

ON THE MECHANISM OF CREVICE CORROSION OF STAINLESS CHROMIUM STEELS

G. KARLBERG

*Department of Applied Electrochemistry and Corrosion Science,
Royal Institute of Technology, Stockholm, Sweden*

Received May 28th, 1970

The mechanism of crevice corrosion of stainless chromium steels in neutral 3% NaCl solution has been studied in a test cell, specially constructed for the purpose. Immediately after the start of an experiment, both pH and potential of the steel surface increase as a result of alkali formation (oxygen reduction) during corrosion of the steel in the passive state and a thickening of the air-formed oxide film. After the oxygen available within the crevice has been consumed, the cathode process is concentrated to the outer surface whereas on the crevice surface only metal dissolution takes place. By hydrolysis of metal ions (Fe^{2+} and Cr^{3+}) the crevice solution is now acidified. After having passed a maximum value of about 10, pH in the crevice is lowered to a steady state value of about 4. The crevice surface is first activated locally (pitting) and finally in its entire extent and potentials of the crevice and of the outer surface are both lowered. On the acid anode (crevice) surface, the Flade potential is raised whereas it is lowered on the outer surface, on which pH is raised due to the cathode reaction. The crevice may therefore be active and the outer surface passive even if their potential difference is quite small (150 mV for 13% Cr, 50 mV for 17% Cr).

Sensitivity towards crevice corrosion is perhaps the greatest weakness of the stainless steels. Besides in actual crevices it occurs also under deposits and is then sometimes referred to as deposit attack. Pitting of stainless steel is quite often connected with crevices or deposits.

A survey of the literature¹⁻¹³ on crevice corrosion of stainless steels shows that relatively few experimental investigations on actual working crevices have been carried out. Conditions in really efficient, *i.e.* quite narrow crevices, such as threads, are not easy to specify or measure. On the other hand, wider crevices, in which measurements may be carried out, are not very effective and crevice corrosion may take very long time to develop or nor be forthcoming at all.

The mechanism of crevice corrosion on passivated metals is usually described as follows: On a free surface the diffusion-limited current density of oxygen reduction will exceed the critical current density for passivation and the metal will remain in the passive state with a corrosion potential above the Flade (or activation) potential. In a crevice, on the other hand, the diffusion-limited current density of the cathode reaction will soon be smaller than the critical current density for passivation and the corrosion potential, *i.e.* the point of intersection between the

cathodic and the anodic polarization curve, will fall below the Flade potential, *i.e.* in the activity range. This means that the outer surface will be maintained in the passive state, whereas the crevice is active and corrodes. The potential difference between outer surface and crevice is assumed to be great and the Flade potential is tacitly assumed to be the same for outer surface and crevice. Special studies have shown that the Flade potential is not changed with the oxygen content of the solution^{2,8,4}. On the other hand, the critical current density for passivation is increased in the presence of chloride ions^{8,14,15}.

The notation of quite a large potential difference between crevice and outer surface seems to be derived from potential measurements on steel specimens immersed in solutions of differing oxygen content. The potential of a stainless steel specimen, immersed in an aerated or a deaerated solution of the same pH may differ about 600 mV. In a study of crevice corrosion, Rosenfeld and Marshakov⁵ measured a potential difference of several hundred mV between a crevice and a free surface of stainless steel, which, however, were not in metallic contact with each other. In an actual, working crevice, the latter is in direct galvanic contact with an outer surface. Since the two electrodes are polarized towards each other, the potential difference in a working crevice corrosion cell would be expected to be much smaller.

France and Greene¹⁶ describe anodic protection of crevices in sulphuric acid and measure potential differences of about 1000 mV between crevice and outer surface, which are both anodes in an electrolytic cell with a special counter electrode as cathode. From the electroplating field it is well known how difficult it is to make the current penetrate into crevices and recesses. The great potential difference between crevice and outer surface in this case has no correspondence, therefore, in an actual crevice corrosion cell.

More than twenty years ago, Uhlig¹ realized that crevice corrosion and pitting are, in principle, the same thing. It has been said¹² that pitting does not require a crevice — it creates its own. It is also true that a crevice attack on stainless steels starts as small pits. The presence of oxygen or some other oxidation agent and chloride ions seem to be necessary prerequisites for both pitting and crevice corrosion of stainless steels. The operation of an oxidant concentration cell between a small, active anode surface in contact with an acidified anolyte and a large, alkalinized and passive cathode surface also seem to be common features. Rosenfel'd and Danilov¹⁷ studied the potential distribution on a surface of stainless steel subjected to pitting and found a potential difference of about 100 mV between the interior of a pit and the surrounding, unattacked surface. Studies of crevice corrosion of titanium have also lead to suggestions of a mechanism similar to that of pitting^{18,19}. Fokin and coworkers¹¹ consider, however, that in the development of crevice corrosion, pH is of greater importance than chloride ions, which seem to be entirely deciding for pitting of stainless steels. As a measure of the sensitivity of a stainless steel towards crevice attacks, they take the pH at which a free, passive electrode is activated.

The mechanism of crevice corrosion of carbon steels, which occurs primarily in inhibited solutions, seems to be substantially the same as that of stainless steels. Whereas the free surface is passivated by the inhibitor, a crevice may become active due to insufficient supply of the inhibitor. With reference to crevice corrosion of carbon steels, Skorcheletti and Golubeva²⁰ explained by means of polarization diagrams why the aerated electrode in a differential aeration cell corrodes less than the non-aerated electrode. Since the cathode reaction occurs more readily on the aerated electrode, pH is raised on its surface and its Flade potential is lowered. For passive electrodes of Fe, Cr and Ni the Flade e_{F1} potential changes with pH according to the relation²¹

$$e_{F1} = e_{F1,0} - 0.058 \text{ pH} \quad (1)$$

Even if the potential of aerated and non-aerated electrode is assumed to be the same, it is possible that this common corrosion potential lies within the passive range of the aerated electrode but

within the active range of the non-aerated electrode. Accordingly, these authors showed that buffering of the test solution prevented passivation of the aerated electrode, which then corroded more than the non-aerated electrode.

It should be noted, on the other hand, that the mechanism of crevice corrosion seems to be substantially different in strongly acid solutions and if metal ion concentration cells (rather than differential aeration cells) are operative. In the latter case, as with copper, the attack may take place on the free surface close to the crevice and not within the crevice itself²². Most cases of crevice corrosion and deposit attack in the atmosphere, finally, are apparently due to the simple fact that moisture and salts are more easily retained in crevices and under deposits than on free and clean surfaces²³. The purpose of the present study was to try to reach a deeper understanding of the mechanism of crevice corrosion of stainless steels by measuring the potential of crevice surface and outer surface and the pH of the crevice electrolyte in an appropriate model apparatus in which crevice corrosion was allowed to develop naturally.

EXPERIMENTAL

Apparatus

The cell was built from transparent polymer material in order to make direct observations of the metal surface possible (See Fig. 1). The cell consists of two separate vessels, which may be screwed together, forming the crevice between them. The construction enables perfect cleaning and degreasing of the walls of the crevice before each experiment. This is necessary in order to make the thin electrolyte film penetrate into the crevice completely and wet the surface of the specimen of thin steel sheet. The width of the crevice is simply varied by placing a rubber gasket of desired thickness between the walls. From the crevice into the electrolyte in the smaller vessel there is a capillary hole, provided for measuring the electrode potential of the crevice part of the specimen. The crevice is connected with the larger vessel via a slot, through which the specimen passes. The specimen is a strip of stainless steel, half of which lies in the crevice, whereas the other half is surrounded by the electrolyte in the larger vessel, which is in contact with the atmosphere. A calomel electrode whose salt bridge ends in the smaller vessel measures the potential of the crevice surface. The same calomel electrode is used as a reference electrode in the pH measurements. For measuring the change of pH within the crevice electrolyte, a glass electrode with a plane glass membrane and intended for pH measurements on surfaces penetrates through the smaller vessel and ends in the wall of the crevice, as shown by Fig. 1. It is fixed by means of a moulding resin. A Luggin capillary of polyethylene tubing from another calomel electrode is pressed against the outer surface of the specimen. An insulated cable is soldered to the free end of the specimen in the large vessel. The soldered joint and its immediate surrounding is molded in a cold curing thermoset or coated with repeated lacquering. No attack (of a crevice or galvanic nature) occurred around the soldering.

The construction makes possible a uniform aeration of the outer surface so that no differential aeration cells are created along the latter. The specimen is well below the electrolyte surface along all its length. Nor will corrosion products accumulate along the crevice by sinking towards its bottom as would be the case with a vertical crevice. Since electrode potential and not galvanic current is measured, an eventual outer resistance in the form of soldered contacts, cables and ampere meter is excluded.

Specification of experimental set-up: Cell material: Corrosion resistant type of poly(methyl methacrylate). Specimen: 0.2 mm steel strip, dimensions 30×1.8 cm, ground with paper No 400, degreased with acetone and kept in desiccator for two hours. Crevice (between metal surface and cell wall): Dimensions 15×2 cm. Average thickness $(a - 0.2)/2$ mm where $a = 0.5 - 2$ mm

is the thickness of rubber gasket. Electrolyte: Aerated, neutral 3% NaCl solution, prepared from distilled water. Glass electrode: Radiometer, Type G 242 C. Moulding resin: Bayer Leukotherm E 571, hardener T 3. Lacquer: Struer edge protecting lacquer.

Specimen analyses: Sample A (notation 13% Cr): 0.10 C, 0.30 Si, 0.29 Mn, 0.016 P, 0.004 S, 13.6 Cr, 0.22 Ni; B (notation 17% Cr): 0.07 C, 0.22 Si, 0.29 Mn, 0.016 P, 0.010 S, 17.3 Cr, 0.14 Ni, 0.01 Mo.

It turned out, that the attack was first developed where crevice was thinnest. Besides, an attack almost always started in the slot, forming the mouth of the crevice. By a slight bending of the specimen an attack could be provoked just opposite the capillary hole. In measuring the crevice potential accurately, a cell without glass electrode was used. In measuring the pH change of the crevice electrolyte it was more important to get the attack opposite the glass electrode and the potential measurement was then only qualitative. The glass electrode was therefore mounted with its membrane a tenth of a mm inside the wall of the crevice. Perfect sealing was required and the glass electrode was therefore surrounded by two concentric Perspex tubes, the outer of which was glued to the cell. The two cylindrical interspaces created in this way were filled with moulding resin.

In order to compare pH values measured in the crevice with critical pH values for general activation of the same stainless steel, time-potential curves were recorded for steel specimens immersed in chloride solutions with varying pH and oxygen content. For these measurements, a cell according to Fig. 2 was used. This cell had a tightly fitting cover. From beneath, through the bottom of the cell, gas mixtures with varying oxygen content could be blown in. The specimens were inserted in the walls of the cell. The surface of the specimen in contact with the cell was coated with lacquer in order to avoid crevice attacks. The specimens were ground with emery paper No. 400, degreased with acetone and then stored in a desiccator 24 h before mounting. Before each series of measurements, the actual gas mixture was passed through the electrolyte for a couple of days in order to reach a stationary state. The pH of the test electrolyte (3% NaCl

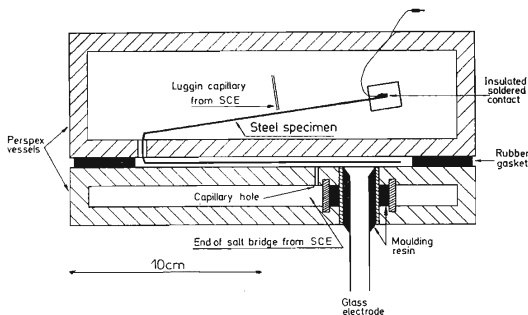


FIG. 1
Top View of Crevice Corrosion Cell

solution) was adjusted by means of a 0.1M acetate buffer and increasing additions of hydrochloric acid.

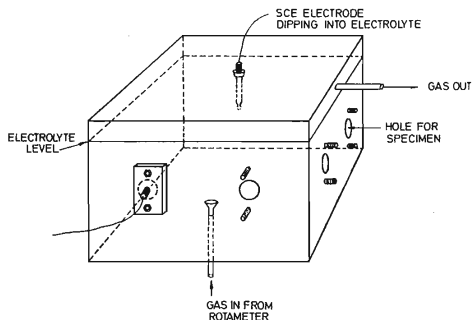


FIG. 2
Cell for Time-Potential Studies

RESULTS

Crevice Corrosion

Initially, the corrosion attacks on the specimen inside the crevice were very small. Quantitative values of the crevice potential (e_{crev}) refer to experiments in which an attack was obtained just opposite the capillary hole. The glass electrode, on the other hand, has such a large area that it must necessarily cover not only a starting attack but also un-attacked surface. A correct value of the pH within an attack cannot be counted upon in short experiments, therefore.

Potentials of outer surface and crevice as a function of time. The diagrams in Fig. 3 show typical changes of potentials for steels A or B, respectively. In the initiation period the potential difference, $\Delta e = e_{\text{out}} - e_{\text{crev}}$ between the outer surface and the crevice was small. In the beginning, both potentials rose to a maximum and then fell, e_{crev} more rapidly than e_{out} . After a few hours, both potentials attained an almost constant value. No rapid potential fluctuations occurred during the course of an experiment.

Influence of steel composition. The attack occurred more rapidly on steel A with 13% Cr than on steel B with 17% Cr. With steel A, furthermore, the potentials e_{out} and e_{crev} finally assumed lower values than with steel B and their difference Δe was greater (150 mV as compared to 50 mV for B).

Influence of electrolyte composition. 3% Na_2SO_4 instead of 3% NaCl as electrolyte did not provoke crevice corrosion within reasonable time.

Influence of crevice width. If the mean distance between cell wall and specimen is increased from 0.15 to 0.9 mm, the potential difference Δe is decreased from 150 mV to 75 mV for steel A.

Influence of crevice depth. The potential difference $\Delta e = 150$ mV was obtained when the potential of the crevice was measured 8 cm from its mouth. If the potential was measured immediately inside the mouth of the crevice, the difference Δe was only 90 mV.

Crevice pH. Initially, the pH of the electrolyte was 6. As shown by Fig. 3, pH began to rise as soon as the electrolyte solution penetrated the crevice. The rise took place more rapidly the thinner the crevice was. After about an hour, pH reached a maximum value of 9.5 and then started to decrease slowly. If localized attack started just opposite the glass electrode, pH started to decrease more rapidly and did not attain such a high maximum value. In order to find out how far pH in the crevice could sink, the cell was allowed to operate for a long time (2–14 days) with steel A. After observation through the transparent cell wall had shown that the main part of the steel specimen within the crevice had been attacked, the crevice solution was collected and its pH was measured. The value obtained was 4.0. Locally, pH might have been somewhat lower, however.

Influence of time elapsed between grinding and assemblage. It proved difficult to provoke a crevice attack within a short time, if the specimen was kept in the desiccator for a long time between grinding and insertion in the cell. This time was therefore limited to 2 h.

Influence of aeration of the crevice. One variant of the experimental cell could be placed vertically, resting upon one of its short sides. The slot (mouth of the crevice) was then parallel with the solution level and located about 1 cm below the latter.

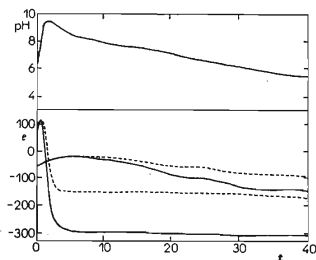


FIG. 3
Time (t , h) Dependence of pH in the Crevice for Steel A and Time Dependence of Potential e (mV) and pH in the Crevice for Steels A and B

Full lines e in the crevice, dotted line e of the outer. Lower pair of lines steel A, upper pair of lines steel B. Width of the crevice 0.15 mm.

Air was bubbled in through a capillary hole at the bottom. This prevented the appearance of crevice attack completely.

Influence of buffering of the test solution. In the test solutions buffered to a pH-value close to the neutral point, crevice corrosion is effectively retarded. Hence, when the 3% NaCl solution was buffered with 0.1M acetate buffer to pH 6, only a small local attack developed just inside the mouth of the crevice within a week.

Critical pH Value for Activation in General Corrosion

Fig. 4 illustrates how steels A and B behave in acetate buffered 3% NaCl solution of different pH and oxygen content. The concentration of the buffer system was 0.1 mol/l. According to Fig. 4A, steel A does not stand pH 3 in argon-saturated electrolyte but corrodes under hydrogen evolution. It does stand pH 4 in argon-saturated solution, however. It is also evident that steel A stands pH 3.5 with oxygen bubbling. The difference of electrode potential of steel A in oxygen-saturated and oxygen-free solution is as high as 700 mV. As regards steel B (Fig. 4B), it stands pH 3.5 but not 3.0 in argon saturated solution. The potential difference for steel B in aerated and deaerated solution is 600–700 mV at pH 3.0.

The test series also comprized some austenitic steels. By experience, it was found that the steels were passive as long as their potential remained above -200 mV on the hydrogen scale. Below 0 mV stable potentials were obtained, above 0 mV, *i.e.* in the passive range, the potentials often fluctuated about 200 mV or even more.

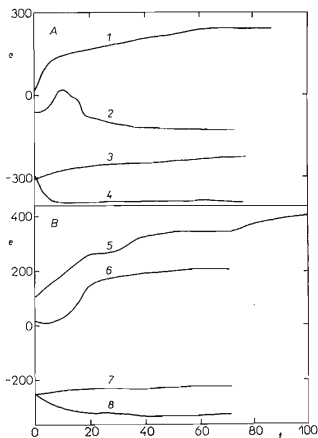


FIG. 4

Time (t , h) Dependence of Potential e (mV) of Free Electrodes in Acetate-Buffered 3% NaCl Solution

A Steel A (13% Cr), B steel B (17% Cr).
 1 O_2 , pH 3.5 (potential fluctuations); 2 air, pH 4.0; 3 Ar, pH 4.0 (bright colour); 4 Ar, pH 3.5 (dark, H_2 evolution); 5 O_2 , pH 3.0; 6 air, pH 3.0; 7 Ar, pH 3.5 (bright colour); 8 Ar, pH 3.0 (dark, H_2 evolution).

Furthermore, the potentials change considerably immediately after immersion in the solution. Continuous measurement of the potential shows very clearly, however, when the critical pH for activation is reached. If pH is lowered continuously, a rapid and distinct decrease of potential is obtained at a certain critical pH value. The potential then remains stable and is not further lowered by a continued decrease of pH (but rather raised somewhat in accordance with the Nernst equation). Bubbling oxygen through the solution lowers the critical pH value about one unit.

In aerated solution, the potential of a newly immersed electrode rises rapidly from a low initial value. This is apparently due to a thickening of the air-formed oxide film. The specimen assumes the same low initial potential in deaerated solution but the potential does not rise with time in this case.

DISCUSSION OF RESULTS

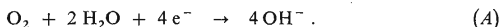
The results show that the initiation of a crevice attack does not involve the development of a great difference in potential between aerated outer surface and air-free crevice. In the beginning, the two potentials are practically the same and the whole of the steel specimen is passive. Its small general corrosion in the passive state consumes oxygen and produces alkali, however. The measurements show that pH on the steel surface rises rapidly during the first part of the initiation period, obviously an example of so-called wall alkalinity. The consumption of oxygen and formation of alkali is particularly rapid immediately after immersion of the specimen, apparently corresponding to the growth of a thicker oxide film than that formed in air. The potential of both the free electrodes exposed in the cell according to Fig. 2 and of the specimen in the crevice cell rises to begin with. If the oxide film is allowed to thicken for a long time in air before exposure to the salt solution, the initial change in pH and potential is smaller, however, and a crevice attack takes much longer time to develop.

After the initial rise of the electrode potential of both crevice surface and outer surface both potentials fall when crevice attack starts. Whereas the potential of the anode (crevice) surface is lowered due to activation, the potential of the cathode (outer) surface is lowered due to cathodic polarization. During the propagation of a crevice attack there develops between anode and cathode a certain, although not very large, potential difference, whose magnitude is a measure of the rate of attack in accordance with Ohm's law. The lower the two potentials are, the greater is their difference. As the active surface within the crevice is increased, the corrosion current increases and so does the ohmic potential drop and the cathodic polarization of the outer surface. Conversely, a small attack within the crevice corresponds to a very small, almost negligible potential difference at relatively high potential values of both the anode and the cathode.

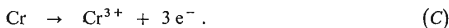
That steel A (13% Cr) gives a larger potential difference than steel B (17% Cr) is apparently due to the fact that the corrosion rate of stainless steel in its active

state also is reduced by an increased Cr content. This means a lower corrosion current and a smaller potential difference at increased Cr content. It is natural, furthermore, that an attack occurs where the crevice film is thinnest since both the oxygen available and the buffer capacity is smallest in a thin film. The influence of the crevice width on the potential difference between anode and cathode is explained by the larger resistance and higher ohmic potential drop along a thin solution film. By the same reason, the potential measured is lower far into the crevice if the attack occurs at its inner end.

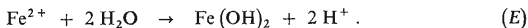
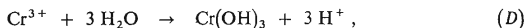
That the pH of the crevice solution is increased rapidly immediately after filling the cell with electrolyte is obviously due to the fact that initially oxygen is consumed and alkali produced also within the crevice according to the cathode reaction:



This pH change occurs all over the specimen surface within the crevice and is adequately shown by the glass electrode. After all oxygen within the crevice is consumed, the cathode reaction (A) occurs entirely on the outer surface whereas on the crevice surface mainly the anode reactions:



occur. When the Fe^{2+} and Cr^{3+} concentrations reach certain values, hydrolysis takes place:



These reactions generate hydrogen ions, which means that pH is lowered again after having passed a maximum value. Since the glass electrode covers both anode and cathode surfaces to begin with, it does not respond adequately to this lowering of pH. In a number of experiments it started however, at the same time as the lowering of potential and then pH sank continuously and slowly for a long time. It seems probable that this subsequent lowering takes place more rapidly just above the attacks. The glass electrode reacts when the anode surface with low pH increases in size. Collection of the crevice solution and pH measurement showed pH 4 after a few days. It seems reasonable to assume that the effect of this acidification due to hydrolysis within the crevice is the same as that postulated in the theory of pitting. That buffering of the test solution prevented crevice attack is also an indication that the lowering of pH is a condition for activation. The relation between the critical

pH for activation of a stainless steel and its tendency to crevice corrosion, reported by Fokin and coworkers¹¹ points in the same direction. It is interesting to note that the final pH value, measured in the crevice solution, coincides with the critical pH required for activation of the steels concerned in deaerated NaCl solution. Below this pH value hydrogen evolution takes place and it seems reasonable to assume that the corresponding consumption of hydrogen ions prevents the crevice pH from sinking to a still lower value. It should be noted, furthermore, that hydrogen ions migrate out of the crevice to an increasing extent as their concentration is raised.

The mechanism of crevice corrosion of stainless steels in neutral aerated chloride solutions, as it emerges from the experiments reported above and the succeeding discussion is illustrated by the schematic polarization diagrams for crevice and outer surface shown in Fig. 5. i_c denotes cathodic polarization curves for oxygen reduction, and i_a anodic polarization curves for stainless steel, which in the passive range are vertical lines. Potential values refer to the time-potential curves for steel A in Fig. 3.

In the beginning, the polarization diagrams for crevice and outer surface are identical. All the steel surface is passive, the air-formed oxide film allowing a fairly high anodic current density, however. The corrosion process consumes oxygen and produces alkali, which partly diffuses away from the outer surface. The redox potential for the cathode reaction (A) above is given by

$$e = e_0 + \frac{RT}{zF} \ln (P_{O_2} / [OH^-]^4), \quad (2)$$

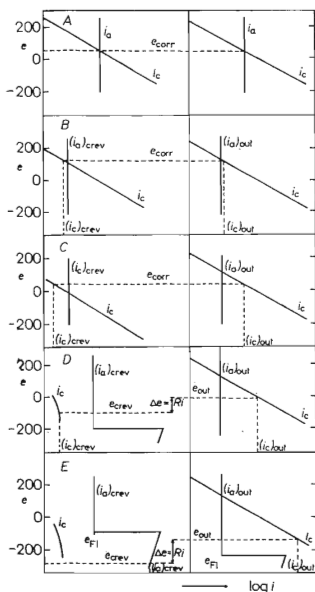


FIG. 5

Mechanism of Crevice Corrosion in the Initiation Stage

i_c and i_a denote cathodic and anodic current densities, subscripts crev and out refer to crevice and outer surface, respectively. R is the internal electrolyte resistance in crevice corrosion cell, e_{F1} denotes Flade potential. Diagram E shows the propagation stage.

which shows that a change of pH causes a potential change four times that caused by a corresponding change of oxygen concentration. Although both a lowering of oxygen content and a rise of pH are factors which cause a lowering of the equilibrium potential, the measured potentials of both crevice and outer surface are initially changed in positive direction, in accordance with Figs 3 and 4 and apparently due to a strengthening of the air-formed oxide film.

The anode curves are moved towards lower currents, both in the crevice and on the outer surface, due to a thickening of the oxide film and corresponding to more noble values of measured potentials. From the crevice towards the outer surface there flows in the solution a small current of the size $(i_a)_{crev} - (i_c)_{crev} = (i_c)_{out} - (i_a)_{out}$, which means that there is an ohmic potential drop in the same direction. This is so small, however, that crevice and outer surface still have practically the same potential.

The difference in oxygen content and cathodic c.d. between crevice and outer surface is now large. In the crevice, the anode reaction dominates over the cathodic reaction, which means that the amount of OH^- ions formed in the crevice is negligible in comparison with that of the Fe^{2+} ions generated. At all times we have the relation

$$(i_a)_{crev} + (i_a)_{out} = (i_c)_{crev} + (i_c)_{out} \quad (3)$$

Hydrolysis of Fe^{2+} and Cr^{3+} ions, result in a lowering of the pH of the crevice solution. With the successively increasing cell current Cl^- ions migrate into the crevice. The result is an acid solution of iron and chromium chlorides. Both H^+ ions and Cl^- ions increase the rate of the anode reaction, H^+ by dissolving the oxide film, Cl^- by peptizing it. The acidification of the crevice solution raises the Flade potential according to Eq. (1) above.

The Flade potential of the crevice surface has now been raised so much that the crevice surface is active whereas the outer surface is still passive. The propagation stage of the crevice attack has been reached. The corrosion current and hence also the potential difference (Δe) between crevice and outer surface is increased. Δe reaches a steady state value of c. 150 mV for steel A and 50 mV for steel B. In the slot (crevice mouth) ferric hydroxide accumulates. It is formed under oxygen consumption and also renders oxygen diffusion into the crevice more difficult. Crevice corrosion is self-propagating (autocatalytic) in the same way as pitting. That pH is not decreased below 4 is apparently due to a certain amount of hydrogen evolution within the crevice and to migration of hydrogen ions out of the crevice. For steel A, e_{crev} in the steady state is below the potential of the hydrogen electrode at pH 4 (i.e. -235 mV).

CONCLUSIONS

Several co-operating factors are necessary for crevice corrosion of stainless steels to occur. These are: The presence of an oxidation agent, usually oxygen, forming a concentration cell between crevice and outer surface. The presence of activating anions, usually Cl^- ions. A low enough buffer capacity to allow a substantial lowering of pH within the crevice.

This study was promoted in several ways by the Sandvik Steel Co., Sweden. The authors are indebted to Mr J. Ch. Carlén, Chief Engineer, and to Dr L. Troselius of this company for fruitful discussions.

REFERENCES

1. Uhlig H. H.: *Corrosion Handbook*, p. 172. J. Wiley, New York 1940.
2. Greene N. D.: *J. Electrochem. Soc.* 107, 457 (1960).
3. Schafer G. J., Gabriel J. R., Foster P. K.: *J. Electrochem. Soc.* 107, 1002 (1960).
4. Evans U. R.: *J. Electrochem. Soc.* 108, 613 (1961).
5. Rosenfeld I. L., Marshakov I. K.: *Corrosion* 20, 115t (1964).
6. Korovin Yu. M., Ulanovskii I. B.: *Corrosion* 22, 16 (1966).
7. Strocchi P. M., Vicentini B., Sinigaglia D.: *Electrochim. Met.* 1, 239 (1966).
8. Ulanovskii I. B.: *J. Appl. Chem. U.S.S.R.* 39, 768 (1966).
9. Bombara G., Sinigaglia D., Tacani G.: *Electrochim. Met.* 3, 81 (1968).
10. Hoar T. P.: *Galvanotechnik u. Oberflächenschutz* 9, 18 (1968).
11. Fokin M. N., Kurteпов M. M., Žuraviev V. K., Oreshkin: *Proc. 1st Inst. Symp. Water Desalination*, Washington D. C., p. 2-531; U.S. Department of the Interior, Washington 1967.
12. Fontana M. G., Greene N. D.: *Corrosion Engineering*, p. 54. McGraw-Hill, New York 1967.
13. Evans U. R.: *The Corrosion and Oxidation of Metals*, First Supplementary Volume, p. 51. Arnold, London 1968.
14. Riggs O. L.: *Corrosion* 19, 180t (1963).
15. Nobe K., Tobias R. F.: *Corrosion* 20, 263t (1964).
16. France W. D., Greene N. D.: *Corrosion* 24, 16 (1968).
17. Rosenfeld I. L., Danilov I. S.: *Corros. Sci.* 7, 129 (1967).
18. Jackson J. D., Boyd W. K.: *ASTM Spec. Tech. Publ.* 432, 219 (1968).
19. Griess J. C.: *Corrosion* 24, 96 (1968).
20. Skorcheletti V. V., Golubeva N. K.: *Corros. Sci.* 5, 203 (1965).
21. Vetter K. J.: *Electrochemical Kinetics. Theoretical and Experimental Aspects*, p. 752. Academic Press, New York 1967.
22. Copson H. R. in the book: *Corrosion Resistance of Metals and Alloys* (LaQue & Copson Ed.) p. 10. Reinhold, New York 1963.
23. Kaesche H.: *Werkstoffe Korros.* 15, 379 (1964).