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oxide films in environmentally assisted
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Abstract

The aim of this literature study has been to evaluate the level of understanding of the role of anionic impurities in environmentally assisted cracking (EAC) of iron- and nickel-based alloys in the coolant conditions of a boiling water reactor (BWR) – type nuclear power plant, mainly under normal water chemistry (NWC). The study has been motivated by a need to find the most relevant experimental approaches that can be applied when looking for correlations between crack growth rate and measurable electrochemical and chemical parameters.

Special crack tip chemistry conditions are established, when trace amounts are present in the BWR coolant and become enriched within a crack. Anions may influence both the conductivity and the pH of the coolant within the crack. In addition, they may influence the composition, structure and properties of the oxide films formed on crack walls either directly via adsorption or incorporation or indirectly via the effect of changes in pH within the crack. Based on the proposed mechanisms for EAC, oxide films formed on crack wall surfaces are likely to play a key role in determining the crack growth rate of structural materials. The prediction of the influence of anionic impurities is thus likely to be facilitated by means of understanding their effect on the films on crack walls. One of the most promising approaches to experimentally clarify this influence is based on investigating the electrochemical behaviour of oxide films Fe- and Ni-based materials in high-temperature conditions simulating the special chemistry within a stress corrosion crack. Results from such studies should be compared and combined with ex situ analytical results obtained using modern electron microscopic techniques. In addition to crack growth, currently available electrochemical techniques should also be applied to find out whether crack initiation can be explained and modelled on the basis of the electrochemical behaviour of oxide films.

Preface

The present review has been written as a part of the subproject "Water chemistry, service reliability and activity levels" within the project "Plant life management" (XVO). The funding from the National Technology Agency (Tekes), Teollisuuden Voima Oy and VTT to this work is gratefully acknowledged.

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Appendix A. Summary of and comments on proposed EAC models

1. Introduction

The aim of this literature study is to collect and evaluate the level of understanding of the role of anionic impurities in accelerating environmentally assisted cracking (EAC) of iron- and nickel-based alloys in boiling water reactor (BWR) coolant conditions, mainly under normal water chemistry (NWC). The study has been motivated by a need to find the most relevant experimental approaches that can be applied when looking for correlation between crack growth rate and measurable electrochemical and chemical parameters.

Environmentally assisted cracking (EAC) can be understood as a localised deformation process accelerated by local corrosion in addition to mechanical stresses or strains. The cracking of structural materials in nuclear power plants may proceed along grain boundaries, i.e. intergranularly (IGSCC), underlining the role of dissolution, or through the grains, i.e. transgranularly (TGSCC), underlining the role of mechanical loading. Generally, the two most studied occurrences of cracking have been that of sensitised stainless steel in BWRs and that of nickel-based alloys (especially Inconel alloy 600) in pressurised water reactors (PWR). As mentioned above, the present text deals mainly with cracking of iron- and nickel-based materials in BWR coolant under NWC conditions, in which the cracks can most often be classified as intergranular. For the sake of generality, we have not made a strong distinction between the cracking of stainless steels and that of nickel-based alloys, and even the cracking of low-alloy steels is occasionally commented when considered useful. Cracking phenomena in PWR environments are also to some extent commented for the sake of comparison or complementary information. Ignoring cracking in PWR conditions in the present kind of discussion could not be considered justified because of the conceptual similarities among all hot water systems, as commented also by Ford and Andresen [1]. For similar reasons, ideas presented in the literature in the context of crevice corrosion are to some extent included in this survey, when they seem to have relevance or bring useful insight into understanding partly similar phenomena in a crack.

In order to focus on the role of chemical and electrochemical phenomena in cracking, we have considered the structural metallurgical properties of the materials to be beyond the scope of the study. In other words, we have treated the metal itself as a “black box”, although its metallurgical properties have a major impact on the absolute crack growth rate. Another decision related to the scope of the present report is that crack propagation has much more emphasis than crack initiation. This restriction is partly a natural consequence of not focusing on the metallurgical properties of materials, because these properties most probably play a significant role in crack initiation [2].

Special crack tip chemistry conditions are established, when trace amounts of anions are present in the BWR coolant and become enriched within a crack, as described in detail later in the present report. Possible routes for the influence of enriched anions on cracking are illustrated in Fig. 1. Anions may influence both the conductivity and the pH of the coolant within the crack. In addition, they may influence the composition, structure and properties of the oxide films formed on crack walls either directly via adsorption or incorporation or indirectly via the effect of changes in pH. Certainly other routes may exist as well, such as possible changes of the composition and properties of the material in the crack tip region. Based on Fig. 1, an alternative definition for the aim of this work can be written as to find ways to clarify which of the routes sketched in Fig. 1 play an important role when assessing the impact of anions in EAC.

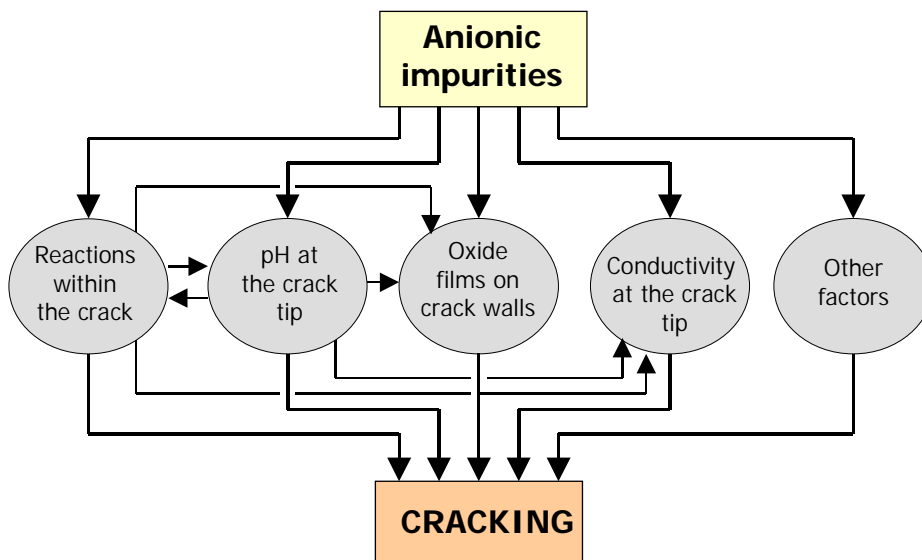


Figure 1. A sketch illustrating possible routes via which anions enriched inside a crack may influence cracking susceptibility of structural materials.

We have on purpose divided the subject in small parts with regard to chemical and electrochemical factors that may contribute to cracking susceptibility. The discussion is accordingly presented so that the influences of bulk environment, of crack tip chemistry, of oxide films on surfaces exposed to the bulk environment and of oxide films on crack walls are treated separately. Although this approach has lead to a considerable length of the text, we believe that this approach serves best our purpose to recognise the most useful experimental approaches. In order to make it easier for the reader to find the context of these small parts on cracking phenomena it would be advisable to read the short descriptions of models proposed for environmentally assisted cracking, attached as Appendix A.

The actual text proceeds, after the introduction and defining the goal of the work, to short comments on the role of metal properties and stress state in EAC in Chapter 3. A

more comprehensive discussion on the role of bulk environment, on the role of crack tip environment and on the role of oxide films external and internal to the crack is given in Chapters 5, 6 and 7, respectively.

We wish that the readers of this text are critical and we welcome all the feedback and comments to the ideas and views presented in this report.

2. Objective of the work

The objective of this work is to collect and evaluate the level of understanding of the role of anionic impurities in the mechanisms of environmentally assisted cracking (EAC) of iron- and nickel-based alloys in boiling water reactor (BWR) coolant conditions. Our main purpose has been to find and define the most suitable and relevant experimental approaches that are needed to find and establish correlations between crack growth rate and measurable electrochemical and chemical parameters.

3. Role of metal properties and stress state in environmentally assisted cracking

We have indicated above in the introduction section that the rate and extent of EAC do not depend only on the corrosive environment but also on the composition and metallurgical properties of the metals exposed to the environment and on stresses. A comprehensive treatment of the effect of metallurgical properties and applied and residual stresses is beyond the scope of this report. It is however worth bearing in mind that these factors influence EAC also indirectly, e.g. by means of changing the environmental conditions.

Brossia and Kelly [3] have for instance commented that the material composition may influence the nature and properties of the passive film both on the surfaces internal and external to the crack, local solution chemistry within the crack and the interfacial electrochemical kinetics. On the basis of the summary of proposed EAC mechanism given in Appendix A, these belong to the key factors in determining the rate of crack propagation.

Page *et al.* [4] have on the other hand reported that the application of dynamic strain to the crack tip may shift the crack tip potential and pH into a regime where chemical reactions different from those occurring under static conditions are expected to occur. Dynamic straining can continuously expose free non-oxidised metal surface to the crack tip electrolyte and by that way maintain dissolution reactions. Elastic stresses have on the other hand been reported to increase the defect content in passive films [5, 6].

The rest of this report is devoted mainly to discussions about the effect of changes in the environment on EAC.

4. Role of bulk environment in environmentally assisted cracking

This chapter provides a short survey of the influence of parameters characterising the bulk coolant on the rate of environmentally assisted cracking. Factors discussed include the temperature and flow rate of the coolant, the corrosion potential (as a measure of the content of oxidising species such as oxygen, hydrogen peroxide and/or chromate), as well as the impurity content and the pH of the coolant. We do not focus in this chapter on any mechanistic aspects but describe instead how and to what extent different factors have been observed to influence EAC in practice.

The temperature is obviously the same at the crack tip as it is at the free surface exposed to the bulk coolant. However, some of the parameters mentioned above, like pH and content of oxidising species, may have different values and may play a different role in the free surface reactions from that in the reactions at the crack tip.

4.1 Temperature

Temperature has been observed to have a clear influence on crack growth rates. The crack growth rate of sensitised stainless steels and nickel-based materials seems to exhibit a maximum at temperatures around 200 °C. Ruther *et al.* [7] have for instance reported that maximum IGSCC crack growth rate (CGR) for Type 304 stainless steel in oxidising conditions occurs at temperatures between ca. 200 and 250 °C in high purity water, while the studied range extended from 100 to 320. Andresen [8] has on the other hand reported a peak in crack growth rate at around 200 °C for both sensitised type 304 stainless steel and Inconel alloy 600 in pure water and/or moderate corrosion potentials (≤ 200 ppb oxygen). The role of the passive film in providing protection from impurities has also been reported to diminish at temperatures in excess of 200 °C. [9].

Temperature cannot be considered an independent parameter for EAC. Instead, it influences the pH of the coolant and the formation, stability and solubility of the different oxides, transport rates of ions etc., which makes its significant influence understandable. It may also have a profound influence on the mechanical properties of some materials even at 300 °C, increasing creep rates and thus the risk of EAC.

4.2 Flow rate

Observations and views about the influence of flow rate on cracking may seem to some extent inconsistent – probably because of different experimental approaches and arrangements.

The possible influence of flow rate on cracking is partly connected with its effect on the corrosion potential (see the following chapter). According to Chai *et al.* [10], crack growth rates increase with water flow rate at low flow rates (< 5 cm/s) at oxygen levels of around 100 ppb, which is likely due to increased mass flow of oxidising species and in this way on corrosion potential. At oxygen levels of 1000 ppb and higher, the influence of flow rate has on the other hand been found insignificant. In this case the high oxygen content is likely to establish a high corrosion potential even under conditions of low flow rate.

According to the views summarised in Ref. 2, a possible increasing effect of water flow on the crack growth rate can be attributed to the increased mass transport out of the crack. Another explanation to the increasing influence of flow rate on crack growth is the increased flux of oxygen to the external surface to compensate for the anodic current due to oxidation in the crack [11]. However, as commented by Turnbull [12], a high flow rate with a suitable flow orientation, i.e. parallel to the plane of the crack, may also flush the crack and thus prevent the formation of occluded cell chemistry that is necessary for EAC to occur. A retarding effect of increasing flow rate to crack growth is also possible in the case of a short crack or a very large crack opening displacement due to excessive plastic deformation, leading to a rinsing of the crack enclave [11].

The initiation of IGSCC in oxygenated water has been found to be delayed in high-flow media, probably due to the fast transport of oxygen to local attacks, promoting repassivation [11]. Another explanation to a decreasing influence of high flow rate on cracking may be connected with its suppressing effect on the transpassive dissolution of chromium, which may play a role in crack growth (see the next chapter). The fact that increasing flow rate decreases the rate of a dissolution reaction may seem unexpected. A possible explanation to this phenomenon is that catalytic species that accelerate the transpassive dissolution are removed from the vicinity of the surface by the high-rate flow [13].

4.3 Potential

The correlation between increasing corrosion potential and increasing crack growth rate of sensitised stainless steels in BWR water at temperatures around 300 °C has been

shown in several investigations (see Fig. 2, Ref. 2 and references therein). The corrosion potential in turn depends on the level of oxygen and other oxidants in the coolant. In certain cases it is likely to be a more uniform parameter to correlate the oxidising nature of the environment to cracking phenomena than the contents of oxidising species in the coolant. IGSCC initiation in the presence of hydrogen peroxide has for instance been found to be faster and occur more frequently than in the presence of only oxygen [14], which shows that the contents of different species cannot be directly compared. An opposite case may be the presence of chromate ions in the solution: they are likely to have a marked effect on the potential, but they have not been reported to have a considerable influence on crack growth rates (see below).

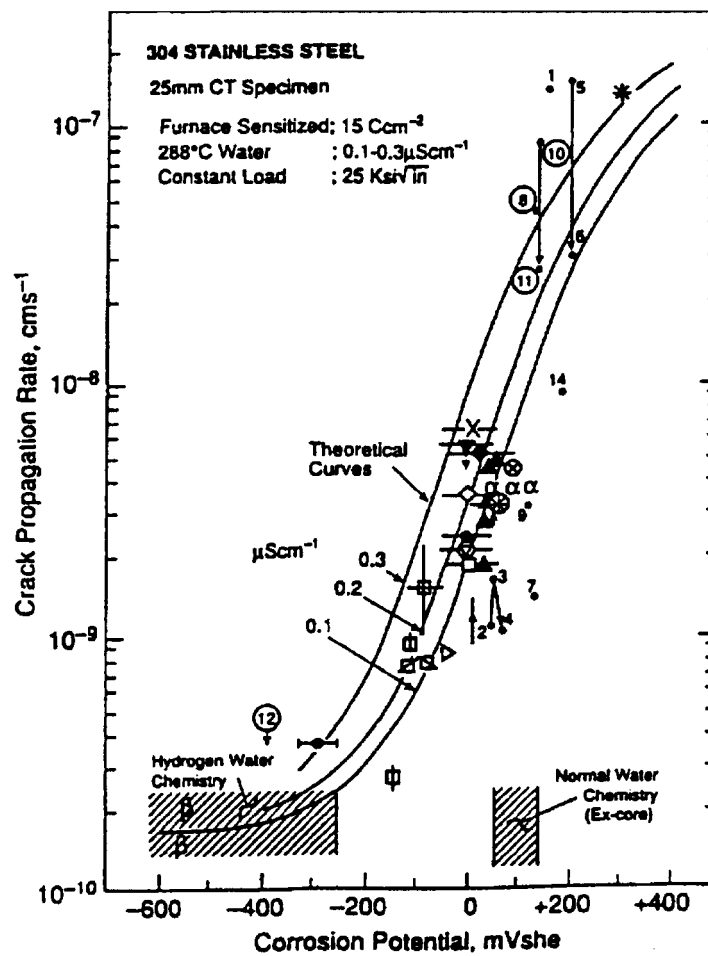


Figure 2. The influence of corrosion potential on the crack growth rate of sensitised stainless steel of type 304 [15].

As indicated by Fig. 2, cracking of sensitised stainless steels in BWR environment has been found to occur mainly above a threshold potential which is around -0.23 V vs. SHE at 288 °C. This value of the threshold potential has been suggested to depend on temperature [16], loading rates, surface condition, solution pH etc. [16]. Recent data

indicates that potentials as high as -50 mV vs. SHE may produce only little increase in crack growth rates, if the purity of the coolant is sufficiently high [17]. It is certainly good to bear in mind that the threshold potential for cracking of stainless steel is relatively close to the onset potential for transpassive dissolution of chromium from the steel at the corresponding temperature [18]. This may be important to the mechanistic modelling of cracking.

Itow et al. [19] have reported that the crack growth rate of Inconel alloy 182 decreases by a factor of 10...30 when the corrosion potential is decreased from 200 mV to -100 mV. This confirms that hydrogen water chemistry (HWC) retards crack growth, although the hydrogen injection rates required to decrease the corrosion potential in plant conditions to -100 mV are relatively high. The crack growth rate seems to be affected immediately after changes in the corrosion potential [19].

At lower temperatures than in the normal operation range of coolant systems in nuclear power plants, a peak in the crack propagation rate vs. potential curve for sensitised Type-304 stainless steel is expected. At 100 °C, a peak is found at around 150 mV [16]. This may have important consequences with regard to cracking during the shutdown and start-up periods.

4.4 Anionic impurities

4.4.1 Generally about anionic impurities

Several kinds of ionic impurities, i.e. sulphate, chloride, carbonate, fluoride, chromate, nitrate and phosphate ions etc., have been reported to be able to accelerate the initiation and propagation of intergranular stress corrosion cracks in various heats of sensitised 304 stainless steel and Inconel alloy 600 in high-temperature water [2, 20]. Impurities affect directly the conductivity of the coolant, and the impurity concentrations can thus be correlated with this measurable parameter. Fig. 3 shows how the crack growth rate of austenitic stainless steel of type AISI 316 can be presented to correlate with the conductivity of the coolant.

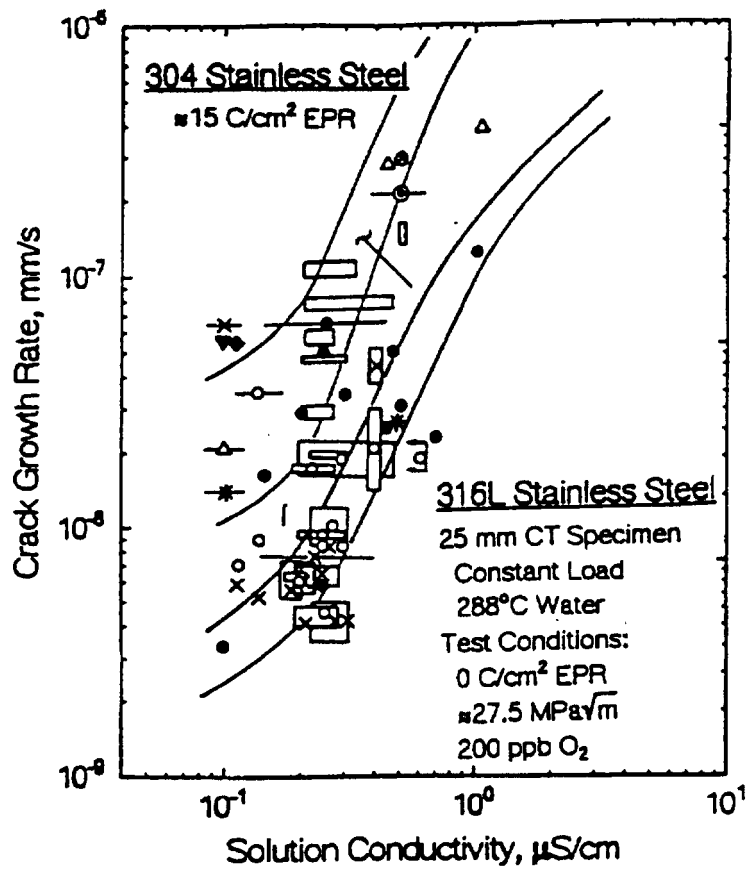
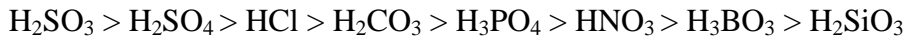
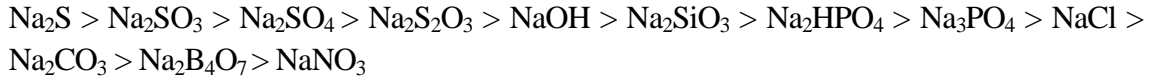


Figure 3. Correlation between the conductivity of the coolant and the crack growth rate of austenitic stainless steel of type AISI 304 and 316L [15].

The contents of anionic impurities are mainly determined by intrusions of resin bed demineralisers which, when exposed to increased temperatures (i.e. close to 60 °C) or irradiation fields or such radiolysis products as H₂O₂, decompose to form acid sulphate and simultaneously release trapped impurities such as chlorides originating from, e.g., condenser leaks [16,21]. Typical contents of sulphates and other anionic impurities mentioned above are of the order of 1 to a few ppb [22] in BWR coolants. Andresen [17] has pointed out that the conductivity levels of 0.2...1.0 μScm⁻¹ characteristic of BWR operation in the 1970s and 1980s have decreased to levels as low as 0.12 μScm⁻¹ over 90 % of the time in several plants as a result of improved coolant clean-up systems. Changing better materials in condenser tubes, i.e. replacing aluminium brass with titanium, has also contributed to the decrease of CI levels in several plants.

Specific impurities are likely to have different effects on the EAC susceptibility independent of their influence on the conductivity and therefore it is important to know which ions are present in the water [2, 23]. Clarifications and rules of thumb for the different effect of different impurities can be looked for by means of comparing various experimental observations.

Ruther *et al.* [7] have studied and ranked both sodium salts and various acids at constant anion concentrations of 100 ppb in the following order with respect to their decreasing effect on the crack growth rate:



This order is in fair agreement with the results of for instance Davis and Indig [23] and Ljungberg *et al.* [24, 25, 26], and also partly with those of Sambongi *et al.* [27]. Ljungberg *et al.* have found that for sensitised AISI 304 stainless steel, sulphate is the most detrimental of the impurities considered. According to Ljungberg *et al.* [24, 25, 26], 100 ppb sulphate enhances IGSCC noticeably in NWC with 200 ppb oxygen, and at 1 ppm oxygen the effect is severe. In HWC with 5 or 15 ppb oxygen, some IGSCC occurs at 25 ppb sulphate, and at 100 ppb sulphate, cracking is nearly as severe as in pure NWC. Chloride also severely enhances IGSCC. However, Ljungberg *et al.* have reported that to achieve similar effects as with sulphate in EAC tests using the constant elongation rate tensile (CERT) technique, 4 to 10 times as much chloride is needed. Ljungberg *et al.* have not found nitrate (200 ppb) and carbon dioxide (1...10 ppm) and sodium carbonate (1 to 24 ppm) to have an increasing effect on crack growth rates, although the results of other experiments have indicated that nitrate and carbonate ions may enhance crack initiation. Also fluoride ions (F^-), SiO_2 and thiosulphate ions ($\text{S}_2\text{O}_3^{2-}$) have been found to be harmful. Inconel alloys 600 and 182 seem to be affected by sulphate and chloride ions in the same way as sensitised AISI 304 stainless steel, but to a smaller degree. Also the results of Toivonen *et al.* [28] indicate that the addition of sulphate ions has a more profound effect on the crack growth of Inconel alloy 182 than on that of sensitised AISI 304.

The observations related to the influence of different anionic impurities on the crack growth rates can be summarised as presented by Andresen [16, 17, 20]:

- Impurities accelerate IGSCC of sensitised Type 304 stainless steel, particularly at temperatures above 150 °C.
- Crack initiation is to a first hand influenced by the pH and not by the type of anion or by the conductivity produced by the impurity.
- Crack initiation occurs more easily in acidic solutions, and is retarded in basic solutions.

- No effect of conductivity on crack initiation has been observed in neutral solutions.
- Crack initiation occurs more easily at elevated temperatures – no effect of impurities on initiation at 125 °C.
- Crack propagation rates are increased in high conductivity solutions, even for neutral and basic pH impurities.
- Crack propagation rates are less clearly affected by the type of impurity (sulphate, carbonate, chloride) than by an increase in conductivity in general.
- Still, acidic impurities may accelerate propagation more than slightly alkaline impurities.

These observations are in fair agreement with the results reported by Zhang *et al.* [29, 30]. They stated that the presence of sulphate ions accelerates crack initiation of Type 304 stainless steel, while crack propagation seems to depend on the conductivity of the coolant rather than on the type of anion. However, it has to be noted that the tests of Zhang *et al.* have been performed in mixed solutions containing sulphate and borate at 95 °C. These conditions differ markedly from those prevailing in BWR environments, and thus the application of the results of Zhang *et al.* [29, 30] to BWR conditions may be misleading.

One approach to assess the impact of anions on cracking susceptibility is to study their influence on the corrosion potential. A decrease of corrosion potential has been reported after the introduction of relatively small amounts of impurities (in the range ≤ 100 ppb) such as H₂SO₄, Na₂SO₄, NaCl, Na₂CO₃, NaNO₃ and NaF [16, 23, 31, 32]. Andresen [16] has reported shifts from about –100 mV to –300...–400 mV for Type 304 stainless steel. These results indicate that the detrimental influence of anionic impurities cannot be correlated directly with the corrosion potential.

One additional observation related to the behaviour of anionic impurities that is certainly worth bearing in mind is the delay in change of crack growth rates with changes in water purity. This has been discussed for instance by Andresen [20, 33], according to whom a certain delay may be required for the crack tip chemistry (see Chapter 5 below) to establish a steady state, at which point the growth rate is higher than when impure water is first introduced. Itow *et al.* [19] have reported incubation times of the order of 100 h for Inconel alloy 182. Considerably longer delays have on the other hand been observed when impure water has been replaced by pure water. It may be possible that exposure to impurities may after subsequent exposure to pure water have effects for at least one week, as indicated for instance by the results of

Toivonen *et al.* [28]. This phenomenon is often referred to as a memory effect, although it seems that this expression was used also for another purpose when discussing the crack chemistry [22, 34] (see also Ch. 6.4).

The delays in the establishment of a steady-state situation and thus in the change of crack growth rates may be affected by the flow conditions. These delays are consequently longer in laboratory autoclaves than in real plants, because the accessible flow rates in the former are usually relatively low.

4.4.2 Sulphate ion as an impurity

The role of sulphate ions in accelerating both the initiation of IGSCC for Type 304 stainless steel and Inconel alloys 600 and 182 and the crack growth rates in Type 304 stainless steel has already been addressed above, and it has been discussed in several reports in the literature [2, 22, 25, 31, 34, 35].

Typical sulphate ion contents in BWR coolants are of the order of 1 to a few ppb [22], but as mentioned in the previous chapter, intrusions of resin bed demineralisers may occasionally lead to significantly higher concentrations. Sulphate has been stated to exist mainly in the form of hydrogen sulphate, HSO_4^- , and only to a small degree as SO_4^{2-} in the bulk BWR coolant at temperatures close to 300 °C [22, 36].

The role of sulphate ions is also strongly emphasised in EPRI guidelines [37], where sulphate ions have been reported to increase the SCC propensity of nickel-based alloys, carbon steel and low-alloy steels. The EPRI guidelines present a chemistry program that can be used by utility personnel as a model for a plant specific program. The guideline value of sulphate content for power operation corresponding to action level 1 is 5 ppb, which can be considered relatively low but accessible during proper operation of the ion exchange resins.

Aaltonen *et al.* [2] have recently surveyed the literature on the effects of sulphate ion concentration on the crack growth rate of stainless steel and nickel-based Inconel alloy 182 weld metal in BWR environment from a fracture-mechanical viewpoint. The survey has revealed that most investigations have been performed with high sulphate ion additions, typically 100 ppb or even 1000 ppb, which remarkably exceeds the sulphate ion levels of operating BWRs. However, some results have been reported also at reasonably low sulphate ion contents (see e.g. Ref. 19). Aaltonen *et al.* have summarised the results from the surveyed literature as follows:

- A time delay of typically some ten hours is observed between a sulphate intrusion and the increase in crack growth rate (as for other ionic impurities – see Chapter 4.4.1 above).
- Sulphate ions concentrate in cracks in appreciable amounts in NWC BWR environment (for further discussion, see Chapter 5.2.4 below).
- After sulphate ion intrusions, higher crack growth rates are sustained for long periods, $\gg 100$ hours, after the bulk environment is nominally clean (see also the discussion on the delays in the change of crack growth rates and on the memory effect in Chapter 4.4.1).
- The CGR of Inconel alloy 182 is higher than that of sensitised austenitic stainless steel of type AISI 304 in clean NWC environment without sulphate ions in the coolant.
- An acceleration factor of about 10 for sensitised AISI 304, and about 4...8 for heat treated Inconel alloy 182 has been reported at a sulphate ion concentration of 30 ppb, compared to the CGR in clean NWC.
- At high amounts of sulphate ions (about 100 ppb), the observed CGRs for sensitised stainless steel and Inconel alloy 182 are similar.

Concerning the effect of sulphate ions in different temperatures, Ruther *et al.* [7] have reported that the temperature range over which maximum susceptibility to cracking has been observed increases by the addition of sulphate ions (100...1000 ppb as H_2SO_4). Andresen [8] has commented that the influence of sulphate ions when compared to that of chloride ions is more pronounced at $T < 250$ °C, while at 288 °C the effects of sulphate and chloride ions added as H_2SO_4 and HCl are similar. These observations deserve attention when assessing the influence of transient situations such as shutdown and start-up periods on crack growth rates.

What comes to cracking in normal (NWC) and hydrogen water chemistry (HWC) conditions, Itow *et al.* [19] have reported that the addition of 16 ppb sulphate ions as sodium sulphate accelerates crack growth of Inconel alloy 182 at lower corrosion potentials (–100...0 mV), while such an addition has no significant influence at a higher corrosion potential of 200 mV. This indicates that the presence of sulphate ions reduces the benefit obtained from HWC. Another possibility is that the crack growth rate at 200 mV is so high that the influence of sulphate ions can no more discerned.

Hermansson and Gott [22] have defined the memory effect in a different way from that used above. They defined it as the number of exposures needed before sulphate affects the crack propagation rate and that the rate increases with the number of exposures. Referring to the work of Lidar, they have commented that exposure of stainless steel to sulphate transients for short periods with high sulphate concentrations had no effect, while repeated exposure periods increase the crack propagation rate [38].

Attempts to assess the effect of sulphate ions on cracking susceptibility by means of studying their influence on the corrosion potential reveals some inconsistency that may be related to different concentration levels of sulphate ions. As mentioned in the preceding chapter, small additions of sulphate ions have been observed to lead to lower corrosion potentials of Fe and Ni-based materials [16, 23, 27, 31, 32]. Previous work carried out at VTT has indicated that the corrosion potential of stainless steel is not affected by sulphate ion addition of 10...30 ppb while that of Ni-based materials decreases with increasing sulphate ion content [39]. The results of Toivonen *et al.* [28] are in agreement with the results on the decreasing influence of sulphate additions on the corrosion potentials of Ni-based materials. Davis and Indig [23] have attributed the decrease in corrosion potential either to changes in solution pH or to active corrosion, i.e. activation of the passive film on the specimen surface. Itow *et al.* [32] have explained by means of the mixed-potential theory the experimental findings about the decreasing effect of impurities on the corrosion potential of stainless steel AISI 304. They based their explanation on the observations of the increasing effect of sulphate ions on the current density of AISI 304 and of the decrease of the transition potential in the passive-to-transpassive region. The observation of the decrease in the corrosion potential may prove to be useful when explaining the effect of impurities on crack growth rates.

Contrary to the results discussed above, McMinn and Page [40] have observed that the presence of 1000 ppb sulphate ions (added as H₂SO₄), simulating a resin intrusion environment, leads to a potential shift of ca. 160 mV in the positive direction for Inconel alloys 600 and 690, Type 316 NG stainless steel, A508 carbon steel weldments made with commercial Inconel alloys 82, 182 and 72 and experimental alloys R-127 and R-135. It is worth noting that this level of sulphate content is considerably higher than in tests discussed in the above paragraph. The observed shift of potentials in the positive direction in the presence of this high contents of H₂SO₄ may be attributed to a decrease in pH and its subsequent effect on equilibrium potentials. Such high amounts of sulphate ions are not anymore relevant with the resin intrusions in BWRs nowadays. Stellwag *et al.* [41] have also reported an increase in corrosion potential of stabilised stainless steel by c. 60...150 mV and in the redox potential as a result of adding sulphate ions either as K₂SO₄ or as H₂SO₄. The added amount of sulphate ions in laboratory tests resulted in an increase of room-temperature conductivity by 10 μScm^{-1} and can thus be

estimated to be about 1250 ppb sulphate added as H₂SO₄. The results of Stellwag *et al.* thus correspond to the cases presented by McMinn and Page, who added relatively high contents of sulphate ions and observed an increase in the corrosion potential.

One interesting feature is that sulphate ions have been observed to enhance the rate of transpassive dissolution of chromium from stainless steels in room-temperature conditions and also at 70 °C [42, 43]. This together with the proposed connection between crack growth rate and transpassive dissolution discussed above in Chapters 4.2 and 4.3 may prove useful when assessing the reason for the influence of sulphate ions.

4.4.3 Nitrate ion as an impurity

The presence of nitric acid may be detrimental in accelerating crack nucleation, while it probably has much less effect on crack growth. This is in line with the fact that the bulk solution pH has a large effect on crack initiation, with acidic solutions greatly accelerating initiation relative to nearly-neutral or slightly alkaline solutions (see Ch. 4.4.1 above).

These statements are supported by experimental observations. Andresen [44] has shown that nitrate has no significant influence on the stress corrosion crack growth rate of sensitised type 304 stainless steel at nitrate levels ≤ 100 ppb, although large increases were observed at 10 ppm. These studies have been performed by adding nitrate both as HNO₃ and NaNO₃ at 270 and 288 °C. As already mentioned in Chapter 4.4.1 above, Ljungberg *et al.* [25, 26] have reported no influence of nitrate on crack growth rates at levels of 200 ppb, while similar levels have been observed to have an enhancing effect on crack initiation [25].

Nitrate ions have been reported to result in a decrease of the corrosion potential [23], although opposite views have also been presented [24].

4.4.4 Chromate ion as an impurity

The influence of chromate ions on crack growth rates does not seem to be entirely clarified. Chromate ions are released from stainless steels and nickel-based alloys in BWR coolants under NWC conditions because of the transpassive oxidation of the material.

Ullberg [45] has reported that the presence of 2...5 ppb chromate ions in BWR coolant raises the corrosion potential of a material corresponding to Type 304 stainless steel and

may thus cause IGSCC. However, chromate ions were observed to have less tendency to cause IGSCC in SSRT tests than for instance hydrogen peroxide at one and the same corrosion potential. Ullberg has commented that the minor effect of chromate may be due to its behaviour as an anodic inhibitor.

5. Role of crack tip chemistry in environmentally assisted cracking

5.1 Specific nature of crack tip chemistry

The chemical conditions within a stress corrosion crack may differ markedly from those in the bulk coolant, and this most probably plays an important role with regard to crack propagation. Several authors have described the physical and chemical phenomena taking place within a crack during crack growth [17, 20, 22, 34, 46, 47, 48, 49 etc.]. These phenomena lead to the establishment of special water chemistry conditions that are often identified as occluded water chemistry. Increased crack growth rates have been ascribed primarily to the occluded chemistry conditions and not to the presence of high amounts of oxygen or high corrosion potential within a crack [17].

Two main processes in the establishment of special crack tip conditions are the formation of oxygen-free regions and the oxidation of the metal at the crack tip. The former is due to consumption of oxygen in cathodic reactions and the mass transfer limitations preventing additional oxygen from entering the crack. The latter is a result of exposure of bare metal surface or of non-protective oxide film to the coolant within the crack. These main processes leading to special conditions are closely similar to those discussed when modelling crevice corrosion. Modelling concepts from crevice corrosion can thus provide useful information for modelling of crack behaviour, and therefore crevice corrosion is discussed to some extent also in this report.

Obtaining information of conditions within the crack is both highly important and very difficult. Turnbull [46] has commented that the major factor hindering progress in the modelling and validation of the developed models for cracking is the difficulty to quantify the local environment and the kinetics of reaction processes at the crack tip.

The chemical conditions within a stress corrosion crack have been attempted to assess by measurements of solution chemistry in real cracks, based on micro sampling techniques [1, 50, 51], measurements of solution chemistry, pH and/or potential in artificial or simulated cracks or crevices [52, 53, 54, 55, 56, 57, 58, 59, 60] and mathematical modelling of the reactions and transport phenomena within cracks or crevices [60, 61, 62, 63, 64]. Recent attempts to study the influence of potential within the crack have been based on micro-polarisation of the crack tip and micro-reference electrodes [1].

The following Chapter 5.2 describes the current understanding of the conditions that may exist within a crack and how these conditions are created. We also describe how the conditions prevailing within a crack influence the behaviour of anionic impurities in

the system, while in Chapter 5.3 we discuss the relevance of crack tip chemistry in proposed EAC mechanisms.

5.2 Description of crack tip conditions and their establishment

The establishment of special crack tip conditions can be ascribed to local deficiency in oxygen and to metal oxidation within the crack, as already mentioned above. This Chapter 5.2 aims at describing how and why these factors lead to the formation of special crack chemistry conditions. We have based our discussion on recent presentations of e.g. by Andresen [17], Engelhardt *et al.* [65] Walton *et al.* [66] (for crevices, aiming at generality), Turnbull [46] and Ferreira and Li [47] etc.

5.2.1 Concept of differential aeration

The basic ideas about the establishment of crevice or crack conditions have been presented a long time ago when the macro cell concept has been introduced [54, 67]. The oxygen/alloy macroscopic electrochemical cell or "macro cell" mechanism can be described as follows: The cell requires one portion of a corrodible structure to be exposed to an electrolyte containing dissolved oxygen, and another portion exposed to oxygen depleted electrolyte. The path between these two regions of electrolyte must provide sufficient resistance to diffusion to prevent significant transport of oxygen from one region to the other. A further requirement is that the metal exhibits some degree of passivation when exposed to the oxygenated environment. This is associated with an electrode potential more positive than in the oxygen depleted region. Under these conditions, oxygen may be reduced at the passive surface, and the metal may be oxidised in the low-oxygen region.

The assumption that the anodic and the cathodic reactions during cracking are spatially separated, i.e. that the cathodic reaction occurs at the outer surface when the anodic reaction occurs within a crack, crevice or pit, and vice versa, has been widely used in early models for cracking and pitting processes. Ateya and Pickering [64] have described how this general belief evolved and that well-separated anodic and cathodic reactions is only a limiting case which is encountered in early stages of crack growth. The general case for base metals has been described to involve distributions of both the anodic and cathodic (hydrogen evolution) reactions, with various intensities at different locations on the internal surfaces of the cracks, along with the reduction of an oxidant at the outer surface for the special case of a freely corroding metal. This kind of distribution of reactions is a result of the potential distribution down the crack (see

below) and the polarisation characteristics of the particular system. At a later stage of cracking, both the anodic and cathodic reactions may occur simultaneously at the same place and at the same rate deep within the crack. This is the other limiting case.

It is worth noting that the cathodic partial reactions may be controlled by the electronic conductivity of the site at which they proceed. This is due to the fact that the cathodic reaction may often be the reduction of such a species in the solution, the reduction of which consumes electrons but does not require transport of ions in the oxide film. The anodic reactions leading to the formation of an oxide film may, on the other hand, depend not only on the electronic conductivity, but the ionic transport properties of the oxide film may contribute as well.

5.2.2 Gradients in oxygen content and corrosion potential

One of the main processes leading to the establishment of occluded chemistry conditions within the crack is the consumption of oxygen and other possible oxidants in the cathodic reaction at the free surface exposed to the bulk coolant as well as on the walls of the crack. Increased reaction rates due to increased water temperature result in fully consumed oxygen at the crack tip even at high oxidant concentrations in the bulk environment. The reduction of oxygen ($O_2 + 2H_2O + 4e^- = 4OH^-$) leads to an initial increase of pH also inside the crack. It also leads to the establishment of a gradient in oxygen content, i.e. differential aeration, because once consumed in corrosion reactions along the crack walls and reactions with reductants like hydrogen mass transfer limitations prevent the entrance of sufficient oxygen to compensate for the consumption [17, 68]. Accordingly, oxygen-free conditions are maintained close to the crack tip, with the steepest change in oxygen content close to the crack mouth. Turnbull [46] has estimated that oxygen is almost totally depleted in the crack already at a distance of ca. 5 % of the crack length from the crack mouth. The calculations were made for a normalised crack depth X .

The crack conditions are characterised by a decrease of the local corrosion potential, i.e. the potential difference between the equipotential metal phase and the solution, $E_{Metal} - E_{Solution}$ or ΔE_{M-S} . Throughout most of the crack, an essentially constant condition of low corrosion potential (typically -0.4 to -0.5 V vs. SHE) in BWR water exists. Thus the difference between the corrosion potentials outside and inside the crack may reach values as high as 500...700 mV, or even 1000 mV [4, 17, 22, 46], depending on the external corrosion potential in BWR water. This kind of potential distribution favours cathodic reactions close to the crack tip and anodic reactions close to the crack mouth. It also leads to a transport of negative ions towards the crack tip. According to Turnbull [46], the potential drop between the bulk coolant and the crack tip has two components:

the drop in the crack and that outside the crack. The latter is significant at high positive corrosion potentials.

Abdulsalam and Pickering [69 and references therein], Wang *et al.* [70] and Cho *et al.* [71] have emphasised the contribution of IR drop in the establishment of a potential difference between the tip and the mouth of a crack or crevice. It seems natural that whenever an oxidation reaction of the crack tip region proceeds and the current passes through the poorly conductive water within the crack, a potential gradient due to IR loss should be present. Due to this IR drop, the potential difference $E_{\text{Metal}}-E_{\text{Solution}}$ or $\Delta E_{\text{M-S}}$ between the metal phase and the solution must be smaller at the crack tip than at the crack mouth. The above authors have performed their experiments using an artificial crack in e.g. Ni in 0.5 M H_2SO_4 . Experiments have shown that the magnitude of the potential drop and the distance into crevice of the passive-to-active transition both increase linearly with increasing applied potential under conditions of constant pH and anion concentration with crack depth.

According to Andresen and Ford [68], the greatly accelerated intergranular crack growth rates observed in tests performed in several laboratories in hydrogen de-aerated water with the addition of ≥ 1 ppm H_2SO_4 show that the potential gradient per se is not the fundamental factor to the crack advance. Their conclusion was based on the assumption that no potential gradient is established along the crack in such de-aerated conditions. Thus they seem to attribute the existence of a potential drop within the crack solely to a possible gradient in oxygen content. However, as indicated above, a potential difference between the crack tip and crack mouth may also be established because of the IR drop in the crack due to the oxidation current passing through the crack. It does not thus seem self-evident to us that de-aeration with hydrogen leads to a total absence of potential gradients.

5.2.3 Metal oxidation and subsequent changes in pH

The exposure of bare metal surface to the coolant within the crack leads to the oxidation of the metal. The metal is dissolved and/or transformed to an oxide film. The dissolution of metal may lead to significant changes in the pH of the crack tip environment.

Metal dissolution and further hydrolysis (e.g. $\text{Me} = \text{Me}^{2+} + 2\text{e}^-$; $\text{Me}^{2+} + \text{H}_2\text{O} = \text{MeOH}^+ + \text{H}^+$, see also Ref. 46) may lead to an acidification of the coolant close to the crack tip, i.e. to a decrease of pH, if impurity anions are available to compensate for the positive charge of the H^+ ions [17, 68]. Impurity anions may originate from the bulk coolant or, alternatively, anions such as S^{2-} can be dissolved from the base metal (see e.g. Refs 52 and 54). In the presence of anionic impurities, the acidification due to hydrolysis of

metal ions is likely to compensate and dominate over the increase in pH due to the reduction of oxygen. The latter takes place in the initial stage while the former takes place during the whole crack growth process. To give an idea of the possible magnitude of pH change, the presence of 0.2 M Na₂SO₄ in artificial crevices with inner diameter of 1 mm prior to testing in 288 °C deaerated water has been found to result in a decrease in the high temperature pH from about 8 to 2.5 [17]. Andresen has however commented that under relevant BWR conditions pH shifts of < 2 can be expected [17].

The development of acidic conditions at the crack tip in the presence of anionic impurities in the bulk coolant may have a profound influence on the composition and properties of the oxide films on crack walls or on the reaction equilibria and reaction kinetics within the crack.

Andresen [17] has pointed out that improved coolant clean-up systems may lead to very low impurity contents and further to alkaline conditions at the crack tip instead of acidification. The generation of highly alkaline conditions is, however, not possible, because it would require the enrichment of metal cations in the crack to compensate for the negative OH⁻ ions. An increase of pH, however, leads to the stability of oxyanions such as HNiO₂⁻ and HFeO₂⁻ instead of the cation form, which prevents further alkalisation [54].

5.2.4 Enrichment of anions in the crack

5.2.4.1 Extent of enrichment

Previous chapters have demonstrated how and why crack tip chemistry is characterised by low local corrosion potential and in most cases by low pH, which increase more or less abruptly when approaching the crack mouth. The potential gradient can act as an “ion pump” moving impurity anions into the crack. Thus even small concentrations of impurities such as SO₄²⁻ and NO₃⁻ ions in otherwise pure bulk coolant may influence strongly the conditions inside the crack and lead to large changes in the cracking behaviour in BWR conditions. [17, 68, 72, 73, 74 etc.].

The anion concentration in the crack has been reported to be roughly 100 times higher than in the bulk coolant [2, 68, 75, 76]. Balachov *et al.* [75] have estimated enrichment factors that may reach values of 300. Andresen and Ford [68] have regarded the possibility of higher enrichment factors as extremely remote. This is supported by the results of Andresen and Young [50], according to which the largest enhancements in environmental crack growth rates for ASTM A533(B) low-alloy steel in simulated BWR coolant with high oxygen contents (10 ppm oxygen; E_{corr} = 100 mV) are

connected with an increase of crack tip sulphur content above 0.5 ppm as S or HS⁻, or above 1.5 ppm as SO₄²⁻. At lower oxygen contents (0 ppb, E_{corr} = -500 mv), the enrichment of sulphur in the crack tip region was much lower (about 5 % of the value at high oxygen contents), and the crack growth rates were low.

The enrichment factors discussed above for anions inside a stress corrosion crack are considerably lower than those reported for crevice corrosion. In crevice corrosion, the solute concentration may increase proportionally with time and heat flux [77, 78], which is a clear difference when compared to SC crack. It seems to remain a bit unclear, how well the theories developed for enrichment in crevices can be compared with to those developed for enrichment in cracks. Despite close similarities, also marked differences between the two phenomena exist: In the latter, the material to solute ratio is much smaller than in the former, in the latter stress are present, in the former heat transfer is often present, etc.

Enrichment factors as low as 100 in stress corrosion cracks have been strongly criticised by Macdonald [74], who claims that even factors as high as 10³...10⁶ should be possible. He has noticed that as Andresen and Ford presented the value of ca. 100 as widely acknowledged, they referred to their own work. Macdonald has also emphasised that enrichment factors determined under fatigue loading conditions, in which convective mixing of the internal and external solutions is significant, are likely to differ a lot from those determined in stress corrosion cracking tests in which the crack enclave is quiescent.

Andresen [73] has presented an illustrative picture of the interrelationships between crack tip chemistry and other contributing parameters in crack growth (see Fig. 4). His scheme can in principle be used to assess the anion contents within the crack when the bulk content and the potential difference between the crack tip and crack mouth are known. Unfortunately, we have not been able to find a complete description of the data used to construct the scheme shown in Fig. 4.

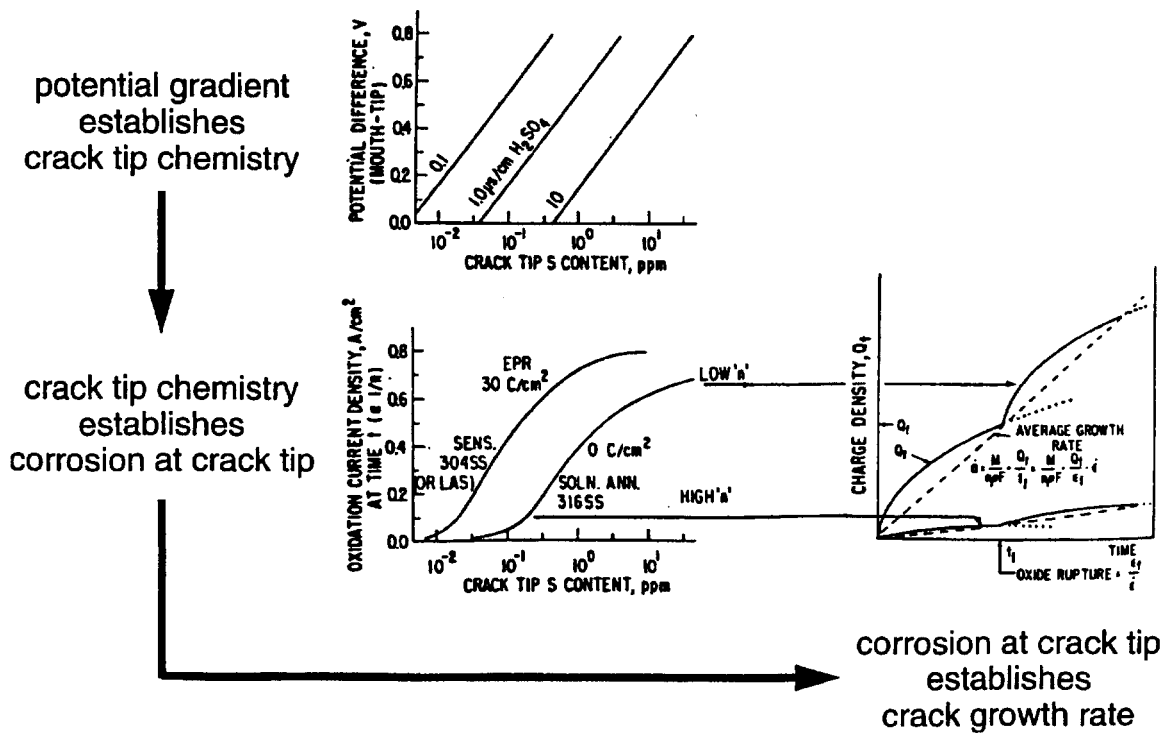


Figure 4. A sketch of the correlation between crack tip solution and material chemistries in determining the crack growth rate [15].

5.2.4.2 Metal as a source of impurities

Metallurgical impurities in the form of sulphides and grain boundary segregants may also contribute to the crack tip chemistry [50, 51, 68, 79]. This is, however, more relevant when discussing the behaviour of low alloy steels used e.g. as pressure vessel steels. Andresen and Young [50] have for instance detected intensive enrichment of sulphur inside a crack in ASTM A533(B) low alloy steel with 0.013 % S in pure simulated BWR coolant. Hänninen *et al.* [51] have on the other hand shown that the dissolution of MnS inclusions from low-alloy steels results in sulphur levels up to 6000 ppb inside cracks simulated by miniature autoclaves. Ljungberg *et al.* [80] have concluded that sulphur originating from the bulk coolant and sulphur originating from the dendrite boundaries of the material would result in the same sulphur species within the crack, which would explain their similar effect on crack propagation. The behaviour of sulphur originating from a low-alloy steel in high-temperature conditions has been discussed in more detail by Moshier and James [81], while Brossia and Kelly [3] have discussed similar phenomena in the case of Type 304 stainless steel in room temperature conditions.

5.2.4.3 Delays in the enrichment behaviour

One interesting feature of the enrichment of anions within a crack is that certain kinds of delays or memory effects exist. This means that if anions are introduced, they tend to remain in the crack for long periods after stopping the addition of the impurity and the bulk water having become clean. Based on the information surveyed and reported in Refs 2 and 38, crack growth rates remain at a higher level for at least 100...300 hours or even longer after the intrusions. Lidar [38] has even reported that the crack growth rate has remained permanently higher and has thus not returned back to the level prevailing prior to transients to high impurity and corrosion potential levels in most laboratory measurements. The deconcentration of impurities is thus much slower than their concentration in normal water chemistry (NWC) environments that has been reported to last for 10...30 hours. [2].

This large difference in the concentration and deconcentration rates must be at least partly due to the existence of a steady-state potential profile along the crack, decelerating the transport of enriched anions away from the crack. It has actually been shown [17] that the recovery back to slow crack growth rates is much faster, if the transient causing an increase in crack growth rates has included both an increase in the anionic impurity level and an increase in potential. If on the other hand a transient only in impurity levels at high corrosion potential conditions is considered, the recovery is much slower, because no change in the potential gradient established within the crack and attracting anions towards the crack tip takes place. By reducing the gradient of the potential of the solution within the crack, i.e., reducing the potential difference between the crack tip and the crack mouth, the recovery can obviously be made faster [2]. This can be done, e.g., by introducing hydrogen in the water environment (HWC). Shinohara *et al.* [82] have determined that the transient times of ion transport are extremely low in a crevice with a very dilute bulk solution. This suggests that the transient times must be low also in a stress corrosion crack, which seems to correlate with the slow changes in crack growth rates with changing bulk environment in BWR conditions. Yet another reason for the slow recovery may be the precipitation of the reduction products of sulphate ions or other anions on the crack walls, retarding the sulphur within the crack.

5.3 Mechanistic interpretations for the role of crack tip chemistry in environmentally assisted cracking

5.3.1 General considerations

The purpose of this chapter is to discuss how the special crack tip chemistry conditions, i.e. the occluded chemistry, may influence the electrochemical and chemical reactions

associated with crack growth. As illustrated in Fig. 1 in Ch. 1, the influence of anions can take place via the solution or via an effect on the composition and properties of the oxide films on crack walls. The influence of crack tip conditions can thus be discussed from different viewpoints:

- Enrichment of anions leads to changes in the conductivity of the coolant within the crack, which in turn may affect the magnitude of the IR drop in the solution within the crack.
- Changes in the chemical environment and pH lead to changes in the reaction and dissolution equilibria and reaction kinetics within the crack.
- The enrichment of oxidising anionic impurities such as SO_4^{2-} , NO_3^- and CrO_4^- may lead to increased oxidation of the material within the crack.
- The changes in the environment and possible adsorption or incorporation of impurities may have a strong influence on the protective properties of the oxide films on the crack walls.

The first three items are briefly addressed in this chapter, while the fourth item is a subject for the Chapter 7 below.

5.3.2 On the behaviour of specific anions

As commented above in Chapter 4.4.2, sulphate has been stated to exist mainly in the form of hydrogen sulphate, HSO_4^{2-} , and only to a small degree as SO_4^{2-} in bulk water at temperatures close to 300 °C [22, 36]. The low corrosion potential and pH values prevailing at the crack tip may lead to the reduction of sulphate ions to polysulphides, thiosulphates and sulphides [4, 22], which may have a large impact on the influence of sulphur species in the crack. If H_2S and HS^- ions are present within the crack, they may, according to the review of Hänninen *et al.* [83], for instance enhance hydrogen adsorption and increase anodic dissolution of the steel. Ljungberg *et al.* [25] have proposed that the formation of sulphides within the crack may lead to an increase of the potential drop along the crack. The kinetics of the reduction reactions of sulphates are, however, not exactly known, and therefore no final conclusions can be drawn about the form of sulphur species in the crack.

Nitrate ions within the crack have been predicted to be reduced to ammonium ions resulting in an alkaline environment [17, 25, 44]. Thus the enrichment of nitrate species in the crack is unlikely. The alkalisation, which when coupled with the importance and

characteristics of metal oxide solubility in high temperature water, has been explained to be responsible for the much lower sensitivity of SCC to nitrate than e.g. to sulphate or chloride ions [44]. Another mechanistic reason to the minor effect of nitrate ions on crack growth may be that after being reduced to ammonium ions, the nitrate-containing species are pushed out of the crack by the potential gradient [1].

The minor effect of CrO_4^{2-} ions to crack growth rates has been attributed to their reduction to Cr_2O_3 , preventing the enrichment of Cr-containing species in the water phase inside the crack [1]. Even when not enriched in the crack but when present only in the bulk coolant, CrO_4^{2-} ions may influence the establishment of crack tip conditions indirectly. As a strong oxidant they may increase the corrosion potential of the material and thus lead to a higher potential difference between the crack mouth and the crack tip, and subsequently to an increased risk for crack growth.

The fact that sulphate ions have a more significant long-term effect on crack growth than chromate and nitrate ions may indicate that the major influence of sulphate ions comes from some partly irreversible effect on the crack walls (see Chapter 7 below). Another possible explanation to the significant influence of sulphate ions is that their reduction products remain in the crack solution unlike the reduction products of chromate and nitrate ions (see above). When remaining in the solution, the ions may increase the solubility of metal via complexation reactions. They also change the conductivity of the solution within the crack.

Although chromate and nitrate ions have been reported not to have a significant influence on crack growth (see above, Ch. 4.4), we think that the contribution and impact of their reduction to Cr_2O_3 and NH_4^+ in the crack should be evaluated, because the reduction must be associated with some oxidation in the system. Similar oxidation reactions of the metal are associated with and may play a role in the presence of sulphate ions, if they are reduced to HS^- or S^{2-} ions in the crack.

The following chapter (5.3.3) is devoted to the role of crack tip chemistry in the slip-oxidation model, while comments related to the other models are summarised in Chapter 5.3.4.

5.3.3 Role of crack tip chemistry in the slip-oxidation model

The influence of anionic impurities on crack growth rates has been explained on the basis of the slip-oxidation model [2, 16, 20, 84] under the assumption that crack growth is controlled by mass transport within the crack. The complexing effect of impurities and their influence on pH may lead to a considerable change in the concentrations of

dissolved metal ions and thus also to changed mass transport conditions within the crack. It may thus seem natural that the impurities have a direct influence on cracking. Andresen [20] has pointed out that for instance the change in the solubility of iron, nickel and chromium oxides is 100...1000 fold per unit change in pH in either direction. Increased concentrations may influence the mass transport via diffusion, migration and convection.

Impurities also increase the conductivity of the solution within the crack and thus decrease the IR drop in the solution down the crack. Thereby they may alter the crack tip potential in the positive direction, leading to increased dissolution rates of e.g. Cr-depleted regions at grain boundaries and thus to higher crack propagation rates, or alternatively to a more rapid formation of a passive layer. However, if the conductivity per se is important, different impurities leading to the same conductivity levels should have quantitatively similar effects. In addition, an increase in conductivity via impurities and via changing temperature should lead to the same increase in crack growth rates. Neither of these has been observed in practice, and it is therefore much more likely that the major effect of anions comes from their influence on metal solubility via pH and complexation. [16, 84].

5.3.4 Role of crack tip chemistry in other models for EAC

The crack tip chemistry has a more or less direct effect on the phenomena contributing to crack growth rates also in several other models, as summarised below:

- The crack tip chemistry influences the (mainly) anodic reactions on the crack walls according to Coupled environment fracture model (CEFM). However, according to CEFM, the anodic reactions do not entirely control the crack growth.
- It influences the surfaces that play an important role in the enhanced surface mobility theory of Galvele.
- It leads to potential changes that may be relevant when considering the internal oxidation model that is favoured when the corrosion potentials are close to the oxidation potential of the solvent metal.
- It influences the oxide films that play an important role in the selective dissolution – vacancy creep (SDVC) model.
- The same is true for the film-induced cleavage model.

- It influences the cathodic reaction of hydrogen evolution that is important in models based on hydrogen induced cracking.

The slip-oxidation model seems, however, to be the only model in which a direct correlation to the rate-controlling step has been made.

The apparently important role of oxide films within the crack is discussed in more detail in Chapter 7 below.

6. Role of oxide films on the free surface in environmentally assisted cracking

It has become evident in the preceding chapters that the role of oxide films formed on material surfaces in controlling the rate of crack growth in EAC deserves careful considerations. This chapter presents available information and views on the correlations between cracking behaviour and the role and properties of oxide films exposed to the bulk coolant.

It may be useful to remember that the oxide films on surfaces exposed to the oxidising bulk coolant, i.e. on the free surfaces, and the films on the crack wall surface differ markedly from each other in BWR conditions under NWC. The films exposed to the bulk coolant in BWR conditions under HWC or to the bulk coolant in PWR conditions do not, on the other hand, exhibit such differences because of the reducing conditions prevailing both inside and outside the crack. Thus the observations about the properties of oxide films on the free surfaces in HWC/BWR and about those in PWR conditions may be directly applicable to draw conclusion about film behaviour in the de-aerated conditions inside a crack.

6.1 Description of the oxide film formed on Fe- and Ni-based materials in BWR conditions

The primary system surfaces exposed to the bulk coolant in BWR conditions are normally protected by a thin passive oxide film. The thickness of the film may vary between tens of nanometers to a few micrometers.

The film formed on stainless steel in BWR conditions can be suggested to be composed of spinel phases [22, 85], although no direct experimental evidence for thin barrier films formed in high-temperatures aqueous conditions exists. In the film formed on stainless steel under normal water chemistry (NWC), a chromite (FeCr_2O_4) or a chromium oxide (Cr_2O_3) layer may be assumed to be situated closest to the metal, while a layer of nickel ferrite ($\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$, $0 \leq x \leq 1$, “trevorite”) may be formed upon it. The interface between these two layers is not sharp. On top of these inner, compact layers, a deposited layer containing hematite in NWC conditions and a mixed spinel in HWC conditions is normally found. Kumai and Devine [86] have detected the presence of $\gamma\text{-Fe}_2\text{O}_3$ in addition to hematite ($\alpha\text{-Fe}_2\text{O}_3$) on steels and observed that the amount of $\gamma\text{-Fe}_2\text{O}_3$ increases with increasing Cr content of the steel. They have also considered the possibility that $\gamma\text{-Fe}_2\text{O}_3$ may contain some Cr, and accordingly they have used a more general designation $\gamma\text{-M}_2\text{O}_3$.

The film structure has been discussed also in Refs 87, 88, and it is illustrated in the sketches of Fig. 5.

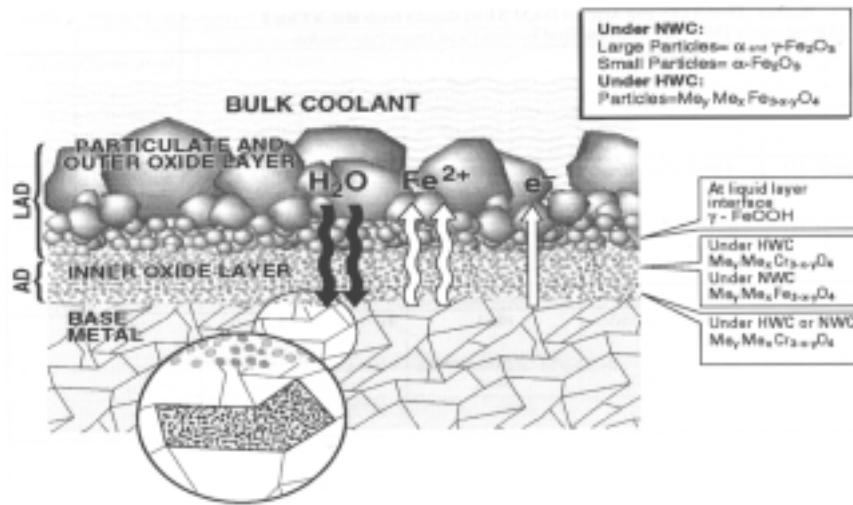


Figure 5. A schematic drawing of the structure of the oxide film formed on the surface of stainless steel exposed to BWR conditions both under normal (NWC) and hydrogen water chemistry (HWC).

The deposited part is not the only one that contains pores and cracks, because in particular the compact trevorite layer is likely to contain cracks and micropores, resulting in a high surface area and paths for easy transport of ions. It might actually be more correct to describe the film as consisting of three parts: a compact part, a cracked part and a deposited, porous part. A detailed description of each of these parts is further complicated by the enrichment of minor alloying elements on oxide grain boundaries, variations in the grain size of the oxide etc. It is very likely that any deviations from ideal homogeneous structure influence the transport rate of ions and ionic defects as well as the electronic conductivity of the film, which in turn influences the behaviour of the film as a cathodic or also as an anodic reaction site.

Based on the analytical electron microscopic (AEM) work and ESCA/Auger analysis of Fish *et al.* [89], the films formed on Ni-based alloys in de-aerated high-temperature aqueous environments are composed of an inner layer of Cr-rich spinel (Fe,Ni)Cr₂O₄ and hexagonal Cr₂O₃ type oxide with Fe and Ni, and an outer layer of (Ni,Fe,Cr) spinel with blocky precipitates of NiFe₂O₄ and NiO. The observation made on Inconel alloy 600 and X-750 were relatively similar. It has to be emphasised that the applicability of the results of Fish *et al.* to BWR environments is subject to some uncertainty.

6.2 Observed correlations between the oxide film on the free surface and cracking

This chapter summarises observations about the possible changes in oxide films on the free surfaces, associated with increased cracking susceptibility. The possible mechanistic interpretations are in turn discussed in Chapter 6.3.

Stahle *et al.* [90] have commented that stress corrosion cracking of steels occurs in such ranges of potential in which the protective film is still protective but marginally unstable. This marginal instability can probably be correlated with the formation of apparently mixed compound surface layers, e.g. $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ on ASTM A533B steel [91] or with the stoichiometric composition of the film on Type 304 stainless steel in oxygen contents leading to high IGSCC risk [92]. Another feature related to the marginal instability is that the occurrence of SCC coincides with the release of chromium via transpassive dissolution from such materials as Type 304 stainless steel [93]. This may lead to subsequent preferential dissolution of grain boundaries. This coincidence has been observed and commented also by Zheng and Bogaerts [94] in the case of cracking of stainless steel in a caustic solution and by Bogaerts and Bettendorf [9] when discussing IGSCC in high-temperature water.

Other observed correlations between the properties of film on the free surfaces and cracking behaviour can be found in the papers by Cubicciotti and Ljungberg [95], Cubicciotti [96] and Congleton and Yang [97]:

Cubicciotti and Ljungberg [95] have reported on the basis of a calculated potential-pH diagram for the Cr-H₂O system with Fe that above the threshold potential where IGSCC mainly occurs, the stable phase is Cr_2O_3 , while below the critical potential the stable phase is FeCr_2O_4 . This suggests that Cr_2O_3 is not protective against IGSCC. In a more recent paper Cubicciotti [96] has reported calculations which showed that a FeCr_2O_4 spinel is formed in BWRs under HWC but not under NWC conditions. In the latter case Fe_2O_3 is formed. The change of stability from Fe_2O_3 to FeCr_2O_4 occurs at the same threshold potential (about -0.2 V vs. SHE) as that at which intergranular stress corrosion cracking rates have been observed to decrease rapidly (see Ch. 4.3). Accordingly, the mitigation of IGSCC risks in plant applying HWC was attributed to the presence of the FeCr_2O_4 spinel.

Congleton and Yang [97] have performed a comprehensive study on the stress corrosion cracking behaviour of sensitised AISI 316 stainless steel in high temperature low oxygen (below 5 ppb) water containing 5 ppm chloride over a temperature range 100...300 °C using SSRT tests, polarisation curves and Auger electron spectroscopy (AES). They have observed SCC in a wide potential range, with an increasing

contribution of intergranular cracking with increasing potential. They commented that a higher susceptibility to SCC correlates with a higher thickness of the oxide, which they attributed to the easier rupture of thicker films. The authors also concluded that the mechanical properties of the surface oxide films are likely to be more important than their chemical properties for crack initiation and propagation during SSRTs. However, a higher susceptibility to SCC was also found to correlate inversely with the increasing concentration of Ni in the surface film, i.e. the chemical composition of the film.

Concerning cracking of Inconel alloy 600, Rebak and Szklarska-Smialowska [98] have pointed out that IGSCC of Inconel alloy 600 in PWR water occurs only when a NiO film is formed during a corrosion process and exists on the metal surface. A high hydrogen content may reduce NiO to Ni and thus decrease the risk for IGSCC. This agrees well with the observations made by Lagerström *et al.* [48], according to which the crack growth rate of Inconel alloy 600 seems to increase with increasing resistance of the surface film formed on the metal. The increase of the resistance can be attributed to a greater amount of NiO at the cost of metallic nickel. The presence of a higher amount of NiO is also likely to lead to a higher number of cation vacancies in the film, which may be a possible explanation to the observed behaviour. Caron *et al.* [99] have on the other hand reported that the crack growth rate in Inconel alloy 600 is almost nil when a Cr-rich film is present and very low when a NiO rich surface film is formed, while the formation of a mixed Ni-Cr oxide leads to a maximum crack growth rate. The observations of Staehle *et al.* [90] give further support to the important role of NiO in the IGSCC behaviour of Inconel alloy 600: they found out that pure nickel is a good model material for studying the SCC of this alloy. The kinetics, extent, and aggravation of grain boundary reactivity related to the sulphur segregation was observed to be the same for pure Ni as for Inconel alloy 600.

Lumsden [92] has reported that in conditions where the stress corrosion cracking risk of Inconel alloy 600 in the presence of thiosulphate ions increases, sulfide is formed in the passive film. He concluded that the formation of sulphide makes the film less protective, which could possibly explain the increased risk for IGSCC.

6.3 Mechanistic interpretations on the role of oxide films on the free surface

The oxide films on the free surface exposed to the bulk coolant may influence either crack initiation or the cathodic reactions taking place on the external surface during crack growth. The influence of oxide films can in principle be based on the electronic, structural and/or mechanical properties or on the permeability and geometry of the film. [16, 22 etc.]

An increase of the electronic resistance of the film may inhibit the cathodic half reaction on the surfaces external to the crack [95, 96]. This reaction is assumed to limit the rate of anodic reactions within the crack and thus to control partly the crack growth rate according to the CEFM model. The observations reported in the previous chapter about such changes in film structure that can be associated with increased cracking susceptibility are mainly associated with increase of the electronic resistance of the film [100]. This suggests that the rate of cracking is not controlled by the cathodic reaction on the external surface.

The mechanical properties of the external oxide films are likely to play a more significant role in crack initiation than in crack propagation. According to Rebak and Szklarska-Smialowska [101], the first step in the nucleation of a crack is the formation of a defect or flaw on the filmed alloy surface. One possible reason for the formation of this defect is the mechanical breakdown of the film due to vacancy accumulation. According to the film-induced cleavage mechanism, a thick or a mechanically hard film may in turn lead to a secondary crack nucleation and brittle fracture [102, 103]. Factors of importance which control the effectiveness of the oxide in initiating the cleavage event include the oxide-matrix misfit, the strength of bonding across the oxide-matrix interface and the oxide thickness and ductility. Turnbull [104] has commented that unlike in the slip-oxidation model there is no continued requirement in the cleavage mechanism to rupture the film and expose bare metal to be dissolved by crack tip straining once cracking has been initiated since it is the film which induces the cracking.

One possible way how the external oxide film may influence cracking is the release of such products from the film that may become enriched in the crack and thus have a detrimental effect on cracking. One theoretically possible candidate is chromate anion released during transpassive oxidation of the surface exposed to the bulk coolant (see discussions above in Ch. 4.4).

6.4 Specific role of oxide films close to the crack mouth

Hermansson *et al.* [22, 34] have distinguished the oxide surface exposed to the bulk coolant in the close vicinity of the crack from the surface further away from the crack when discussing the effect of sulphate ions on cracking. Because of the preliminary and speculative nature of their discussion, we give only a short summary of it for the sake of documentation.

Hermansson *et al.* [22] have proposed that the oxide close to the crack acts as a cathode on which pH and also the potential are higher than on the surrounding surfaces. They presented the hypothesis that the crack growth rate is controlled by the cathodic

processes on this oxide surface close to the crack mouth. They accordingly suggested that the rate-limiting step of crack growth might be adsorption, transport, chemical transformation or precipitation in which hydrogen sulphate and/or sulphate ions take part. The formation of hydrogen sulphate may in turn lead to a neutralisation of the coolant close to the crack mouth. They also assumed that sulphate ions and other sulphur-containing species influence the permeability, geometry, growth and extension of the cathodic oxide surface exposed to the bulk coolant.

Hermansson *et al.* explained that bulk anions are transported to the surface because of the positive surface potential and that adsorption of transported anions occurs more quickly on the surfaces in the cathodic region than in the regions outside it because of the higher potential. They also suggested that SO_4^{2-} can be expected to be more strongly adsorbed than HSO_4^- because of its higher charge and because its concentration is higher close to the cathodic region due to the higher pH. This may lead also to migration of adsorbed anions towards the cathodic region. This was used as an explanation for the retaining of sulphate ions close to the crack opening and thus for the "memory effect". As mentioned above in Ch. 4.4.1, their definition for the memory effect is slightly different from the more common one. They defined it as the number of exposures needed before sulphate affects the crack propagation rate, and that the rate increases with the number of exposures.

7. Role of oxide films formed on crack wall surfaces in environmentally assisted cracking

This chapter summarises observations, views and theories on the properties of oxide films within the crack and their role in environmentally assisted cracking. We have already discussed above that the establishment of crack tip chemistry influences not only the conductivity and pH of the water in the crack but also the reactions, their equilibria and rates within the crack, as well as the oxide films on crack wall surfaces (see also Fig. 1). During the discussion below, it is worth bearing in mind that the properties of oxide films formed on Fe- and Ni-based materials in high-temperature electrolytes differ markedly from those formed in room-temperature conditions. Profound changes take place in oxide films when increasing the temperature above 150 °C [105, 106], and understanding these changes may help to understand the effect of oxide films on crack wall surfaces on EAC.

As in the case of oxide films on the free surfaces exposed to the bulk coolant, the influence of oxide films on crack wall surfaces on EAC may be based on changes in their electronic, structural and/or mechanical properties or on the permeability and geometry of the film [16, 22 etc.]. These changes may be caused by:

- Oxidation due to the enrichment of oxidising anionic impurities such as SO_4^{2-} , NO_3^- and CrO_4^{2-} .
- Adsorption and incorporation of anionic impurities on and in the oxide surfaces.
- Change of reaction and dissolution equilibria due to changes in pH and potential.
- Change of reaction rates due to changes in pH and potential.

We focus in this chapter on the description of the special nature of the films on crack wall surfaces, i.e. inside the crack, on their role in different proposed EAC mechanisms and on the influence of enriched anionic impurities on these films.

7.1 Description of the oxide films on crack wall surfaces in BWR conditions

The gradient in the corrosion potential and pH inside a crack formed in stainless steel or Ni-based materials in BWR conditions under NWC is accompanied by a gradient in the thickness and composition of the oxide film on crack wall surfaces. Variations in oxide film composition along the crack may also be caused by differences in composition

between grain boundaries and the bulk alloy, and by re-precipitation of metal ions that exceed the solubility of the solution at the crack tip (see e.g. Ref. 89).

The gradual change in the structure of the oxide film in stress corrosion cracks formed in AISI 304 stainless steel exposed to BWR coolant has been described as follows [107 and references therein]: The film near the crack mouth is similar to that on the bulk surface exposed to oxidising coolant. In other words, it is a duplex film, the outer layer of which is composed of closely packed crystallites of a ferrite in addition to Fe_2O_3 particles. The inner layer is apparently a spinel oxide. Deeper inside the crack, a single-layer compact film is present with large ferrite crystals (10...50 μm across). Very few Fe_2O_3 particles are found near or at the crack tip. The single-layer film is an Fe-Ni oxide with varying amount of Cr, depending on the distance away from the crack mouth. The crack mouth region is depleted of chromium, whereas the crack tip region contains up to 15% chromium. Accordingly, also the formation of Cr_2O_3 close to the crack tip is possible. These observations are supported by the ideas presented by Segal *et al.* [108], who have concluded that the oxidation state and chromium content of the oxide film inside the crack change gradually with the distance from the crack mouth. Saito and Sakamoto [109] have reported supporting observations about the Cr content in the oxide film formed on the free surface and in artificial crevices for Type 304 stainless steel and Inconel alloy 600 at 280 °C. The low-Cr films on free surfaces were also characterised by a higher film thickness.

Recent advances in the specimen preparation techniques have enabled detailed transmission electron microscopic studies of crack tips of stress corrosion cracks [89, 110, 111, 112, 113, 114, 115, 116]. Most of the crack-tip investigations so far has been performed at the Pacific Northwest Laboratory, PNNL by Bruemmer and his co-workers. However, the data published in the open literature in on crack tip specimens from PWR environments, and the data is mainly on Inconel alloy 600 [89, 110].

Recent results, although not yet published in the open literature, exist on crack tip specimens of guide beams made of AISI 304 stainless steel removed from a clean BWR environment [113]. Thomas and Bruemmer [113] have detected intergranular cracking at a fluence level of about $5 \times 10^{20} \text{ n/cm}^2$, $E > 0.1 \text{ MeV}$ (i.e., about 1 dpa) with no grain boundary chromium depletion. They have observed that the cracks are filled with a continuous, relatively non-porous oxide film, the thickness of which may reach 100 nm. The film on the crack wall is an epitaxial Cr-Fe spinel, while the film in the center of the crack is large-grained magnetite. Thomas and Bruemmer have also observed finger-like porosity in the metal at the leading edge along the grain boundary and depletion of Cr and Fe in the metal close to the crack tip. The deformation of the matrix at the crack tip has been found to be moderate, indicating that the role of localisation of deformation would be insignificant. These observations suggest that crack growth could be

associated with some kind of a selective oxide formation reaction. They do not, on the other hand, give any support to intermittent crack growth, or, in other words, to a mechanism that requires the rupture of the film for the crack growth to proceed. Thus the slip-oxidation mechanism is not supported by the most recent observations. Thomas and Bruemmer have, however, commented that the crack tip structures may be different in irradiated and non-irradiated stainless steels. In a PWR environment, the recent results of Thomas and Bruemmer [113] on crack tip specimens taken from irradiated baffle bolts made of cold-worked 316 SS show, that the crack tip interfaces are stepped and filled with a porous film consisting of a chromium rich spinel to the very tips of the cracks. Further the crack tips are blunted. Based on the results, the authors have evaluated that the leading mechanism in BWR and PWR environment is different.

A major part of the data published in the open literature has been on crack tip specimens from PWR secondary side. One crack tip from a mill annealed AISI 316 stainless steel part has been investigated [110] after operation in deoxygenated environment at 250 °C, corresponding roughly to conditions in a steam generator of a PWR plant. However, sodium phosphate and sodium sulphite had been added to the environment. The results show that the grain boundaries are filled with oxide until the very tip of cracks. The crack flanges have been found to be covered with a layer of epitaxial FeO next to the base metal, and a porous polycrystalline spinel on top. The polycrystalline spinel has been found to be enriched in chromium together with many minor solution constituents, and depleted in nickel compared to the composition of the base metal. As the polycrystalline spinel was not present to the tip of the oxidised zone it was concluded that this oxide is formed by a solid-state process. According to Bruemmer and Thomas [110], the oxide structure on Inconel alloy 600 specimens in PWR steam generator tubes is different, as the investigations on crack flanges from intergranular attack have revealed an inner (non-protective) porous layer, while that in the case of AISI 316 stainless steel has been found to be dense and protective. The corrosion product at the attack tips is Cr₂O₃, even though the predominant oxide at some distance (>100 nm) from the tip is NiO. The presence of porous NiO on Alloy 600 grain boundary crack walls has earlier been reported by the same authors [112], but then the very narrow chromium oxide was not reported.

Fish *et al.* [89] have applied the same technique for the films formed on Inconel alloy 600 in PWR primary water conditions. They have reported that the oxide at the crack tip consist predominantly of NiO, containing some Fe and Cr. These observations seem to be in reasonable agreement with the results reported by Bruemmer and Thomas [110] for cracks formed in secondary side conditions.

The oxide films growing on stainless steel and Ni-based alloys in conditions simulating oxygen-free high-temperature BWR crack chemistry have been found to reach

unexpectedly high thickness values in the range of a few to several 100 nm [117]. This range, however, agrees relatively well with results obtained by Thomas and Bruemmer [113] for a crack grown in a 304 SS sample in BWR conditions and with the results of Schneider *et al.* in oxygen-free borate buffer electrolytes [118], although the latter cannot be considered to correspond directly to conditions within a BWR crack.

7.2 Oxide films as sites for anodic and cathodic reactions

Concerning the transport properties of the films on the crack wall surfaces within a crack, both electronic and ionic conductivity are of interest, because both anodic and cathodic reactions take place within the crack. The electronic properties of the films within a crack are likely to be associated with the cathodic partial reaction that is most likely a reduction of a species in the solution. On the other hand, the protectiveness of the film (i.e. ionic transport properties of the film) is likely to be associated with the anodic oxide growth, because the growth requires transport of species through the oxide film. This is in contrast to the oxide films exposed to the bulk coolant, on which most probably cathodic reduction reactions of a species in the solution dominate. Therefore, the electronic transport properties of the films on the free surfaces are likely to play an important role. In addition, anodic reactions such as the transpassive dissolution of Cr as chromate may proceed at this external surface.

7.3 Mechanistic interpretations on the role of the oxide film on crack walls

Because the composition and properties of oxide films on crack wall surfaces are closely connected with the crack tip chemistry, the following discussion about the role of these films in different EAC mechanism is closely connected with the discussion presented above in Ch. 5. The different models are accordingly discussed in the same order as in Appendix A. It becomes evident below that at least the enhanced surface mobility theory of Galvele, the internal oxidation model, the selective dissolution – vacancy creep model, the film-induced cleavage model and the models based on hydrogen induced cracking are likely to involve steps the rate of which is controlled by the oxide film properties inside the crack.

The electrochemical properties of oxide films on crack walls have not been considered to play a rate-determining role in the slip-oxidation model. Their influence is included in the predictive equation given by Andresen and Ford [84] in the strain-to-fracture parameter ϵ_f . This model is to a great extent based directly or indirectly on anodic reaction processes. Once initiated, the SCC of iron- and nickel-based alloys has in the

slip-oxidation model been suggested to proceed in increments. Each increment consists of the following steps at the crack tip [72, 119, refs 11 and 12 in Ref.120]:

- a) activation, i.e. exposure of new metal surface by mechanical fracture
- b) dissolution of the active surface
- c) repassivation mechanism

The protectiveness of the oxide film on the crack walls can be correlated with the tendency of the oxide to rupture as a result of slip emergence. A mechanically weak film may lead to easier rupture of the film.

Another factor how oxide films on crack walls may contribute to cracking is the fact that the anodic and corresponding cathodic reactions within the crack proceed partly on or in the oxide films on the crack wall surfaces. The slip-oxidation model does not, however, assume that the rate-limiting process for cracking can be found in the oxide films on crack walls.

The oxide films on crack wall surfaces should not play a significant role in the cracking process according to the coupled environment fracture model (CEFM) formulated by Macdonald and Urquidi-Macdonald [121], either. This model also assumes crack advance to occur via the slip-dissolution-repassivation mechanism, but mainly the cathodic reaction is assumed to limit the rate of anodic reactions within the crack and thus to control the crack growth rate. Accordingly, the oxide films on crack walls should not limit the rate of cracking. Turnbull [46] has commented that in some cases oxides within the crack could restrict transport and in the limit prevent coupling of the crack tip with the external surface. This would however not be compatible with the observed dependence of crack growth on potential.

The properties of oxide films within a crack play an important role in the enhanced surface mobility theory of Galvele [122, 123, 124]. The theory of Galvele suggests that the properties of the oxide film on the crack walls can be correlated with the rate of surface diffusion: the surface mobility is higher on a less protective oxide. The surface mobility SCC mechanism also includes the postulate that SCC takes place by capture of surface vacancies in the metal close to the crack tip.

Concerning the internal oxidation model, the oxide films on crack walls may either prevent or facilitate the entry of oxygen to the substrate material and thus play an important role in cracking.

The oxide films on crack walls have a dominating role in the selective dissolution – vacancy creep (SDVC) model [125]. It includes the postulate that SCC takes place by the influence of vacancies in the metal close to the crack tip. The formation of these vacancies and thus also the whole cracking process has been explained to be controlled by the transport of cation vacancies through the oxide film. Interstitial cations are another possible candidate for the species to be transported through the film (see Ch. 10.5). The protectiveness, i.e. the transport properties of the oxide film should thus be directly correlated with cracking susceptibility.

The mechanical properties of the films formed inside a crack play a role in the film-induced cleavage model [102, 103], if a secondary crack nucleation and brittle fracture occurs because of the presence of hard films on crack walls. Turnbull [104] has commented that unlike the slip-oxidation model, there is no continued requirement in the cleavage mechanism to rupture the film and expose bare metal by crack tip straining once cracking has been initiated since it is the film which induces the cracking.

In the models based on hydrogen induced cracking [126, Ref. 20 in Ref. 101], the entry of hydrogen through the crack tip fracture zone plays an important role. Totsuka and Szklarska-Smialowska [127] have concluded on the basis of slow strain rate tests, voltammetric and AC impedance measurements that IGSCC of Inconel alloy 600 occurs only under such environmental conditions under which a sufficiently large amount of hydrogen is absorbed by the strained alloy. In this case the protective properties of the oxide films on the alloy surface in the sense of preventing hydrogen from entering the alloy play a significant role.

7.4 Influence of impurities on the oxide films on crack walls

Available information of the influence of impurities on oxide films on crack walls in relevant conditions is scarce. Accordingly, this chapter serves only to present some preliminary input for further studies.

7.4.1 Adsorption and incorporation of anions

The first step in the possible influence of anionic impurities on the oxide films within the crack is likely to be their adsorption on oxide surfaces. The results summarised below indicate that sulphate and also chloride species may become adsorbed and strongly incorporated into oxide films on stainless steel and nickel-based alloys, even at high temperatures.

Dumbill [111] have applied scanning transmission electron microscopy and energy dispersive analysis to investigate crack tip specimens from laboratory C(T) specimens made of sensitised AISI 304 stainless steel and tested earlier at Studsvik Nuclear for the effect of sulphate transients [38]. They have found sulphur to be incorporated into the spinel oxide on the crack wall. Sulphur has also been found to be present as nickel sulphide precipitates within the crack oxide and also ahead of the crack at the grain boundary. The storage of sulphur in the precipitates could perhaps explain the long accelerating effect of temporary sulphur spikes on the crack growth rate of stainless steels.

Andresen [16] has reported that structural and electronic changes occur in the passive film on sensitized type 304 stainless steel at temperatures in excess of 150 to 200 °C. These changes are indicated by the SIMS observations, according to which the films readily incorporate and permit diffusion of anions at temperatures above 200 °C. Depth profiling of the passive films on stainless steel has shown that sulphate and chlorides can readily penetrate into the full depth of 2...30 µm of the passive film at 288 °C, in contrast to studies performed at 100 °C. Once incorporated, the anions are not easily washed out [16].

Sawochka and Duong [128] have compared the adsorption behaviour of sulphate, chloride, potassium and sodium ions on stainless steel and Inconel alloy 600. They have observed a maximum adsorption of sulphate of approximately 350 µg/m² at a bulk water sulphate ion content of approximately 40 ppb in laboratory tests simulating neutral PWR conditions at 300 °C, contrary to the considerably lower adsorption detected for the other species. Decrease of temperature and increase of pH was found to result in less adsorption.

The room temperature investigations of Thomas *et al.* [129] in 0.01 M NaClO₄ solutions (pH ca. 5.6) have indicated that thiosulphate ions are adsorbed on type 304 stainless steel over a wide potential range, the maximum coverage being less than a monolayer. This accumulation is reversible on 316 and irreversible on 304, which may be due to Mo segregated on the surface on 316.

7.4.2 Protectiveness of the film

Several investigations point to the poorer stability and protectiveness of the film formed on the crack wall surfaces in crack tip chemistry conditions when compared to films formed on the free surfaces exposed to bulk coolant. The poor stability is in line with the tendency to incorporate impurity species discussed in the preceding chapter. Possible reasons for the poorer protectiveness may be a higher content of ionic defects,

the formation of new compounds such as sulphides in the presence of sulphate ions [4] or changes in the thickness of the film.

Based on the survey in Ref. 16, a Fe-10Cr-10Ni alloy can become passive in a pH 4 solution of H₂SO₄, but no more at pH 3. The latter pH is possible to be found in crack tip conditions. Passivity has been observed in similar tests conducted in 0.01 N Na₂SO₄ (pH = 6.5) in alloys with as little as 8 % chromium (Fe-8Cr-10Ni). The role of the passive film in providing protection from impurities has been reported to diminish at temperatures in excess of 200 °C [9, see also 4.1]).

According to Drogowska *et al.* [130], passivation of iron in sulphate solutions has been found to be highly inefficient. Their experiments in 0.1...0.5 M Na₂SO₄ and Na₂SO₄ + NaHCO₃ solutions of pH 8 at 25 and 50 °C have indicated that the surface exhibits continuous pit nucleation and repassivation, i.e., a certain instability when compared to the situation in the absence of sulphate ions. It is worth mentioning that the passivation of Fe in nearly neutral sulphate solutions is much more inefficient than in a borate buffer solution of pH 8.4 because of the enhanced dissolution of Fe in such solutions and formation of unstable salt films [131, 132]. In addition, the repassivation of Fe- and Ni-containing materials has been found to be much less efficient in the presence of low-valency sulphur species [133]. The observations of McIntyre *et al.* [134] also support the poor stability of films formed on Ni-based alloys in the presence of sulphate ions. Their electrochemical measurements have shown that the polarisation resistance of oxide-covered Inconel alloys are roughly one order of magnitude lower in the presence than in the absence of sulphate ions. The results of Shibata and Fujimoto [135] suggest on the other hand that the presence of sulphate ions may be responsible for the breakdown of the passive film on Ni-Cr alloys at temperatures above 130 °C.

Bojinov *et al.* [117] have observed that the oxide films formed on AISI 304, AISI 316 L(NG), Inconel alloy 182 and Inconel alloy 82 are considerable thinner in the presence of sulphate contents simulating crack tip conditions than in the absence of sulphate ions. The lower thickness of the film may be an explanation to a poorer protectiveness of the film. Andresen has on the other hand reported that the thickness of the oxide film on sensitized type AISI 304 stainless steel at 288 °C may increase 10 fold following a 24-hour exposure to deaerated sodium bisulphate when compared to pure water [16]. This is an indication of a dramatic influence on the properties determining film growth rate. Concerning the effect of sulphate ions on the morphology of oxide films, Bojinov *et al.* [117] have reported that needle-like crystals are formed on Fe- and Ni-based materials in de-aerated conditions containing sulphate ions. Gebert *et al.* [136] have on the other hand observed that the addition of sulphate ions to a borate buffer solution at 250 °C leads to the formation of a fine-crystalline, dense layer instead of a coarse-crystalline, porous layer.

7.4.3 Impurities from the metal

The impurities originating from the metal may also in some cases have an influence on oxide films within a crack. As discussed for instance in Chapter 5.2.4.2, certain sulphur-containing species may enter the crack from the metal. Hwang *et al.* [137] have discussed the importance of precipitated or segregated phases at the grain boundary close to the crack tip with respect to the establishment of crack tip conditions in Ni-based alloys. They have commented that the formation of galvanic couples may lead to considerable changes in the chemical conditions in the crack. Fish *et al.* [89] have on the other hand reported that the formation of Cr carbides or other precipitates in Ni-based alloys does not lead to accelerated corrosion, except for Ti and Nb rich carbides.

8. Comments on the role of potential control in EAC investigations

Finding the most useful experimental approach to study the influence of anionic impurities on cracking has been defined as one of the major goals of this survey. An essential question related to this is whether cracking and crack electrochemistry should be studied under open circuit conditions or whether potentiostatic experiments are also possible and relevant.

A potentiostatic experiment simulates in one aspect a cracked specimen well, because separation of the sample (working electrode) and the counter electrode can be considered closely analogous to a (partly) separated macrocell in a cracking system. However, using a potentiostat and a conventional electrode arrangement usually requires a fair conductivity of the solution in which the experiments are performed. Due to the poor conductivity of a simulated BWR coolant, supporting electrolyte such as Na_2SO_4 has often been added to make potentiostatic experiments possible. This may however lead to enrichment of anions of the supporting electrolyte in the crack or crevice, subsequent acidification and erroneous results [54].

We have tried to solve part of the problems related to potential measurement and control in poorly conductive BWR coolants by using a controlled-distance electrochemistry (CDE) arrangement [138]. Even when using such an arrangement, the potential at the crack tip of a cracked specimen cannot be properly controlled (see e.g. Ref. 1). This is due to the IR drop along the crack and due to the establishment of pH and potential profiles along the crack length. The remaining solution when studying crack tip conditions is to simulate crack tip chemistry in the entire experimental environment.

9. Conclusions

The main focus of the present report is on crack growth, and phenomena related on crack initiation have been discussed in a relatively brief manner. Before proceeding to the conclusions and proposal for future research, we briefly summarise the main observations of the work as follows:

About sulphate ions and other anionic impurities:

- Sulphate ions belong to the most detrimental anionic impurities with respect to increased risk of environmentally assisted cracking (EAC) in high-temperature aqueous electrolytes in nuclear power plants.
- Possible reasons for the influence of anionic impurities on EAC may be their effect on conductivity, on pH, on reactions rates or equilibria, on oxide films etc. (see also Fig. 1).
- The specific nature of the impurity anion plays a significant role. In other words, increase in conductivity is certainly not a sufficient explanation.
- Anionic impurities become strongly enriched within the crack in BWR conditions under normal water chemistry.
- Sulphate ions have been observed to deteriorate the protectiveness of oxide films formed on Fe- and Ni-based materials.
- Until now clear understanding of the mechanism of the effect of anionic impurities on EAC does not exist.
- No good explanation has been given to the memory effect in the influence of anions, either.

About EAC mechanisms:

- A general agreement on the validity of different EAC models does not exist. Common to all proposed models is the assumption that the crack tip material undergoes deformation, creep, environmentally enhanced creep, purely mechanical deformation or film-induced cleavage. Various descriptions are given in different models about how environmental effects can influence and accelerate these processes.

- Several proposed EAC mechanisms involve an important contribution of oxidation reactions and oxide films within the crack.
- Also the kinetics of repassivation within the crack seem to be assigned a key role in most of the models of EAC.
- The use of transmission electron microscopy combined with novel sample preparation and elemental analysis has recently proven to be a very powerful tool to investigate real cracks formed in NPP environments and to draw conclusions about the cracking mechanism.

These observations indicate that understanding of the occluded conditions and properties of oxide films within a crack may provide useful insight into the cracking mechanism and into the accelerating influence of anionic impurities on cracking. As a starting point, we recommend as the most fruitful approach to look for correlations between crack growth rates and the properties of oxide films within the crack. This is likely to result in identifying in which cases the rate-limiting step of the crack growth can be located in the oxide film on crack walls.

Such correlations can be found at different bulk impurity contents by investigating the conditions in real cracks and analysing the films formed on real crack walls. The latter can be best done by means of modern transmission electron microscopic (TEM) techniques. Another approach is to assess the occluded chemistry conditions by means of theoretical calculations and subsequently investigate material behaviour in a simulated crack environment. We consider this approach also very promising, because it makes possible versatile electrochemical studies on the behaviour and properties of oxide films formed in conditions corresponding to the occluded crack tip chemistry. It also makes possible to study in relatively short-term experiments the influence of a variety of different impurities and impurity concentrations in a range of temperatures within the crack. In addition, it makes possible to utilise the most recent understanding of the electrochemical behaviour and properties of oxide films in high-temperature, possibly even under dynamic straining conditions. Mechanistic understanding and prediction of crack growth rates and their dependence on the presence of anionic impurities in practice may thus be facilitated.

In addition to correlating measurable quantities with crack growth data, an effort to clarify the role of oxide films in crack initiation is certainly worthwhile. Access to modern electrochemical techniques makes it possible to investigate for instance possible connections between crack initiation and transpassive oxidation of construction materials in the oxidising conditions prevailing in the reactor core. The possibility to perform this kind of electrochemical studies under dynamic straining conditions is also

worth taking into account. It seems to us that understanding crack initiation is at a very preliminary level and that any reasonable hypothesis that can be experimentally tested is worth considering.

To summarise, oxide films formed on crack wall surfaces are likely to play a key role in determining the crack growth rate of certain structural materials. Thus the prediction of the influence of anionic impurities may also become possible by means of understanding their effect on the films on crack walls. One of the most promising approaches to clarify this influence experimentally is based on investigating the electrochemical behaviour of oxide films on Fe- and Ni-based materials in high-temperature conditions simulating occluded chemistry within a stress corrosion crack. Results from such studies should be compared and combined with ex situ results obtained using modern electron microscopic techniques. In addition to focusing on crack growth, currently available electrochemical techniques should also be applied to find out whether crack initiation can be explained or modelled on the basis of the electrochemical behaviour of oxide films.

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APPENDIX A. Summary of and comments on proposed EAC models

The purpose of this chapter is to give a short summary of the variety of possible EAC mechanisms and models proposed in the literature. Thus this chapter serves as a background information for the actual report but does not aim to present a comprehensive discussion of the alternative models. For more detailed treatments, several excellent reviews on the alternative mechanisms of EAC have been published. These include the surveys by Galvele [1], Hänninen *et al.* [2], Turnbull and Psaila-Dombrowski [3], Turnbull [4] and Rebak and Szklarska-Smialowska [5].

Before proceeding it is worth realising that a single mechanism can most probably not explain in detail the complex phenomena related to the EAC of different materials. This view has been expressed for instance by Rebak and Szklarska-Smialowska when discussing the stress corrosion cracking of Inconel alloy 600 [5]. They have also pointed out that almost no explanations have been given in the literature to the events leading to the crack nucleation of this alloy. This seems to be true also for other materials: the mechanisms presented in the literature deal mainly with crack propagation but not with crack initiation.

The order of the models and mechanisms reviewed below is arbitrary and does thus not take a stand on the validity of the models.

The slip-oxidation model

The slip-oxidation model for EAC gives a mechanistic interpretation of the phenomena leading to crack propagation and it can be used for predicting crack growth rates of different materials stainless steels and nickel-based alloys such as Inconel alloy 182 in different environments (see for instance Refs 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27). According to Turnbull [4], the slip-oxidation model is increasingly perceived to be relevant only to intergranular cracking, though not as an exclusive mechanism even for this purpose.

The slip-oxidation model is to a great extent based on early ideas and concepts of cracking presented for instance by Vermilyea [28] and others, as reviewed by Ford [19, 21]. These early ideas relate crack propagation to oxidation reactions at the crack tip. The concepts of a model based on anodic dissolution control have been supported e.g. by Congleton and Yang [29] and Shoji *et al.* [30].

A simplistic view of the slip-oxidation process is shown in Fig. 1 [8]: The formation of an oxide film on a bare surface is followed by the rupture of the oxide film near a grain boundary. Subsequently, the dissolution of the grain boundary occurs and the crack advances. The oxidation of the metal leads to passivation, until the oxide ruptures again and the process repeats. Fundamentally, this process requires both corrosion and mechanical phenomena working together to advance the crack.

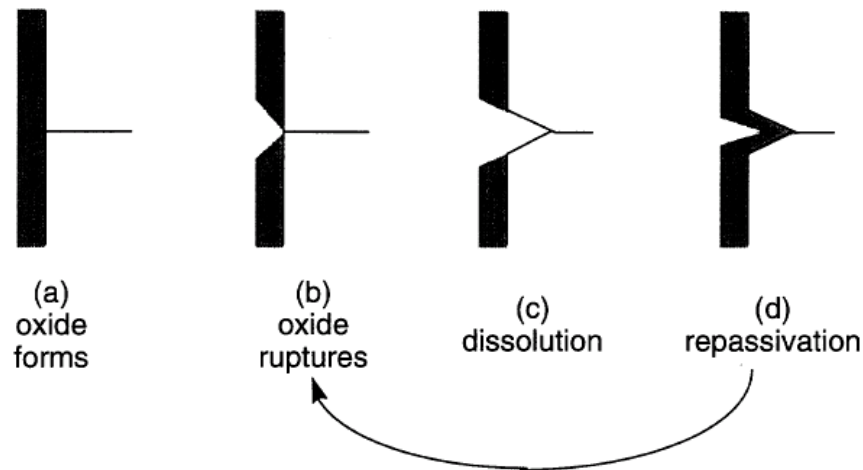


Figure 1. Simplified scheme of the slip-oxidation process for crack advance: a) an oxide film forms on a bare surface, b) the oxide film ruptures near a grain boundary, c) dissolution of the grain boundary occurs and the crack advances, d) the metal oxidises and passivates until the oxide ruptures again and the process repeats. [8].

The crack advance is proposed to be correlated with the oxidation charge density (see Fig. 2) associated with the dissolution and passivation of the bare metal surface exposed to the coolant as a result of the rupture. This correlation is based on the idea that a slip emergence at the crack tip induces a structural damage on the passive film. In order to restore the earlier state, a certain degree of oxidation has to take place. Various environmental metallurgical and mechanical variables are explained to affect the localized crack tip system. These effects can be divided into mechanical effects that control the crack tip strain rate and thereby the periodicity of oxide rupture (e.g. loading, creep rate, yield strength, oxide ductility, crack growth rate) and chemical effects that determine the repassivation response at the crack tip (e.g. crack tip microstructure and microchemistry, and crack tip chemistry, which is influenced by corrosion potential, impurities, flow rate etc.). [16, 18]

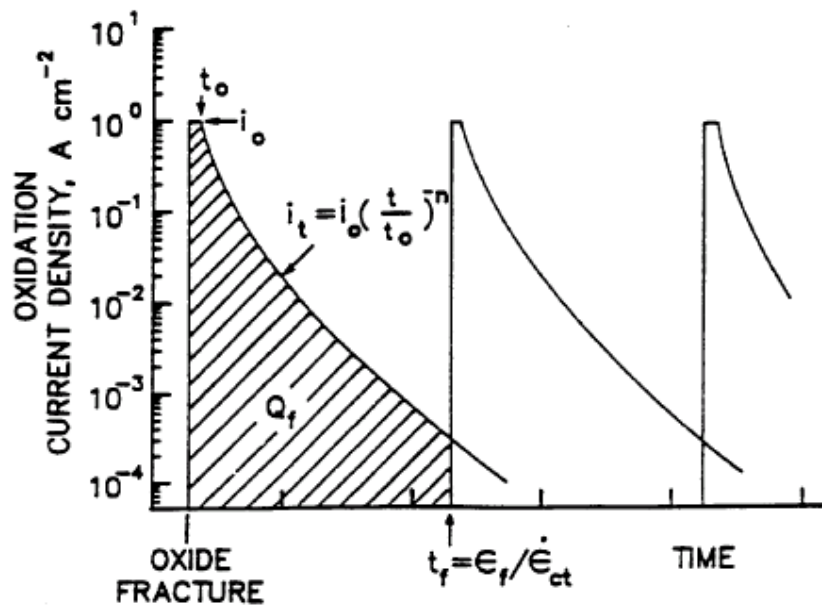


Figure 2. Schematic presentation of oxidation current density vs. time following repeated oxide rupture events. [8]

As shown in Fig. 3, the slip-oxidation model assumes that anodic reactions take place within the crack, while cathodic reactions may take place both within the crack and on the surface external to the crack. The anodic and cathodic reactions within the crack are assumed to be spatially separated. This spatial separation has been supported by the SIMS measurements performed by McIntyre *et al.* [31]. The cathodic reactions on the external surfaces do not control or limit the anodic processes within the crack. In other words, the slip-oxidation model assumes that the crack tip is essentially decoupled from the external driving force of oxygen reduction on the surfaces external to the crack (see also Ref. 32).

It seems that the main purpose in the development of the slip-oxidation model has been to find a predictive equation for crack growth rate. The predictions of material behaviour have been based on the expression reported by Ford and Andresen for the crack velocity as a function of stress intensity and a parameter n (see for instance Refs 5 and 21). Nearly all of the re-passivation aspects in the slip-oxidation model are incorporated into the parameter n , which is the empirically determined slope of the current decay curve of re-passivation. It thus depends on the corrosion potential, solution conductivity and material characteristics. The predictive power of the proposed equation has proven to be good in many cases [5], which is a significant factor in favour of the slip-oxidation model.

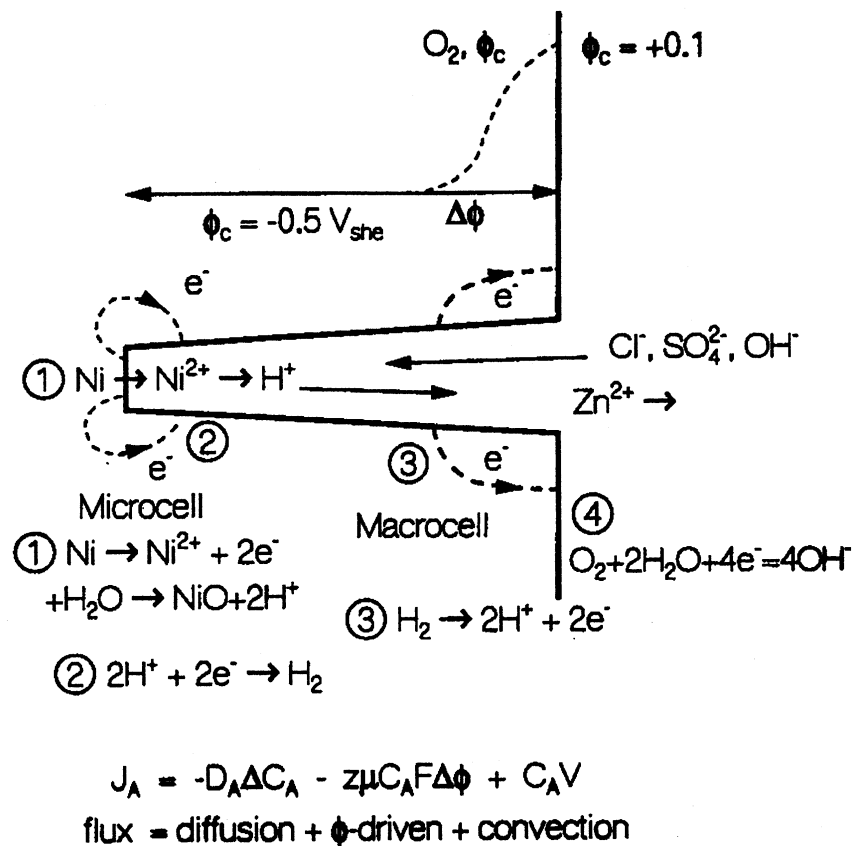


Figure 3. Sketch of the processes during growth of a stress corrosion crack; concepts based on the slip-oxidation model [10, 22].

The views on the rate-controlling step of cracking according to the slip-oxidation model have changed during the years. When deriving the predictive equation discussed above, a clear stand on the rate-determining step of crack growth has not been necessary to take. In a paper published in 1985, Andresen [11] has stated that various parameters may control the growth of stress corrosion cracks:

- The rate of film rupture, which is proportional to the strain rate at the crack tip.
- The extent of dissolution following rupture occurrences.
- The rate of transport of various reactants to or from the reaction surfaces.

Earlier Andresen [9, 11] himself has been in favour of the rate-controlling role of mass transport in the solution within the crack in the case of both iron and nickel-based alloys. He has presented the following evidence to supported his views:

- Increase of temperature decreases the solubility of iron and nickel oxides, contributing to a less effective role of mass transport.

- Determination of activation energies for crack propagation indicate a change in mechanism at around 150...200 °C, the corresponding values suggesting a change from an oxidation-dissolution control to mass transport control. (The former most probably refers to a kinetically controlled process.)
- Variations in the value of the critical threshold potential for cracking indicate that the corrosion potential is not the single factor contributing to crack growth rates.
- A correlation established for crack length and time can be explained by assuming mass transport control.
- The shape of current–time transients simulating current flow after film rupture can be explained assuming a diffusion-controlled process.
- The effect of impurity additions on crack growth rates is larger at high temperatures, at which mass transport and thus also the transport of impurities is assumed to be rate-determining.
- With low stress ratios ($R = 0.9$ and 1.0), when the pumping effect is low, the crack advances much faster at crack edges than in the centre. This can be understood via the increased rate of mass transport close to the bulk solution.

In spite of the above list, the proof for mass transport control in the solution within the crack is not very convincing. For instance, any conclusions based on the magnitude of activation energies can be considered only very tentative. In addition, most of the facts listed above can be associated with mass transport in a solid phase as well.

In the latest discussions of the slip-oxidation model Andresen and co-authors [8, 21, 22] recognise that the kinetics of repassivation, i.e. the formation and growth of the passive film on the freshly exposed surface at the crack tip, is the main rate determining factor of the crack growth rate. Thus in material-environmental conditions where the crack tip chemistry is aggressive, the growth rate is predicted to be high as much oxidation and dissolution may occur between oxide rupture events.

The rate-controlling step of cracking has been and is still subject to debate also in the literature: Taylor [33] has at an early stage proposed that aqueous diffusion within the crack rather than the kinetics of alloy dissolution controls the rate of crevice corrosion of Inconel alloy 600 in high-purity water at 288 °C. Based on thermodynamic considerations, Congleton and Parkins [34] have suggested that the cracking mechanism is electrochemically controlled, with the detailed nature of the surface film formed being of utmost importance. Contrary to the views of Andresen presented above, Ruther *et al.* [35,36] have proposed that the more likely rate controlling step in the cracking of Type 304 stainless steel according to a slip-oxidation mechanism involves the cathodic reaction, e.g. reduction of oxygen or the reduction of such oxyanions that contain a

central atom which has multiple oxidation states, e.g. As^{5+} . Other alternatives may be for instance MoO_4^{2-} and CrO_4^{2-} anions.

The slip-oxidation model has also been subject to some criticism. The strongest arguments against it have perhaps been presented by Macdonald, according to whom the model of Andresen and Ford violates Faraday's law and conservation of charge [37]. Rebak and Szklarska-Smialowska [5] have on the other hand commented that the slip-oxidation model does not explicitly address variables such as temperature, pH, presence of carbides at the grain boundaries etc. The slip-oxidation model has also been criticised by Turnbull and Psaila-Dombrowski [3], because at least part of the test results used in the development of the model have been obtained using a simulated crack in a Teflon compact tension specimen. This kind of arrangement leads to the ignorance of reactions on the crack walls, their influence on conductivity and potential profiles within the crack, current magnitudes etc. [3].

In our view the slip-oxidation model seems to be based on several well-established concepts, but its evaluation is complicated by the difficulty to distinguish between experimentally proven facts, assumptions and conclusions. Summarising, this model seems to be a good example of a cross-correlation between well established theoretical issues of crevice and crack chemistry and completely empirical characteristics of a process of which little is fundamentally known in BWR environments, i.e. oxide breakdown and repassivation.

Coupled environment fracture model (CEFM)

The coupled environment fracture model (CEFM) presented by Macdonald and Urquidi-Macdonald [38] is based largely on the same ideas as those of Ford and Andresen in their slip-oxidation model. Macdonald and Urquidi-Macdonald, however, emphasise the strong coupling of the external and internal environments and that charge conservation has to be carefully taken into account in the formulation of the model concepts. The latter means that the sum of currents within the crack and of the currents due to the oxidation of hydrogen, the reduction of oxygen, the reduction of hydrogen peroxide and the dissolution of metal at the external surfaces has to be zero. A sketch of the CEFM is shown below in Fig. 4.

The CEFM has been proposed originally for sensitised 304 SS in LWR environments, and at the moment it is used to model and to serve as a base for mitigation of cracking of stainless steels [39, 40, 41].

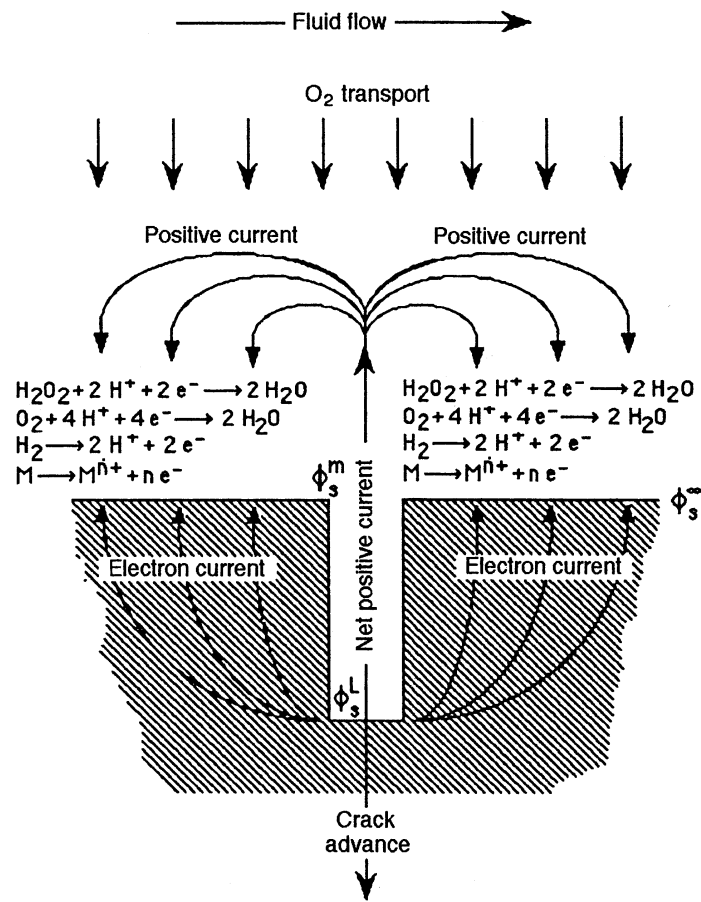


Figure 4. A sketch of the coupling of the external and internal environments in the CEFM. [39].

In analogy to the model presented by Ford and Andresen, the CEFM thus assumes crack growth to proceed via anodic dissolution. Partly in contrast to the ideas of Ford and Andresen, the CEFM takes a clearer stand in the rate-limiting step of crack growth: it was considered to be the cathodic reaction on the external surface of the crack. Because of the relatively small currents emanating from the crack, mainly the cathodic reactions for regions close to the crack mouth are assumed to play an important role [39]. Macdonald and co-workers [42] have done extensive work to show that a dominating part of the cathodic reactions proceeds at the external surface of the crack. They have also speculated that the unexpectedly high current during crack propagation may be due to microstructure events along grain boundaries ahead of the main crack. These events have been proposed to be due to hydrogen.

CEFM is continuously under active development [37, 40, 41]. Macdonald [37] has for instance relatively recently partly relaxed his statement of the dominating role of the cathodic reaction on the external surface. He has accepted that the anodic currents are partly compensated for by small cathodic currents on the crack walls. Based on his

experimental results, he still strongly argues that a considerable current exits the crack and is consumed on the external environment. This has earlier led to the treatment of the crack current as anodic, although it is actually a sum of anodic and small cathodic currents. At the present stage, the CEFM divides the crack into three parts (starting from the crack tip) [43]:

- First region: The current that is produced at the tip is consumed by cathodic processes.
- Second region: the potential passes through a plateau, where the cathodic current density approximately compensates the anodic current density (=> current that flows through the solution in the crack is very small).
- Third region near the crack mouth: the cathodic current on the crack sides cannot compensate the anodic passive current.

A fast algorithm for estimating crack growth rates introduced recently by Engelhardt *et al.* [43] is based on the concepts of the CEFM, and it emphasises again the strong coupling of the external and internal environments. The importance of this coupling has been emphasised also for instance by Turnbull [32], who recognized the importance of the hydrogen and water reduction reactions in the crack as well.

The CEFM leads to essentially the same accuracy of prediction of actual crack growth as depending on potential and solution conductivity (i.e. anionic impurities) as the slip-oxidation model [39]. CEFM, however, requires less calibration data for the prediction of crack growth in given conditions than the slip-oxidation model. Currently, a theory of crack initiation in terms of the Point Defect Model for passive films is currently being incorporated in the predictive algorithms, and this is likely to increase the determinism of the model by taking into account the role of the passive film in the coupling of the electrochemical reactions during crack growth [40]. The fact that the current densities of repassivation at the crack tip are fundamentally different from the passive current density at the crack walls has been also taken into account [41].

Several assumptions and concepts of the CEFM have been stated to be controversial, and a discussion on the validity of the model has been going on (see e.g. Refs. 14, 37, 20) The criticism towards the idea of cathodic reactions taking place only on the external surfaces [e.g. 3] has led to further development of the CEFM, as discussed above. Another factor criticised by Andresen and Ford has been that the CEFM does not account for the dramatically different SCC responses of the different impurity anions even at identical conductivity, but it instead considers only the value of the total conductivity [14]. Macdonald [37] has however commented that the CEFM takes into account the specific ion issues, because they are reflected in the equivalent conductances and in the kinetics of the charge transfer reactions. Andresen and Ford

[14] have also criticised that the CEFM relies upon only a potential gradient for transport of species down the crack, but also this criticism has been rejected by Macdonald [37].

Other points subject to criticism have been the simplifying assumptions concerning:

- the geometry of the crack [32]
- the lack of equilibrium reactions (referring most probably to solution equilibria), solubility limits and interactive effect of environment on crack tip kinetics [32, 3].

In addition, the CEFM has been criticized for its lack of ability to explain the occurrence of cracking in Inconel alloy 600 at open circuit potential and at applied negative potentials [5], and because of the use of Laplace's equation ($\nabla^2\Phi = 0$), although this equation is invalid in the presence of steady-state concentration gradients. However, the Laplace equation has been used also by Turnbull in another elaborated treatment of the occluded chemistry within the crack [32].

One of the values of the CEFM has been considered to be in recognising the possible effect of the net current flowing from the crack on the potential distribution just outside the mouth of the crack [3]. Another additional value is certainly in the active discussion that has been given rise to as a result of the conceptual difference in the CEFM and the slip-oxidation model. Our view is that albeit the CEFM and the slip-oxidation model have approximately the same predictive force, the more deterministic and scientifically sound base of the CEFM deserves to be recognized.

The enhanced surface mobility theory

The enhanced surface mobility model of Galvele gives an alternative mechanistic interpretation to crack growth of several materials. The model can also be used to predict crack growth rates. The model has been originally presented in 1985...1986, fully formulated in 1987 [44], and an improved version has been given in 1993. It is still under active development, as shown by the recent results reported in 1997 and 2000 [45, 46]. According to Turnbull [4], Galvele has developed this model, because in his view the measured high crack growth rates cannot be explained by oxidation currents at the crack tip. For instance, at crack velocities $> 10^{-7}$ m/s the current densities would be so high (0.3 Acm^{-2}) that the cracks would become plugged with corrosion products.

The enhanced surface mobility model of Galvele [1] is based on the transport of an atom at the crack tip by surface diffusion from its highly stressed location to a new site at the less stressed sides, advancing thereby the crack by one atom spacing for each such

movement (see Fig. 5). The crack propagation is explained to result from the capture of vacancies by the stressed lattice at the crack tip. A clear stand is taken in the rate-limiting step: the movement of ad-atoms along the surface of the crack is stated to control the rate of crack growth. These atoms are then lost by dissolution or by the introduction of surface vacancies. The environment can be explained to affect the rate of surface diffusion through enhancement of the rate of consumption of ad-atoms or through the effect of surface compounds on the surface diffusivity of the metal or alloy.

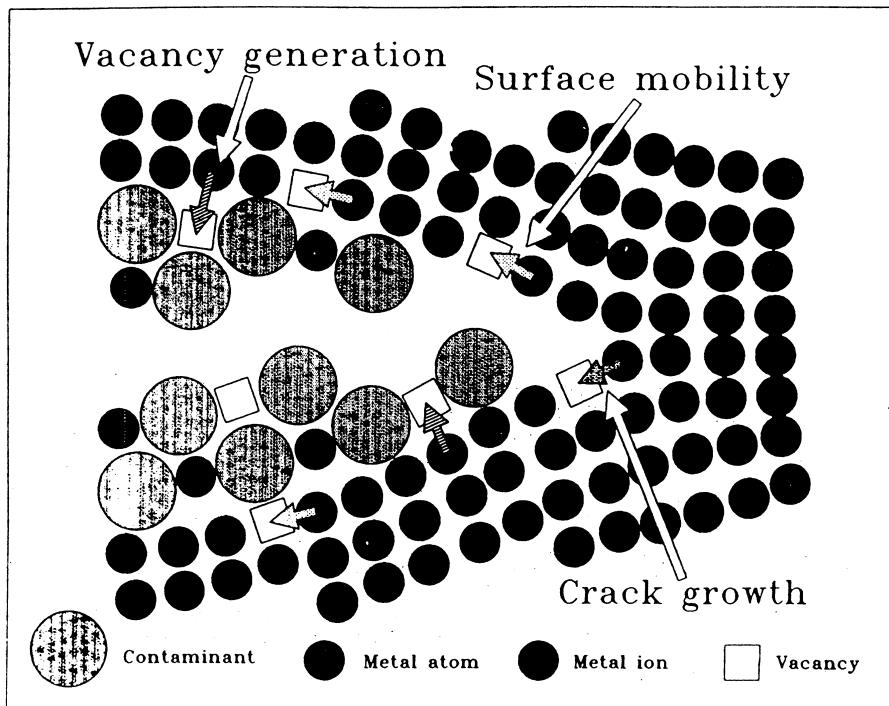


Figure 5. A sketch of the concepts underlying the enhanced surface mobility model [47].

Galvele has also given a predictive equation for the crack propagation rate as a function of the surface diffusion coefficient, the diffusion path length, the atomic diameter, the maximum stress at the crack tip and temperature. The model of Galvele seems comprehensive and versatile, and its predictive power has been found to be good [49].

One point subject to criticism has been overestimating stress corrosion crack velocities in ductile fcc metals by about 14 orders of magnitude [48]. Galvele [49] has pointed out that this criticism was based on calculations in which the role of the environment was ignored. He commented that the environment greatly increases the injection of vacancies into the metal surface, leading to predicted stress corrosion crack growth rates that correspond well with practical observations. Turnbull [4] has criticized the validity of the assumptions about the surface mass transport behind the surface mobility model. He has also commented that although the local chemistry has been described to

determine the nature of surface films, the model lacks any relationship between the environment and the film.

The internal oxidation model

The internal oxidation model is originally based on the concepts developed for oxygen embrittlement of grain boundaries of nickel and its alloys at temperatures in excess of 500 °C. Scott and Le Calvar [50, 51, 52] have suggested that the same phenomena may be involved in the intergranular stress corrosion cracking of nickel-based alloys, in particular Inconel alloy 600, in PWR environments.

As indicated above, the internal oxidation model is based on the diffusion of oxygen into the metal lattice. The reason for embrittlement has been explained to be either the presence of a layer of oxygen atoms at the grain boundary or the formation of gas bubbles such as CO and CO₂. Scott and Le Calvar [50, 51] have argued that the narrow range of potentials in which IGSCC in PWRs occurs can only be associated with an oxidation process controlling the cracking mechanism. The high value of activation energy on the other hand has been stated to rule out liquid or gas phase diffusion as a rate-controlling step. The importance of the anionic conductivity of the protective film has been pointed out by Combrade and Scott [53].

The internal oxidation model has been explained to be favoured when the corrosion potentials are close to the oxidation potential of the solvent metal [50]. As described in Ref. 51, under such conditions less noble minor alloying elements of an alloy may oxidise within the material while leaving the main metallic element of the alloy largely untouched. This can be considered a particularly severe problem for nickel-based alloys in atmospheres with very low partial pressures of oxygen which satisfy the thermodynamic requirement that the less noble minor alloying elements (Fe, Cr) can oxidise while the more noble solvent metal Ni does not. The concentration of the oxidisable species such as chromium must be below a critical minimum value in order to avoid formation of a protective external film by that species alone. Internal oxidation has been stated to be transgranular at temperatures higher than 700...800 °C or intergranular at lower temperatures.

An equation to predict crack growth rates has been given by Scott and Le Calvar, taking into account the temperature, the grain boundary diffusion coefficient of oxygen in the alloy, the surface energy, the interatomic spacing, the grain boundary thickness, the surface solubility of oxygen, the number of sites explored per gas atom jump, yield stress and the stress intensity at the crack tip.

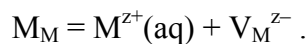
The predictive power of the internal oxidation model is not as good as that of the models discussed above. In addition, its assumptions and basic concepts are not strongly supported by experimental observations. One thing worth commenting is that observations of oxide films in microscopic images at a significant distance ahead from the crack tip may become interpreted to be a proof for the internal oxidation. This kind of 2-dimensional microscopic data are, however, extremely difficult to use as a proof for such a model, because cracking is certainly a 3-dimensional process and a crack may thus advance also at levels above or below that of the image, leading to a false impression of its continuity in a two-dimensional image.

The internal oxidation model is probably not very relevant in BWR conditions, in which the corrosion potentials are not close to the oxidation potential of the solvent metal. It may, however, have some relevance in conditions prevailing inside the crack, where the local corrosion potentials may be relatively low because of the depletion in oxygen in the water phase.

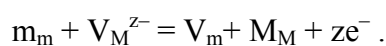
The selective dissolution – vacancy creep (SDVC) model

Aaltonen *et al.* [54] have presented the selective dissolution – vacancy creep (SDVC) model for crack growth in Inconel alloy 600 in PWR conditions. The model is based on the idea that the formation of vacancies in the metal contributes to crack growth via their accumulation in the near-surface layers and subsequent diffusion in the bulk causing significant changes in the defect distribution and structure of the bulk metal. Vacancies can interact with crack tip dislocations advancing crack tip deformation together with applied external loads. This leads to passive film breakdown at the crack tip and repeated selective dissolution, vacancy generation, deformation cycle.

One of the original assumption of this model is that the crack growth rate is determined by the transport of cation vacancies (V_M^{z-}) through the oxide film on the crack walls. These cation vacancies can be formed at the film/solution interface in the following reaction [55]:

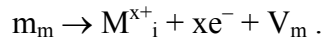


When the cation vacancies reach the metal/film interface, they react with the substrate metal, leading to the formation of vacancies in the metal as follows:

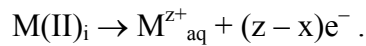


When the concentration of vacancies migrated in the bulk metal becomes high enough, they can cause changes in the dislocation structure of the metal affecting the initiation and growth of stress corrosion cracks.

According to the mixed-conduction model (MCM) developed recently to explain the conduction mechanism in passive films on ferrous alloys [56, 57], another important route for the generation of vacancies in the metal substrate, V_m , can be the injection of interstitial cations M^{x+}_i at the metal / film interface



The interstitial cations are transported through the passive film and are dissolved at the film/ solution interface [56, 57]



It has been suggested that the conduction in passive films formed on ferrous alloys at potentials lower than ca. -0.3 V vs. SHE in a tetraborate solution at $200\text{--}300^\circ\text{C}$ is dominated by interstitial cations [58]. Thus it can be expected that the interstitial route of metal dissolution through the film may dominate at the low potentials close to the crack tip. The extent of the influence of anionic impurities on that dissolution route remains to be quantified.

The most significant value of the SDVC model is in its comprehensive treatment of the generation and transport of vacancies in the metal (see also Refs 59, 60, 61). The processes within the oxide, however, have not yet been quantitatively clarified. This certainly deserves more attention in the future, especially because the rate-limiting step of the cracking has been proposed to be in the oxide film.

The (SDVC) model differs fundamentally from the slip-oxidation model and the CEFM model in that it does not involve the rupture of the oxide film as a necessary cause for the propagation of the crack. Instead, the rupture of the film in the SDVC model can be considered to be a consequence of the accumulation of vacancies in the near-surface layers of the metal and subsequent processes in the metal.

Film-induced cleavage model

Paskin *et al.* [62] and Sieradzki and Newman [63] have presented a film-induced cleavage mechanism, according to which secondary crack nucleation and brittle fracture may occur via cracks that are nucleated because of the presence of hard films on existing cracks.

Ford [19] has described EAC via a film-induced cleavage as a combination of oxidation related, i.e. slip-oxidation, and brittle-fracture mechanism. He has summarised the film-induced cleavage model as follows: Initially, the crack front moves forward by an oxidation process governed by the same rate-determining steps as those in the slip-oxidation model, but when the oxide rupture event due to an increment in strain in the underlying material occurs the crack in the oxide may readily penetrate a small amount into the underlying ductile metal matrix. The extent of this additional “environmentally-assisted cleavage” component of crack advance may be governed by the state of the coherency between the oxide and the matrix, and the fracture toughness of the substrate. Factors of importance which control the effectiveness of the oxide in initiating the cleavage event include the oxide-matrix misfit, the strength of bonding across the oxide-matrix interface and the oxide thickness and ductility.

According to Turnbull [4], the range of applicability of this kind of film-induced cleavage mechanisms remains contentious and requires further work. Andresen [6] have on the other hand proposed that the film-induced cleavage model explains better than the slip-oxidation model how crack growth via transgranular cracking proceeds.

Models based on the role of gaseous components

Another approach to modelling EAC is based on the role of gaseous components formed during the cracking. These models have generally not been developed to a quantitative stage.

Hydrogen induced cracking is one of the most popular models for Inconel alloy 600 [64, 5], although the present evidence has been stated to provide only weak support that hydrogen plays a predominant role in environmental cracking in hot water [18]. Hydrogen is likely to be formed in the cathodic reactions within the crack as a result of the low corrosion potential at the crack tip. The formation of gaseous hydrogen during corrosion fatigue crack propagation at the open circuit potential has been proven for instance on 316L stainless steel in MgCl₂ solution at 117 °C using video optical microscopy [65]. The formation of hydrogen may subsequently result in diffusion of atomic hydrogen into the alloy. Ruther *et al.* [35] have proposed that the rate-controlling step of cracking via hydrogen embrittlement may in analogy to the slip-oxidation model be liquid diffusion, passivation and oxide rupture, because these factors may influence the ad-atom coverage and subsequent hydrogen permeation.

The entry of hydrogen through the crack tip fracture zone plays an important role in the model developed by Hall [66] for the intergranular stress corrosion cracking (IGSCC) of Inconel alloy 600. This model is based on thermally-activated dislocation creep

mechanism. The crack growth rate is assumed to be controlled by a diffusion controlled creep process. It has been shown to depend, among other factors, on the local hydrogen overpotential, pH and the hydrogen permeability of the crack tip corrosion film. According to Rebak and Szklarska-Smialowska [5], the use of this model for predictive purposes requires extensive assumptions.

Another mechanism based on the influence of gaseous components has been proposed by Shen and Shewmon (Ref. 67 in Ref. 5). They have postulated that high-density bubbles of methane may be nucleated at the grain boundaries as a result of the reaction of carbon and hydrogen under stresses and pressure. According to this model, the anodic dissolution controls the amount of hydrogen injected into the alloy, while the crack growth rate is controlled by grain boundary diffusion. No experimental evidence of the presence of methane or the formation of bubbles ahead of the crack tip exists.

Magnin *et al.* (Refs 68, 69 and 70 in Ref. 5) have proposed a model that takes into account the corrosion deformation interactions (CDI) observed during creep tests. It thus has a strong mechanical component, and it combines the effects of hydrogen and anodic dissolution. This model cannot, however, be used for quantitative prediction of crack growth rates.

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Title Facts and views on the role of anionic impurities, crack tip chemistry and oxide films in environmentally assisted cracking			
Abstract <p>The aim of this literature study has been to evaluate the level of understanding of the role of anionic impurities in environmentally assisted cracking (EAC) of iron- and nickel-based alloys in the coolant conditions of a boiling water reactor (BWR) – type nuclear power plant, mainly under normal water chemistry (NWC). The study has been motivated by a need to find the most relevant experimental approaches that can be applied when looking for correlations between crack growth rate and measurable electrochemical and chemical parameters.</p> <p>Special crack tip chemistry conditions are established, when trace amounts are present in the BWR coolant and become enriched within a crack. Anions may influence both the conductivity and the pH of the coolant within the crack. In addition, they may influence the composition, structure and properties of the oxide films formed on crack walls either directly via adsorption or incorporation or indirectly via the effect of changes in pH within the crack. Based on the proposed mechanisms for EAC, oxide films formed on crack wall surfaces are likely to play a key role in determining the crack growth rate of structural materials. The prediction of the influence of anionic impurities is thus likely to be facilitated by means of understanding their effect on the films on crack walls. One of the most promising approaches to experimentally clarify this influence is based on investigating the electrochemical behaviour of oxide films Fe- and Ni-based materials in high-temperature conditions simulating the special chemistry within a stress corrosion crack. Results from such studies should be compared and combined with ex situ analytical results obtained using modern electron microscopic techniques. In addition to crack growth, currently available electrochemical techniques should also be applied to find out whether crack initiation can be explained and modelled on the basis of the electrochemical behaviour of oxide films.</p>			
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