latter. This indicates that

Fig. 9 Effects of stress cycle frequency on dynamic SC crack growth rates of a 300M high-strength steel in a 3.5% NaCl solution at 298 K and at $R = 0.94$.

the crack growth was dominated by hydrogen embrittlement. At higher K_{max} levels, however, ductile transgranular cracking became dominant over the fracture surfaces, which means that corrosion fatigue prevailed over the fracture.

As is proved from the results mentioned above, the fracture area fractions are closely related to the fracture mechanisms, and the inter- and transgranular fracture area fractions were calculated by the image processing technique, as is shown in the typical process of Fig.10⁽²²⁾; the converted digital image being divided into small rectangles (Fig. 10(a)), the intergranular rectangles were identified without human assistance by using the algorithm by gray-level spatial dependency proposed by Haralick

(a) Scanning electron microphotograph. Arrow shows crack growth direction.

(b) Identification of intergranular cracking by manual analyses (IG: intergranular cracking, TG: transgranular cracking).

(c) Identification of intergranular cracking by image processing technique (IG: intergranular cracking, TG: transgranular cracking).

Fig. 10 Calculating process of inter- and transgranular fracture area fractions by computer image processing technique (static SCC of a 300M steel in a 3.5% NaCl solution at 298 K).

et al.⁽²³⁾, i. e., co-occurrence matrices. From the figure, it is clear that there was a very good agreement between the results by the computer image processing technique (Fig. 10(c)) and by manual analysis (Fig. 10(b)).

2.2.3 Effects of temperature SC crack growth is considered to be a thermally activated process⁽²⁴⁾. As was discussed before, dynamic SC crack growth of ZK141 alloy is brought about by the alternating mechanism of intergranular dissolution, which is prevailing in static SCC, and subsequent transgranular hydrogen embrittlement. Therefore, temperature dependence of crack growth of dynamic SCC is considered to be different from that of static SCC. The effects of temperature on static and dynamic SC crack growth rates ranging from 278 K to 343 K are shown in Fig. 11⁽²⁵⁾. Compared at the same temperature, da/dt for dynamic SCC was higher than that for static SCC with lower K_{DSCC} than K_{ISCC} over the temperature range examined. However, threshold values were independent of temperature with and without vibratory stresses. This implies that static strength (static SCC) and fatigue strength (dynamic SCC) of the passive films, and deformation strength of the base metal were independent of temperature.

On the other hand, da/dt for both static and dynamic SCC increased with increasing temperature: the higher the temperature, the higher the crack growth rates. Apparent activation energies for static SC crack growth were approximately ranged from 78 kJ/mol to 83 kJ/mol. The fracture surfaces of static

SCC principally exhibited intergranular cracking; an enhancement of da/dt with increasing temperature was caused by an increase in intergranular dissolution rates. That is to say, the values of activation energies, 78–83 kJ/mol, would be those of intergranular dissolution in this material^{(26),(27)}.

For dynamic SCC, however, thermally activated Region II crack growth had two apparent activation energies. At $T \leq 318$ K, dynamic SC crack growth was brought about by the alternating fracture mechanism of intergranular dissolution and subsequent transgranular hydrogen embrittlement in a ligament zone. Therefore, the apparent activation energy at lower temperatures, 21–29 kJ/mol, would be correlated with this alternating fracture mechanism. As temperature increased further, intergranular cracking dominated over the fracture surfaces similarly to static SCC, and the activation energies became higher and closer to that of static SCC (about 84 kJ/mol). This was caused by not only an enhancement of intergranular dissolution but also suppression of transgranular hydrogen embrittlement. At higher temperatures, hydrogen embrittlement had little detrimental influences on crack growth.

2.3 Effects of crack length on SC crack growth

Similarly to fatigue in air⁽²⁸⁾, a small crack size effect appears which unpredictably accelerates SC crack growth, with lower threshold values than longer cracks^{(29),(30)}, even though the crack is long enough in the mechanical or metallurgical sense, showing no influence of crack length on fatigue crack growth in an inert environment. Gangloff⁽³¹⁾ first observed these important phenomena in cyclic SCC and pointed out that the crack growth acceleration as "chemically short crack" is attributed to the influence of crack size on localized convection, transport, and reaction in an occluded environment in cracks, which constitute the chemical driving force in an aggressive environment.

Figure 12⁽³⁰⁾ shows the influence of crack size on static and dynamic SC crack growth in terms of K_{max} . The material tested was a 523 K tempered high-strength 4135 steel ($\sigma_b = 1770$ MPa) immersed in a 3.5% NaCl solution at 298 K. The crack length from a notch root was above 1.12 mm for static SCC in an aerated solution ($DO > 6.1$ ppm), above 1.52 mm for dynamic SCC, and above 2.81 mm for static SCC in a deaerated solution ($DO \leq 0.2$ ppm). The crack length for a long crack was longer than 6.72 mm from a notch root. The dynamic loads were sinusoidal waves with R of 0.9 and f of 30 Hz. Table 1 summarizes the threshold values and their crack length from a notch root.

Compared at the same testing condition, threshold values for a short crack were smaller than those

Fig. 11 Effects of temperature on static and dynamic SC crack growth of a ZK141 aluminum alloy immersed in a 3.5% NaCl solution at 298 K.

for a long crack, and at the same time small vibratory stresses decreased dynamic SCC thresholds, similarly to the case of long crack discussed before. Fracture surfaces near thresholds were intergranular, irrespective of the crack length and testing condition. However, the most marked differences existed in dissolution: dissolution of the fracture surface was more prevalent in short cracks than in long cracks. That is to say, a decrease in threshold values of short cracks was considered to be caused by an accelerated hydrogen uptake at the crack tip associated with increased dissolution of fracture surfaces as compared to long cracks.

In the case of cyclic SCC of the same material at $R=0.1$ and $f=0.1$ Hz⁽³⁰⁾, no influence of crack length sized above 1.18 mm from a notch root was observed. At $R=0.5$, however, crack growth rates of short cracks (0.61 mm–4.87 mm from a notch root) in terms of ΔK_{eff} were highly accelerated compared to long cracks (crack length >5.96 mm). One must note that the unpredictable crack acceleration of short cracks occurred especially at a high stress ratio including dynamic SCC.

For lower strength materials insensitive to SCC, on the other hand, an acceleration of short cracks in a corrosive environment is considered to be due to corrosion-product-induced wedge effects (crack closure) being less effective in a shorter crack length. Figure 13⁽³²⁾ shows crack growth curves of notched

Fig. 12 Effects of crack length on static and dynamic SCC crack growth of a 4135 high-strength steel in a 3.5% NaCl solution at 298 K. ($R=0.9$ and $f=30$ Hz)

specimens of a 0.15% C steel in a 1% NaCl solution, which were subjected to rotating bending at $f=35$ Hz. The growth rates of a short crack sized below 1 mm from a notch root (a^* included notch depth of 1.1 mm) was faster than that of a longer crack. An acceleration in shorter cracks is attributed to corrosion-product-induced wedge effects not being effective in a shorter crack size. Figure 14⁽³³⁾ also shows crack growth rates of a 3.5 NiCrMoV steel in a 5% NaCl + FeCl₃ solution. Here, crack closure was measured and the figure contains the typical subtracted load-displacement Curves. In the case of short cracks (0.2 mm–1.5 mm) shown by open symbols, crack closure was not observed, whereas in long cracks, crack closure was distinctly observed; the difference of crack closure behavior between long and short crack explained an unexpected acceleration of short corrosion fatigue crack growth in terms of ΔK .

The chemically short crack problems have recently come into consideration, and the crack size effects, an acceleration in short crack, are strongly dependent on the material/environment system itself, especially marked in high-strength materials. However, the researches in this field have mainly dealt with steels in aqueous environments, not with materials sensitive to

Table 1 Threshold values and crack length from a notch root of static and dynamic SCC of a 4135 steel in a 3.5% NaCl solution at 298 K

	SCC Aerated soln.		SCC Deaerated soln.	DSCC Aerated soln.
Long crack (MPa·√m)	24.1	24.3	18.4	13.1
l (mm)	6.86	7.39	9.78	8.12
Short crack (MPa·√m)	13.4	15.7	14.1	9.28
l (mm)	2.66	2.21	2.81	1.52

Fig. 13 Crack growth curves of 0.15% C steel in 1% NaCl solution. (rotating bending at $f=30$ Hz; a^* includes notch depth of 1.1 mm)

an APC type of SCC such as aluminum alloys or austenitic stainless steels in high-temperature water. Doig and Flewitt⁽³⁴⁾ theoretically derived a more prevailed dissolution in short cracks than in long cracks, resulting in higher crack growth rates, though almost no experimental results in such materials are available; systematic studies concerning mechanisms of short crack problems in corrosive environments are necessary in materials sensitive to both HE and APC types of SCC.

3. Corrosion-product-induced Wedge Effects

Corrosion-product-induced wedge effects^{(32),(35)–(38)} have great potential in influencing corrosion fatigue crack growth rates. In 1971, Elber⁽³⁹⁾ pointed out that residual plastic deformation remaining in the wake of the crack during fatigue crack growth caused crack closure, which plays an important role in influencing fatigue crack growth behavior. In addition to this type of crack closure, i.e., plasticity induced crack closure, corrosion products are formed within the crack in a neutral corrosive solution, leading to an earlier crack contact between the surfaces; the effective stress intensity factor is decreased from the one in an inert environment, resulting in deceleration in corrosion fatigue (CF) crack growth. This type of crack closure, termed "corrosion-product-induced wedge effects",

Fig. 14 Effects of crack length on corrosion fatigue crack growth of a 3.5% NiCrMoV steel in a 5% NaCl + FeCl₃ solution.

was first observed in CF crack growth of a 0.15% C steel in rotating bending tests⁽³²⁾, whose crack growth curves are shown in Fig. 13. As was explained, the slower crack growth rates above a^* of about 1.5 mm were due to this type of crack closure.

This crack closure is well explained by crack closing simulation using a three-dimensional image processing technique^{(18)–(20)}, which was mentioned before. Figures 15⁽¹⁹⁾ and 16⁽¹⁹⁾ show stereo-pairs of matching scanning electron microphotographs of corrosion fatigue of an 80 kgf/mm² class high tensile strength steel, HT80, in synthetic seawater, and their processed bird's-eye views, respectively. The matching surfaces were then superimposed, and the one surface was translated, rotated, and tilted so that two surfaces were properly aligned. After this processing, the spacing between the surfaces was incrementally decreased until an access distance D of 5 μm from the first contact between the two surfaces, i.e., $D=0$ μm . Figure 17⁽¹⁹⁾ shows the matching cross sections taken along the A-A and B-B lines in Fig. 15 at $D=5$ μm . In the figure, the shaded zone indicates corrosion products adhered. Crack closure occurred along the B-B line, where the corrosion products adhered so much, whereas a gap between two cross sections was still remained along the A-A line, where the corrosion products scarcely adhered.

In order to discuss CF crack growth behavior, the influences of the corrosion-product-induced wedge effects should be taken into consideration. Figure 18⁽³⁸⁾ shows the typical subtracted load-strain curves of CF of a high tensile strength HT50 steel ($\sigma_B=580$ MPa) immersed in a 1% NaCl solution at stress intensity

Fig. 15 Stereo-pairs of matching scanning electron microphotographs of corrosion fatigue of a HT80 steel immersed in synthetic seawater. Arrows show crack growth direction.

factor range of about $10 \text{ MPa} \cdot \text{m}^{1/2}$. The curves were divided into three regions of I, II, and III⁽³⁷⁾. A crack was fully open in Region III, and was fully closed in Region I. Region II was the transition between Regions I and III. The ΔK values computed from Region III correspond to the well-known effective stress intensity factor range, ΔK_{eff} .

Corrosion-product-induced wedge effects result from i) solid-like corrosion-product-induced wedge effects (ECC) and from ii) viscoelastic or viscous corrosion-product-induced wedge effects (VCC)⁽³⁶⁾. At $R = -1$ or $f = 5 \text{ Hz}$, ECC dominated over the crack closure, because corrosion products were strongly adhered on crack wakes by compressive loads at $R = -1$, or at $f = 5 \text{ Hz}$ a large amount of corrosion products were formed and crack closing rates were small.

Fig. 16 Bird's-eye view of Fig. 15. Arrows show crack growth direction. The heights in bird's-eye view (a) are inverted, making easier to compare with the other matching topograph, (b).

Fig. 17 Crack closure simulation along the A-A and B-B cross sections in Fig. 15.

This was also supported by the fact that subtracted load-strain curves did not change before and after vacuum drying⁽³⁷⁾. At $f = 50 \text{ Hz}$ with $R = 0.1$ and 0.5 , VCC was superimposed on ECC, resulting in different paths between loading and unloading periods. However, the load sharing capacity by VCC is negligible⁽³⁶⁾, and therefore, an increase in crack opening stress was mainly caused by ECC. In the case of $R = -1$, the crack was thickened by dissolution, thereby moving the perfect closing load, P_{op1} into the compressive side.

The retardation effects by corrosion-product-induced wedge effects can be quantitatively evaluated by ΔK_{eff} -based methodology⁽⁴⁰⁾. However, in the low crack growth rate region⁽³⁷⁾⁽³⁸⁾, or under the cathodic polarization condition in synthetic seawater⁽⁴¹⁾, where Ca-Mg deposit⁽⁴²⁾-induced wedge effects become predominant, the driving force due to the load sharing in Region II must be taken into account of⁽³⁷⁾⁽³⁸⁾.

In the laboratory tests, the above-mentioned corrosion-product-induced wedge effects are inevitable. On one hand, stress-assisted dissolution is dominant in low-stress, long-term CF crack growth of actual components. Under such circumstances, plasticity-induced crack closure as well as corrosion-product-induced wedge effects are not expected⁽³⁵⁾, because the crack tip is blunted and is greatly thickened⁽⁴³⁾. Consequently, from a conservative standpoint, it is reasonable to assume $\Delta K_{\text{eff}} = \Delta K^{(35)}$ (or $\Delta K_{\text{cont}} = \Delta K^{(44)}$) for long-term CF crack growth. Here ΔK_{cont} is the modified effective stress intensity factor range, considering the load sharing in Region II⁽³⁷⁾⁽³⁸⁾, a proposal to estimate long-term CF crack growth characteristics have been presented elsewhere⁽³⁵⁾⁽⁴⁴⁾.

Corrosion-product-induced wedge effects affect

Figure 18 Typical subtracted load-strain curves of a HT50 high tensile strength steel immersed in a 1% NaCl solution at 298 K.

CF crack growth measurement in laboratory test. Therefore, the measured CF crack growth should be correlated with ΔK_{eff} or ΔK_{cont} , not with ΔK , in order to eliminate the reduction of the mechanical driving force due to the corrosion-product-induced wedge effects.

4. Mechanical Factor Controlling Crack Initiation at Corrosion Pit

SC or CF cracks are sometimes initiated at the bottom of a corrosion pit: e.g., see Fig. 6. In this section, the mechanical factor controlling the crack initiation will be discussed. Figure 19⁽¹²⁾ shows the relationship between the maximum principal stress, $\sigma_{1,max}$, and pit depth with and without cracks of the multiaxial cyclic SCC tests shown in Figs. 3 and 4. From the figure, it is clear that a cyclic SC crack was initiated after the pit depth exceeded a threshold value. Assuming a corrosion pit with a crack as a sharp semielliptical surface crack, the Mode I stress intensity factor at the bottom of a corrosion pit was calculated by using the Newman-Raju equation⁽⁴⁵⁾. Here, the maximum principal stress, $\sigma_{1,max}$, was substituted for stress. Ten pits with a crack were randomly chosen in each fractured specimen, and K_I values were calculated; the relationship between the minima in each specimen and $\sigma_{1,max}$ is shown in Fig. 20⁽¹²⁾. The data, except at high stress levels, were almost constant, and average value of K_I , K_{IFSCC} , was obtained at $5.4 \text{ MPa} \cdot \text{m}^{1/2}$.

The relationship between $\sigma_{1,max}$ and the pit depth at K_{IFSCC} are plotted in Fig. 19 with aspect ratios of 1.0, the maximum aspect ratio $((b/a)_{max})$, of 0.77, the average of the mean value of each specimen $((b/a)_{mean})$

Fig. 19 Relation between pit depth and maximum principal stress, $\sigma_{1,max}$, in multiaxial cyclic SCC tests of a 4135 steel in a 3.5% NaCl solution at 298 K.

and of 0.55, the average of the minimum $((b/a)_{min})$. The threshold pit depth above which a crack was initiated at the bottom of a corrosion pit coincided with the line of $K_{IFSCC} = 5.4 \text{ MPa} \cdot \text{m}^{1/2}$. These results well support that the mechanical condition dominating the crack initiation at the bottom of a corrosion pit is the stress intensity factor calculated on the assumption of a corrosion pit being a surface crack.

Similar methods also provide useful tools to evaluate the mechanical condition of CF crack initiation at the bottom of a corrosion pit^{(46),(47)}. The relation between stress amplitude, σ_a , and pit depth is shown in Fig. 21⁽⁴⁶⁾. The materials tested were the following high tensile strength steels: 50 kgf/mm² class steel, HT 50, 50 kgf/mm² class thermomechanically controlled process steel, HT50-TMCP, and 80 kgf/mm² class steel, HT80. Rotating bending loads at $f = 0.17 \text{ Hz}$ were applied to round-bar specimens immersed in synthetic seawater. It is also quite clear that CF cracks were initiated when the pit depth exceeded a threshold value.

Similarly to the cases of cyclic SCC mentioned above, the stress intensity factor range at the deepest point of a pit was calculated by the Newman-Raju's equation⁽⁴⁵⁾, assuming a corrosion pit having a crack as a sharp crack. Figure 22 shows the relation between ΔK ($=K_{max}$) and pit depth of interrupted tests. The figure also contains the average values of ΔK , ΔK_{CF} and pit depth, $\bar{a}$, at each interrupted cycle. As shown in Fig. 22, it is clear that the pit depth increased with increasing cycle ratio n/N , where N is the cycles to fracture. However, ΔK did not increase with an increase in the pit depth and the cycle ratio, and the average values of ΔK , ΔK_{CF} , whose values are shown in the figure, were almost kept constant; ΔK_{CF} of pits with a crack remained

Fig. 20 Relation between stress intensity factor, K_I and maximum principal stress, $\sigma_{1,max}$, in multiaxial cyclic SCC tests of a 4135 steel in a 3.5% NaCl solution at 298 K.

Fig. 21 Relation between stress amplitude, σ_a , and corrosion pit depth of high tensile strength steels, HT 50, HT50-TMCP, and HT80 immersed in synthetic seawater at $f=0.17$ Hz and $R=-1$.

constant, though pit depth increased with stress cycles after crack initiation. Namely, the average values of ΔK_{CF} , ΔK_{CF}^* , are better parameters than the minimum values of ΔK in relating to the mechanical condition dominating the CF crack initiation.

The lines in Fig. 21 represent the relation between σ_a and pit depth at ΔK_{CF}^* and the average aspect ratios of pit, α_{mean} , of these three steels; it is concluded that the mechanical condition of whether or not a crack was initiated was clearly determined by ΔK_{CF}^* values obtained by assuming the corrosion pit as a sharp crack.

5. Concluding Remarks

The investigations on environmental strength of materials are increasingly important from the standpoints of not only purely scientific interests but also the development of reliable design basis for machines and structures. In the field of SCC, one must note that SCC behavior under various dynamic loading conditions has been systematically understood. In the field of CF, various international, or national cooperative round-robin test programs have been developed, whose objective is to obtain design basis and life prediction methods.

From the standpoints of methodology, well-known fracture mechanics approaches have been widely used, and the advanced technology is coming into use, including computer image processing, electrochemical new techniques characterized by scanning vibratory electrode technique⁽⁴⁸⁾ and noise analyses⁽⁴⁹⁾; these advanced techniques shall help us realize substantial progress of knowledge concerning the environmentally induced degradation of materials. The materials investigated are now extending from conventional metallic materials to advanced compos-

Fig. 22 Relation between stress intensity factor range, ΔK , and corrosion pit depth, " a ", in interrupted tests of high tensile strength steels, HT 50, HT 50-TMCP, and HT 80 immersed in synthetic seawater at $f=0.17$ Hz and $R=-1$.

ite materials such as fiber reinforced plastics (FRP) and metal matrix composites (MMC). Since environmental strength results from time-dependent phenomena, long duration is required to investigate its characteristics. Unsolved problems still remain and further systematic studies are required.

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