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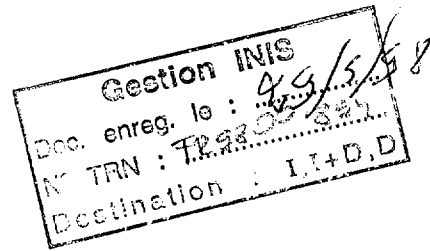
**CORROSION SOUS CONTRAINTE DE L'ALLIAGE 600 DANS
DE L'ACIDE BORIQUE EN PRESENCE DE CHLORURES**

*CHLORIDE STRESS CORROSION CRACKING OF ALLOY 600
IN BORIC ACID SOLUTIONS*

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SYNTHÈSE :

Cette étude montre que la très bonne résistance à la corrosion sous contrainte de l'alliage 600 en présence de chlorures, due à sa teneur élevée en nickel, n'implique pas une immunité complète. La fissuration est possible en présence de chlorures de 100 à 360°C lorsque le milieu est rendu suffisamment agressif. C'est en particulier le cas des milieux chlorurés aérés, dans lesquels une acidification locale peut se produire. Cette fissuration éventuelle en milieu chloruré est un point intéressant pour les études sur le comportement des tubes de générateur de vapeur dans les zones confinées du milieu secondaire.

EXECUTIVE SUMMARY :

The high nickel austenitic alloys are generally considered to have good resistance to chloride stress corrosion cracking. In the standard boiling magnesium chloride solution tests, alloys with more than 40% nickel are immune. Nevertheless, more recent data show that cracking can occur in both Alloys 600 and 690 if the solution is acidified. In other low pH media, such as boric acid solution at 100°C, transgranular and intergranular cracking are observed in Alloy 600 in the presence of minor concentrations of sodium chloride (2g/l). In concentrated boric acid at higher temperatures (250 and 290°C), intergranular cracking also occurs, either when the chloride concentration is high, or at low chloride contents and high oxygen levels. The role of pH and a possible specific action of boric acid are discussed, together with the influence of electrochemical potential.

CHLORIDE STRESS CORROSION CRACKING OF ALLOY 600 IN BORIC ACID SOLUTIONS

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INTRODUCTION

A number of nickel base alloys, such as the 600 and 690 grades, have been developed for their resistance to stress corrosion cracking (SCC) in the presence of chlorides. However, various experiments carried out by EDF have shown that cracking can occur in these materials in the presence of chlorides, in the temperature range between 100 and 360°C. After a brief review of existing data, the present article describes cracking observed in Alloy 600 exposed to chloride-containing solutions during laboratory studies performed by EDF. The results are interpreted in the light of the available evidence.

I. LITERATURE SURVEY

A. Comparative Behavior of Stainless Steels and Nickel Base Alloys

The susceptibility of stainless steels in chloride-containing environments is well known, and decreases with rising nickel content (Fig. 1 [1]). In boiling magnesium chloride solution, a maximum sensitivity is obtained for steels of the 18-10 type, while in Alloy 800, with 30-35% nickel, although cracking still occurs, it is much slower [1, 2]. The parameters which enhance the aggressivity of the medium, such as acidity and the concentration of Cl^- ions, increase the tendency for cracking. For applications concerning PWR power plants, these effects have been studied in chloride-containing concentrated boric acid solutions at about 100°C [3].

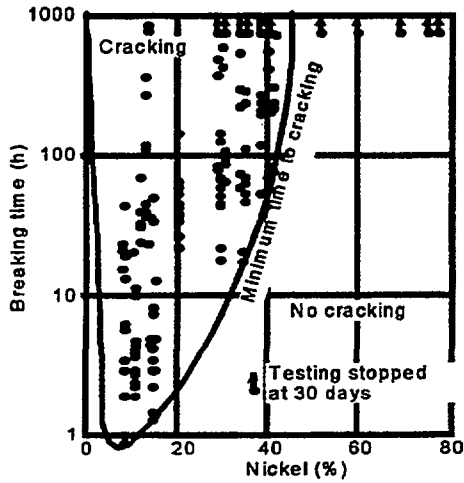


Figure 1: Time to cracking of Fe-Ni-Cr wires in boiling 42% magnesium chloride [1]

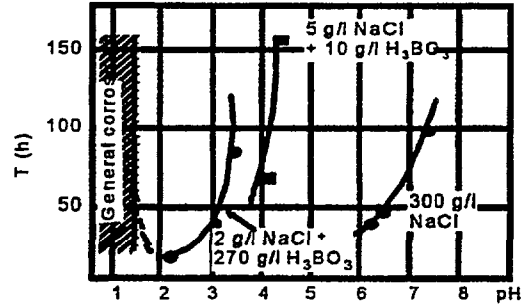


Figure 2: Influence of pH on SCC of 316 steels in 27% boiling boric acid [3]

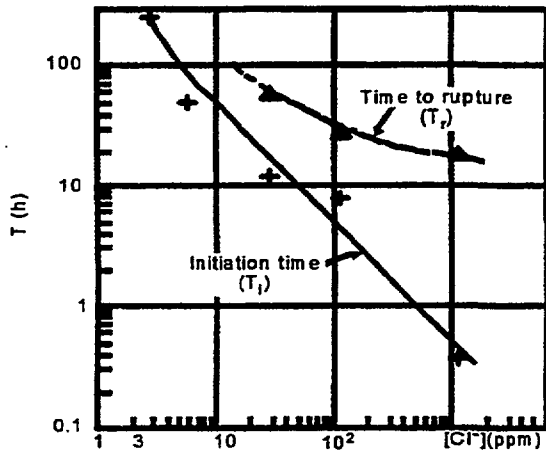


Figure 3: Influence of chloride concentration on SCC of 316 steels in 27% boiling boric acid [3]

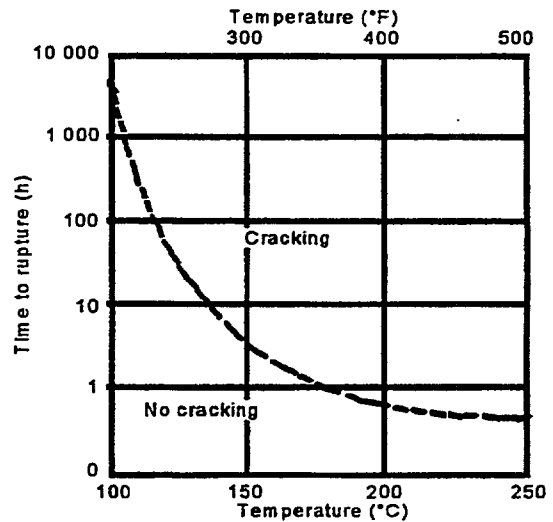


Figure 4: Influence of temperature on 304 SS in neutral chloride solutions. Chloride content ranging from 0.1 to 33% NaCl [4]

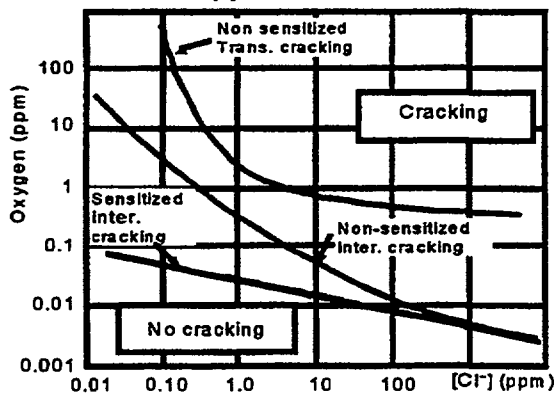


Figure 5: Effect of chloride and oxygen content on SCC of Stainless steels in water at 250°C [5]

Conditions of this sort can arise due to local concentration of boric acid caused by leakage of the primary medium, for example at seals. The results obtained (Figs. 2 and 3) clearly show that cracking increases with the aggressivity of the medium, except when the latter reaches excessive levels where general depassivation occurs.

Temperature is another key parameter, and it is generally recognized that cracking is difficult below 60°C and that the risk increases with rising temperature (Fig. 4). Thus, stainless steels crack readily at high temperature in neutral solutions, even at low chloride concentrations, the susceptibility depending on the concentrations of chloride ions and dissolved oxygen (Fig. 5). Transgranular cracking is observed in Alloy 800 in these media, oxygen content being an aggravating factor. However, even in the absence of oxygen, cracking can occur in this alloy at 350°C [6]. Although SCC in stainless steels in chloride-containing solutions is generally considered to involve transgranular cracking, intergranular cracking can also be obtained in these conditions in non-sensitized materials. This has been observed in high temperature water (Fig. 5) and also in magnesium chloride solution, in which it has been shown that intergranular cracking can be obtained by diminishing the aggressivity of the medium or by increasing the applied stress or strain rate in a given environment (Fig. 6 [7]).

In the case of Alloy 600, numerous studies have shown its good resistance to SCC in chloride-containing media at low temperatures (< 200°C). This behavior is attributed to the beneficial effect of nickel and has been observed in a wide range of media, including highly aggressive ones (Fig. 1 and Table 1). However, Alloy 600 can show cracking at high temperatures in pure water (Table 2), where the accelerating effect of chloride ions is not marked in the absence of oxygen (Table 2, test 14). In contrast, the *simultaneous* presence of chlorides and oxygen sharply accelerates SCC by comparison with the usual PWSCC, and in this case, the presence of crevices is detrimental (Table 2, test 15), perhaps due to local acidification.

Data published in the literature reveal that Alloy 690 shows very good SCC resistance in chloride-containing media at all temperatures. This has been confirmed by tests in different solutions, at various chloride concentrations, with and without dissolved oxygen (Table 3). However, in tests performed by EDF (Table 6), a small crack was observed in this material in boiling magnesium chloride solution acidified to pH 1.

B. Unresolved Questions

This review reveals that, in spite of the very good SCC resistance of Alloy 600 in chloride-containing media, a few cases of cracking have nevertheless been observed, either in acid media, or in situations where a locally acidified solution has been able to form at a crack tip due to hydrolysis of metal ions in the presence of oxygen and chlorides. Indeed, tests on stainless steels in a chloride-containing boric acid medium have shown that a simple shift in pH is sufficient to cause the appearance of cracking (Fig. 2).

These considerations indicated the need to determine whether there is a risk of cracking in Alloys 600 and 690 in certain acidic chloride-containing media. In particular, this situation could arise in the event of concentration of boric acid in the primary medium, or in locally acidified solutions formed on the secondary side of steam generators. The experimental studies described in the present article were undertaken in order to examine this possibility.

II. MATERIALS AND EXPERIMENTAL TECHNIQUES

Tests of different types were performed in chloride-containing solutions of variable composition. These included tests in magnesium chloride solution of variable pH at 153°C. It is known that the equilibrium pH of a 42% magnesium chloride solution at 153°C is about 2.3 [7], corresponding to the hydrolysis reaction :

Table 1 - Alloys 600 and 690 : SCC tests in chloride-containing media at low temperatures.

Material	Chemical Conditions	Temperature (°C)	Duration (h)	IG/TGSCC **	Ref.
600	3,5% NaCl + 0,5% CH ₃ CO ₂ H + H ₂ S	30	5 040	NC	[8]
	50% H ₂ SO ₄ + 3% NaCl	30	5 040	NC	
	NaCl	100	5 040	NC	
	NaCl saturated (pH 4)	109	5 040	NC	
	42% MgCl ₂	154	1 680	NC	
	85% ZnCl ₂	180	1 680	NC	
690	MgCl ₂ U-bend	154	2 325	NC	[9]

Table 2 - SCC tests on Alloy 600 in chloride-containing media at high temperatures.

N°	Chemical Conditions	Temperature (°C)	pH _T	Duration (h)	IG/TGSCC **	Ref.
2	Water + 100 ppm Cl ⁻ (saturated with oxygen)	200	5.7	3 000	NC	[10]
3	Water + 100 ppm Cl ⁻ + O ₂	288	5.6	4 000	NC	[11]
4	Water + 100 ppm Cl ⁻ + 50 ppm O ₂ (pH 2.8 - 6.5 - 10.5)	300	-	13 940	NC	[12]
5	AVT + 500 ppm Cl ⁻ + O ₂	316	-	>12 000	NC	[13]
6	Water + sodium orthophosphate + 5 ppm Cl ⁻ + 0.5 ppm O ₂ (pH 9)	320	-	10 000	NC	[14]
7	NaCl 400 g/l (pH _{25°C} 3 to 6)	332	4.8	2 000	NC	[15]
8	NaCl 200 g/l + FeCl ₃ 200 g/L	332	1.5	840	NC	[15]
9	FeCl ₃ 127 g/l (E = ERFH)	332	2.7	5 000	NC (IGA)	[15]
10	NaCl + NH ₄ Cl + sulfates (sulfates/chlorides = 0.01 à 0.17)	315	4 to 5	-	C	[16]
11	Water + 600 ppm Cl ⁻ , saturated with oxygen	350	5.5	10 000	C	[17]
12	37 ppm HCl + 600 ppm H ₃ BO ₃	320	3	-	C	[13]
14	Pure water (4-point bending)	360	5.5	14 000	C	[13]
	Water + 100 ppm Cl ⁻ + 3 ppb O ₂ (4-point bending)			14 000	C	
15	Water + 100 ppm Cl ⁻ + 20 ppm O ₂	360	5.5	2 500	C	[13]
				Double U-bend	1 500	
16	NaCl 10 ⁻² m, sat. O ₂ at RT, CT specimen	250	5.6	~ 200	C	[18]
18	NaCl 10 ⁻² m + Na ₂ SO ₄ 10 ⁻¹ m, sat. O ₂ at RT, CT specimen	250	6.8	~ 200	NC	[18]

Table 3 - Tests on Alloy 690 in chloride-containing media.

Chemical Conditions	Temperature (°C)	Type of specimen	Duration (h)	Result	Ref.
500 ppm Cl ⁻	260	double U-bend	3 024	NC	[9]
875 ppm Cl ⁻	260	double U-bend	1 344	NC	[9]
600 ppm Cl ⁻ + 150 ppm Na ₂ HPO ₄ (non-deaerated solution)	260	double U-bend	1 344	NC	[9]
100 ppm Cl ⁻ (CuCl ₂ + NiCl ₂ + seawater)	288	double U-bend double C-ring	4 000	NC	[11]
500 ppm Cl ⁻	300	double U-bend	1 000	NC	[9]
Deaerated water + 500 ppm Cl ⁻	316	double U-bend	16 128	NC	[19]
100 ppm Cl ⁻ + 50 ppb O ₂	320	capsules	14 000	NC	[19]
AVT + 400 g NaCl (pH 3 - pH9)	333	-	2 000	NC	[20]
AVT + 200 g NaCl + 200g FeCl ₂ (pH3 - pH5)	333	-	840	NC	[20]
1000 ppm Cl ⁻	350	capsules	21 000	NC	[20]
100 ppm Cl ⁻ + 300 ppb O ₂	350	capsules	15 000	NC	[20]

NC : not cracked



In order to evaluate the risk of cracking in this medium at more acid pH levels, HCl additions were made, to obtain solutions with pH values of 2.3, 1.6 and 1.0. Tests were also carried out between 100 and 290°C in solutions containing from 3 to 40% by weight of boric acid with chloride contents from 0 to 50 g/l. The conditions of the different tests performed are summarized in Table 4.

A. Materials

The materials studied were an AISI 304 stainless steel tube, four tubes and a sheet of Alloy 600, and two tubes of Alloy 690. Their chemical compositions and heat treatment conditions are given in Table 5. Alloy 600 was studied in the mill-annealed (MA) condition, after grain boundary sensitizing by treatment for 1 h at 700°C (S), and after thermal treatment for 14 h at 700°C (TT) to produce intergranular precipitation without sensitizing.

B. Test-pieces

The test-pieces used were of the C-ring, U-bend or reverse U-bend (RUB) types. The ends of the C-ring specimens, which initially formed an angle of

60° with the center, were clamped together. The U-bend specimens were 10 mm wide strips cut from tubes, deformed to produce parallel arms by bending to a U shape on a 10 mm diameter mandrel (outer surface in tension). Finally, the RUB specimens were obtained from half-tubes about 110 mm long, bent first of all to 45°, then deformed to produce parallel branches. In addition, a few electrochemical measurements were made in acid media at 102°C. The specimens used for Constant Extension Rate Tests (CERT) were 88.4 mm long by 3.5 mm wide strips cut from tubes.

C. Tests

The tests performed at 100 to 153°C were carried out in glass vessels equipped with a reflux cooling system. In the magnesium chloride media, the pH of the acidified solutions was adjusted by adding HCl and the solutions were renewed at weekly intervals. The tests in boric acid media at higher temperatures (250 to 360°C) were carried out in autoclaves, generally made from Hastelloy. The constant strain rate tests were conducted in a simulated primary medium (2000 ppm B + 1 ppm Li), either deaerated or with a 5 bar overpressure of oxygen introduced at 125°C. The imposed strain rate was $2.5 \times 10^{-7} \text{ s}^{-1}$.

Table 4 - Test conditions.

Chemical Conditions					
T (°C)	H ₃ BO ₃	Chlorides Species [Cl ⁻]	Observation	Material	
100-102	27% (50 g/l B)	NaCl	0	pH _r 2,3	600
			2 g/l	pH _r 2,3	
			2 g/l	pH _r 2,3 (HCl)	
153	0	MgCl ₂ 44	pH _r 1, 1,5, 2,3	304, 600, 690	
250	0	NaCl	50 g/l	pH _r 2,0	600, 690
	3%		(FeCl ₂ 0,2M)		
290	40%	NaCl	50 ppm	pH _r 3,0 300 ppm O ₂	600
	40%		50-128 ppm	pH _r 3,0 [O ₂] = 0	
	-		78-260 ppm	pH _r 5,6	
360	B 1000 ppm + Li 2 ppm	NaCl	0,7 ppm 20 ppm	pH _r ~8,2 [O ₂] = 0 pH _r ~8,2 PO ₂ 4 bar (125 °C)	600

Table 5 - Chemical compositions and heat treatments of the experimental materials.

Alloy	Identification	Heat treatment *	SCC specimens	Chemical composition (wt %)				
				C	Cr	Ni	Fe	Mo
600	6R, tube	MA (1' at 980°C), TT	U-Bend	0.032	16.03	76.2	6.6	0.05
	6S, tube	MA, TT	U-Bend	0.019	15.35	73.7	9.48	0.08
	6M, tube	MA (1' at 980°C),	U-Bend, C-ring	0.035	16.15	72.5	9.74	0.01
	U134, tube	S	U-Bend, C-ring	0.031	16.10	73.9	8.90	0.02
	U 572, tube	MA, S	RUB	0.028	15.25	74.5	9.25	-
	WF 242 R	MA, S	ERT spec., RUB	0.03	16.05	73.30	9.20	0.03
	T40, sheet	MAS**	U-Bend, C-ring	0.072	16.03	73.5	8.60	0.13
690	9 E1, tube	MA (1040°C)	RUB	0.028	28.72	61.3	9.16	0.040
	U 455, tube	MA	RUB	0.018	28.90	59.3	10.95	<0.01
304L	U118, tube	MA 1100°C	RUB	0.023	18.15	11.4	67.4	0.50

* MA : Mill-annealed TT : Thermally treated, MA + 14 h 700°C under vacuum S : sensitized 1 h 700°C

** MAS : This sheet is mill-annealed, but due to the high carbon content, it is already sensitized to intergranular corrosion

III. RESULTS

A. Magnesium Chloride Tests

The results of the magnesium chloride tests are summarized in Table 6. The type 304 stainless steel cracked in less than 24 hours in all the solutions. Alloy 600 did not crack at a pH of 2.3, whereas a intergranular crack appeared after 1500 hours at a pH of 1.6 for the non-sensitized condition. The depth of the crack was unable to be determined by metallography due to faulty sampling. In the case of Alloy 690, a 60 µm deep intergranular crack was observed after 288 hours in the most strongly acid medium (pH = 1), and was found to have initiated at the bottom of a pit (Fig. 6). Indeed, numerous pits were observed on both alloys, with depths of up to a few hundred microns.

These results are quite new compared to the data obtained by Copson [1], since they show that

an increase in the aggressivity of the solution shifts the field of chloride SCC to nickel contents higher than those previously reported. However, they confirm the very good resistance of nickel-rich alloys in these environments, since in spite of the aggressivity of the medium, cracks were obtained only after long times, and remained fairly shallow, with depths less than those of the pits which formed simultaneously.

B. Tests in Chloride-Containing Boric Acid Media

All the SCC results obtained in the different chloride media, with and without boric acid, are summarized in Table 7.

1. Tests at 102°C

Alloy 600 does not crack in boiling 27 wt. % boric acid solution in the absence of chlorides. In

Table 6 - Results of the boiling magnesium chloride tests (RUB Specimens)

Alloy	Identification	Heat treatment	pH		
			1	1.6	2.3
304	U118	MA	F <24	F <24	F <24
600	U572	MA	NC 1500 h	F 1500 h	NC 1500 h
		S	NC 1500 h	NC 1500 h	NC 1500 h
690	U455	MA	F 288 , 60 µm	NC 1200 h	NC

* MA : Mill-annealed TT : Thermally treated, MA + 14 h 700°C under vacuum S : sensitized 1 h 700°C

Table 7 - Results of the SCC tests on Alloy 600 in chloride-containing boric acid solutions.

Chemical conditions				Material			Results
T (°C)	H ₃ BO ₃	Cl ⁻	remarks	Heat	specimen	heat T.	
100-102	27%	0	pH _T 2.3	6M U134 T40	C-ring C-ring U-bend	MA S S*	NC 4470 h (0/12) NC 4470 h (0/12) NC 4470 h (0/12)
	27%	2 g/l	pH _T 2.3	6M U134 T40	C+U C+U U-bend	MA S MAS*	NC 5200h (0/16) F 1260 h (9/16) to 2460 h (12/16) IG 650 μm F 330 h (8/12) to 760h (9/12) TG 90 μm
				U134 T40	C-ring U-bend	S MAS*	F 1410h (1/2) IG 700 μm NC 2350h (0/14)
				T40	U-bend	MAS*	F 840h (6/10) TG 160 μm
0	2 g/l	pH _T 2.3 (HCl)	6M U134 T40	C+U C+U C+U	MA S MAS*	NC 1940h (0/16) F 1260 h (2/16) to 2400h (12/16) IG+TG 220 μm F 1260 h (5/16) to 3200h (12/16) TG 100 μm	
250	0	50 g/l	pH _T 2.0 (FeCl ₂)	6R, 6S 6R, 6S U134	U-bend	MA TT S	F 2000h (1/4) IG 10 μm NC (0/4, 2000h) F (2/2, 2000h) IG ~ 1000 μm
	3%			6R, 6S 6R, 6S U134	U-bend	MA TT S	F 2000h (4/4), IG 60 μm F 2000h (1/4) IG 10 μm F 2000h (2/2) IG ~ 1000 μm
290	0	78-260 ppm	pH _T 5.6 [O ₂] = 0	6R	RUB	MA	NC 3000 h (0/1)
	40%	50 ppm	pH _T 3.0 300 ppb O ₂	6R	RUB	MA	F 742h (3/3) IG, 700 μm
		51-128 ppm	pH _T 3.0 [O ₂] = 0	6R	RUB	MA	NC 3030h (0/2)
360	1000 ppm B + 2 ppm Li	0,7 ppm	pH _T ~8.2 [O ₂] = 0	WF 242R	RUB	MA	NC 4250 h (0/2)
					RUB	S	NC 4250 h (0/2)
					CERT 2.5 10 ⁻⁷ s ⁻¹	MA	F 342 h, IG 50 μm
			pH _T ~ 8.2 P _{O2} 4 bar (125 °C)	WF 242R	RUB	S	NC 3250 h (0/2)
					CERT 2.5 10 ⁻⁷ s ⁻¹	S	NC
20 ppm	WF 242R	CERT 2.5 10 ⁻⁷ s ⁻¹	MA	F 35 h, IG 750 μm			

* MA : Mill annealed TT : Thermally treated, MA + 14 h 700°C under vacuum IG : intergranular cracking
S : sensitized 1 h 700°C MAS : mill annealed, but sensitized as-received TG : transgranular cracking

contrast, the addition of 2 g/l of chlorides to this medium promotes the formation of cracks as soon as 330 h of exposure in the sensitized condition (Table 7 and Fig. 7). A remarkable feature is that either transgranular (TG) or intergranular (IG) cracks can be obtained under these conditions. In the absence of boric acid, but with 2 g/l of chlorides and the same pH of 2.3 fixed by the addition of HCl, IG or TG cracks also appear, after exposure for about 1300 h in the sensitized condition (Table 7).

Electrochemical tests were performed on Alloy 600 in these media (Fig. 8). The corrosion rate in the absence of chlorides is low and the corresponding potential is high, indicating good passivity. The behavior deteriorates as the chloride concentration increases, the corrosion current rising and the potential falling. Measurements of the free

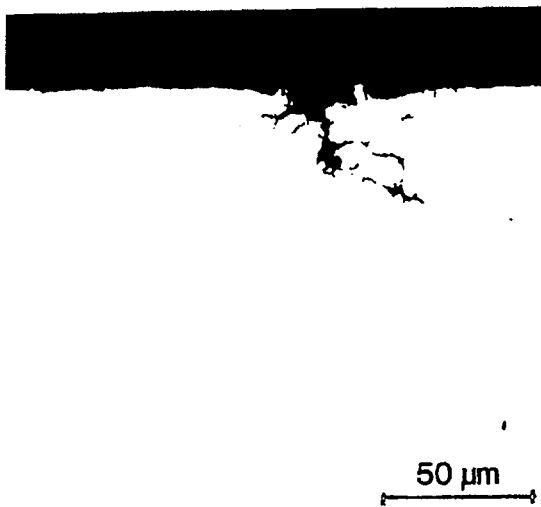


Figure 6 : Alloy 690 in Boiling $MgCl_2$ at pH 1 (312 h) - RUB

potential performed on samples in the sensitized condition show that cracking occurs in a range of potential close to -350 mV/SCE, corresponding to the beginning of the active zone (Fig. 9). This behavior differs from that of 18-10 type stainless grades, which crack in the passive region in the same medium. It is not what might have been expected assuming a local slip step dissolution mechanism at the crack tip. Whereas the resistance and the passivity of the alloy are excellent in the presence of boric acid alone (Fig. 9, curve a), the latter is clearly detrimental when combined with chloride ions. The cracks obtained are longer in the presence of boric acid and the passivity is not as good as in solutions where the boric acid is replaced by HCl to obtain the same acidity (Fig. 9, curves b and c).

2. Tests at 250°C

Tests were carried out, on Alloy 600 at 250°C in deoxygenated 50 g/l chloride solutions, acidified to $pH_T = 2.0$ by the addition of 0.2 M of ferrous chloride. Intergranular cracks were obtained in 2000 h in the absence of boric acid (Table 7).

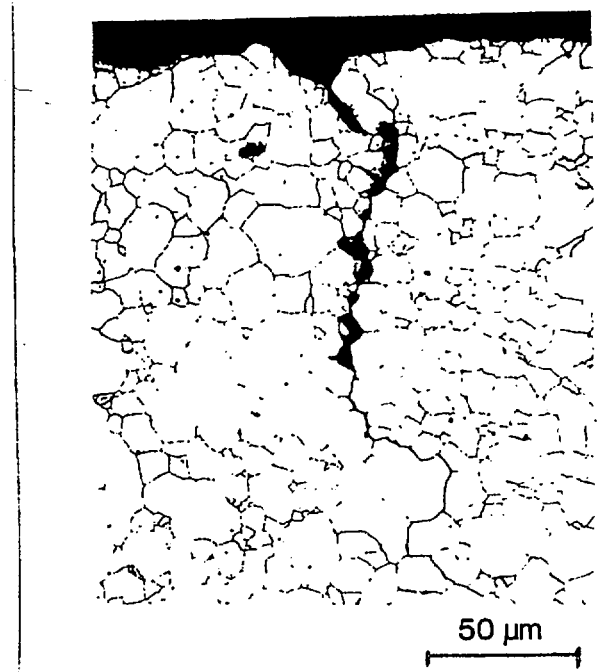


Figure 7 : Alloy 600 in Boiling Boric acid (27 % B) + Cl^- (2 g/l) (1410h) C-Ring

They were deep for the sensitized condition, shallow for the mill annealed condition and absent for the TT condition. Cracking was markedly accelerated by the addition of boric acid, since cracks were obtained in the TT condition and those in the mill annealed condition were deeper. Furthermore, the results show that the sensitized material is more prone to cracking, while the 14 h at 700°C treatment is beneficial. No cracks were observed in Alloy 690 in either of these media, either in the mill annealed or TT conditions.

3. Tests at 290°C

At 290°C, deaerated 40 wt. % boric acid solutions containing 50 ppm of chloride ions produce no cracking in mill annealed Alloy 600 (Table 7). In contrast, the simultaneous presence of oxygen (300 ppb) and chlorides (50 ppm) causes the formation of deep intergranular cracks after about 750 hours. This is due to the deleterious effect of oxygen in the presence of chlorides already mentioned (cf. Table 2) and not to any specific effect of boric acid.

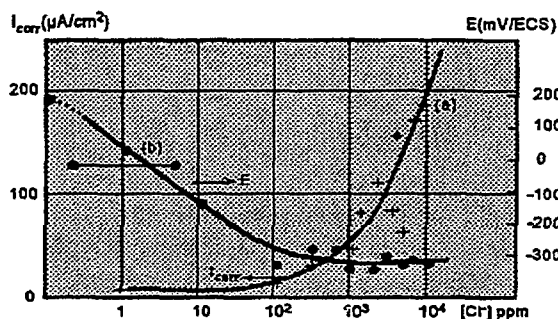


Figure 8 :
Effect of chlorides concentration on the corrosion rate (a) and the rest potential (b) of Alloy 600 (T 40 - sheet). The corrosion rate is deduced from the polarisation resistance ($i_{corr} = B/R_p$ where $B = 33 \text{ mV}$)

4. Tests at 360°C

Experiments at 360°C were performed on Alloy 600 in a simulated primary medium (1000 ppm B + 2 ppm Li), on RUB specimens or in imposed strain rate tests (CERT). The results show (Table 7) that the presence of oxygen alone is not detrimental in the absence of significant amounts of chloride. None of the specimens, even in the sensitized condition, revealed any cracking in oxygenated media without chlorides, whereas the addition of 20 ppm of chlorides is sufficient to induce the rapid formation of deep intergranular cracks.

IV. DISCUSSION

All these tests show that nickel base alloys can undergo chloride stress corrosion cracking in a wide range of temperatures and media. In boiling magnesium chloride solutions at 153°C, acidification of the medium to $\text{pH}_T = 1$ or 1.6 enables cracking to be obtained in Alloys 600 and 690, albeit in long times and at high stresses. In solutions containing 2 g/l of chlorides acidified to $\text{pH}_T = 2.3$, numerous inter- and transgranular

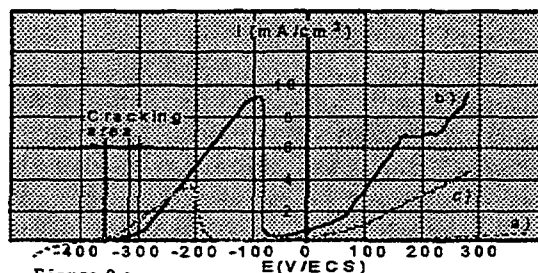
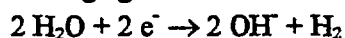


Figure 9 :
I-E curves obtained in boiling solutions on Alloy 600 (sweep rate 36 or 360 mV/h)
a) boric acid 27% (T40, M.A., sensitized)
b) boric acid 27% + Cl^- 2g/l (T40, M.A., sensitized)
c) Cl^- 2g/l + HCl 5.10^{-3} M , pH 2.3 (T40, M.A., sensitized)

cracks were obtained in Alloy 600 at about 100°C. Similar behavior was observed at 250°C in media acidified to $\text{pH}_T = 2$, with and without boric acid. At both 100°C and 250°C, boric acid is detrimental, but is not essential, while sensitization is also an aggravating factor.

At higher temperatures, 290 or 360°C, the media investigated were less aggressive, due to their lower acidities ($\text{pH}_T = 3$ to 8.2) and much lower chloride contents ($< 300 \text{ ppm}$). The results have demonstrated that the presence of chlorides alone, without oxygen, does not induce cracking, and that similarly, a high concentration of oxygen is not at all harmful in the absence of chlorides. Only the simultaneous presence of chlorides and oxygen causes cracking, over the range of pH_T studied, from 3 to 8.2. This can clearly be related to the well known acidification phenomenon which occurs in aerated media in confined zones of stainless alloys, and is the general source of pitting and crevice corrosion in these materials. Once an initial defect has been created, the driving force for local acidification is the hydrolysis of Cr^{3+} ions in the crack, the electrons liberated by the corrosion being consumed by reaction with oxygen outside the

crack. In a deaerated medium, there is no local acidification, since the acidity due to the hydrolysis reaction is consumed inside the crack by reduction of the oxidizing agent :



Acidification is accompanied by an increase in chloride ions to maintain the electrical neutrality. In aerated solutions, this mechanism can involve ions other than chlorides, but the latter are probably more effective than sulfates, for example, whose solubility is lower.

All the cases of SCC encountered can therefore be incorporated in a general pattern, chloride SCC being possible in Alloy 600 provided that the medium is made sufficiently aggressive. The required aggressivity can be induced by different combinations of acidity, chloride concentration and temperature. At low temperatures, the phenomenon is observed only for strong acidities and high chloride concentrations, and is associated with pitting corrosion. At higher temperatures, the necessary acidity level can be attained by local acidification in confined zones.

An interesting question is the role of boric acid. Apart from its effect on the pH, an intrinsically deleterious influence in the presence of chlorides has been demonstrated by the SCC tests at 100 and 250°C. Moreover, the electrochemical measurements have shown that Alloy 600 is effectively passive in the presence of boric acid alone (borates are known to have a passivating influence), whereas in chloride-containing solutions, boric acid appears to be detrimental. The mechanism of this effect is not yet understood.

Finally, it is noteworthy that the cases of transgranular cracking observed are quite rare for Alloy 600, although similar behavior has been reported in lead salt solutions.

Although Alloy 690 has not been studied systematically, it showed good SCC resistance at

250°C in a medium where Alloy 600 underwent cracking. The only case of cracking observed was a small 60 µm deep crack formed after 288 hours in highly acidified boiling magnesium chloride solution, i.e. under extremely severe conditions.

V. CONCLUSIONS

This study has shown that the extremely good SCC resistance of Alloy 600, due to its high nickel content, does not imply complete immunity to this type of attack. Cracking is possible in the presence of chlorides when the medium is made sufficiently aggressive. In particular, this is the case for aerated chloride solutions, in which local acidification can occur. Boric acid can be detrimental in the presence of chlorides, due not only to the associated acidity, but apparently also to an intrinsic effect whose mechanism is not yet understood. The possibility of the occurrence of SCC in Alloy 600 in chloride-containing solutions is of particular interest for studies of cracking in steam generator tubes in the confined secondary medium.

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