UNITED STATES OF AMERICA
NUCLEAR REGULATORY COMMISSION



BEFORE THE ATOMIC SAFETY AND LICENSING BOARD

| | | |
|---|---|---|
| In the Matter of | ) | |
| | ) | |
| METROPOLITAN EDISON COMPANY, ET AL. | ) | Docket 50-289 |
| | ) | (Steam Generator Tube Repairs) |
| (Three Mile Island Nuclear | ) | |
| Generating Station, Unit 1) | ) | |

## JOINT INTERVENORS RESPONSE TO LICENSEE'S SECOND SET OF INTERROGATORIES

Responses are here provided to Licensee interrogatories using Licensee's letter, number designations as noted in "II Interrogatories".

A. General Interrogatories

II - 1 - Norman O. Aamodt prepared all interrogatory answers.

II - 2a - No proposed witnesses are named.

B. Interrogatories on Contention 1(2)

II - 1(2) - 1(a) - It might have been a cause.

(b) - It may pose a significant threat of future IGSCC.

2(a) - See "Observations On The Cracking Process - Role of Sulfur", Pg. 1157, 8 of "Historical Review Of The Principle Research Concerning The Phenomena Of Cracking of Nickel Base Austentitic Alloys" (hereafter referred to as "The Paper" (attached).

(b) - See subsequent answers.

3 - See answer to II-1(2) - 2(a).

4 - I do not know.

5 - I do not know.

6 - NA

7 - Hot water, some oxygen, some tensile stress and time. In essence, the IGSCC is "incubating" with time being the key variable. With high nickel content, some moderate level of carbon and even trace amounts of sulfur, sensitized Inconel 600 will crack in an aqueous environment which is not free of oxygen.

8 - The Paper.

9 - All operating conditions.

10 - The Paper; see answer to II-1(2)2(a).

11 - Same as 10.

12 - Rate of IGSCC initiation, or time to generation of cracks, can be expected to shorten with increased nickel or sulfur content, increased oxygen or chlorine level, increased water temperature and increased stress level.

13-(a) See answer to 12.

(b) I do not know outer bounds.

14 - See The Paper.

15 - I do not know, other than those that cause increased oxygen levels.

16 - NA

17 - High nickel and carbon content.

18 - See The Paper.

19 - I do not know; "coupling" effects described in The Paper may provide clues.

20 - NA

21 - The Paper. It is short and topically developed as discussed above.

22 - I do not know.

23 - NA

24 - Yes

25 - oNote (2) of The Paper.

oNote (5) of The Paper. Note absence of contaminants in aqueous environment.

oNote (6) of The Paper.

oNotes (8), (9), (10) of The Paper.

oNote (11) of The Paper.

26 - I do not know.

27 - NA

28 - I do not know.

29 - NA

30 - See above answers.

31 - I do not know yet.

32 - I do not know yet.

33 - I do not know yet.

C. Interrogatories on Contention 1(3)

II-1(3)-1 - I allege that islands of IGA may be precursors of IGSCC, that all that is needed for IGSCC to develop may be a additional time for "incubation" to be complete.

-2 - See Note (1) (Pg. 1149) of The Paper.

- As noted by Third Party Review, IGSCC was frequently observed in areas of concentration of IGA islands.

- Threfore: Role as precursor is reasonably deduced.

3 - Yes

4 - See answers to B.

5 - Yes

6 - o Additional exposure to oxygen, chlorides, lead, etc. might shorten "inclubation" period.

o I do not know which elements or compounds could serve as synergists, nor their concentrations (though trace amounts would probably suffice for synergistic effects to occur.)

7 - o Potential corrodents are described in Third Party Review of The Paper.

o Synergists - Personal experience with anti-oxidant systems.

8 - See 7.

9 - I do not know yet.

10 - I do not know yet.

11 - I do not know yet.

D. Interrogatories on Contention 1(5)

II 1(5)-1 - Low valence carbonions which could mimic activity of sulfur in sulfide forms.

2 - Chemical similarities of carbon and sulfur.

3 - o Valence lower than 4.

o "Carbonaceous" is almost meaningless apart from the fact that carbon is present in some undefined form(s).

4 - Yes, possibly.

5 - I do not know and, unfortunately, GPUN does not, nor is it evident than any one else does.

6 - NA

7 - Same as 5.

8 - NA

9-a- I do not know.

b- I do not know.

c- Mechanism probably would be similar to that with sulfur. I do not know what synergists might be present.

10 - NA

11 - Any and all that might occur in the system. Note: A "synergist" is not a synergist if it does not produce a synergistic effect.

12-a- I do not know, but GPUN should.

b- I do not know, but GPUN should.

c- I do not know, but GPUN should.

13 - GPUN should know whether or not synergistic effects are likely to occur (or have occurred) if GPUN is to develop a suitable confidence level with regard to any prediction of anticipated IGSCC initiation.

14, 15, 16 - No questions.

17 - PhD., Chemistry, many years on Staff of Bell Telephone Laboratories, inventor of various chemical systems dependent on synergistic effects, widely published. I do not have his resume.

18 - See 17. This work supports Contention 1(5) in that the operable element of expertise is knowledge of synergism, per per se.

19 - I do not know.

20 - NA

21 - If we should use Dr. Hansen as a witness or source of help, I will provide this information immediately. I do not have access to this information at this time.

22 - I do not know yet.

23 - I do not know yet.

24 - I do not know yet.

Norman O. Aamodt for Joint Intervenors

February 27, 1984

Conf. June 12-16, 1973 Unieux-Firminy, France
International Corrosion Conference Series NACE-5 NACE 1977 Houston, Texas

# HISTORICAL REVIEW OF THE PRINCIPAL RESEARCH CONCERNING THE PHENOMENA OF CRACKING OF NICKEL BASE AUSTENITIC ALLOYS[(1)]

*J. Blanchet, H. Coriou, L. Grall, C. Mahieu, C. Otter, and G. Turluer**

In a number of studies,[1-3] we have shown that austenitic alloys (nickel-chromium-iron) with high nickel contents (Ni = 77%), such as Inconel 600, are susceptible to the phenomena of stress corrosion. The cracking is essentially intergranular and appears in demineralized water, at 300 and 350 C, in the absence of oxygen, chlorides, and traces of certain harmful impurities (lead),[4] and at the bottom of recess zones. It is significant that the period of incubation preceeding the appearance of cracks is long (on the order of several months under our experimental conditions). Inconel 600 type alloys are often recommended for the construction of various reactor components that undergo stress: steam generators and internal structures of high-pressure water reactors. We will review some previous results in the first part of the paper. (1)

## Tests in Water at 350 C

The nominal compositions of the alloys are as follows: (1) Cr 17%, Ni 10%, (2) Cr 17%, Ni 35%, (3) Cr 17%, Ni 45%, (4) Cr 17%, Ni 77%, (5) Cr 20%, Ni 45%, Mn 5%, and (6) Inconel 600.

We have performed experiments with 1 mm sheet specimens in the quench annealed condition. The exact compositions of these alloys are given in Table 1.

TABLE 1
(Compositions Expressed in Percent)

| Types Cr/Ni | C | Cr | Ni | Mn | Si | Ti | Nb | S | Fe |
|---|---|---|---|---|---|---|---|---|---|
| 18/10 | 0.012 | 17.1 | 10.3 | 5 | 0.3 | | | 0.010 | Remainder |
| 18/25 | 0.025 | 17.3 | 34.7 | 0.9 | 0.5 | | | 0.010 | Remainder |
| [illegible]45 | 0.014 | 17.3 | 44.3 | 1.0 | 0.5 | | | 0.007 | Remainder |
| 20/45 | 0.030 | 19.2 | 45.5 | 4.9 | 0.7 | | 0.34 | 0.005 | Remainder |
| 18/77 | 0.002 | 18.0 | 77.3 | 1.0 | 0.5 | | | 0.007 | Remainder |
| Inconel 600 | 0.040 | 14.9 | 78.4 | 0.12 | 0.2 | 0.24 | | | Remainder |

### *Pure Water*

These alloys have been tested under the three following conditions: (1) medium: demineralized and deoxygenated water ($O_2 \leq 3\ \mu g \cdot kg^{-1}$); (2) temperature: 350 C, and (3) stress applied by flexure (0.5% permanent deformation).

Cracking of the alloy Cr 17%, Ni 77% is noted after 6 months of testing, and that of Inconel 600 after 9 months. Figures 1 and 2 show the micrographic aspect of the cracking for these two materials. The cracking occurs almost always intergranularly with, however, a few rare transgranular paths for the alloy Cr 17%, Ni 77%. The other alloy types: Cr 17%, Ni 10%; Cr 17%, Ni 35%; Cr 17%, Ni 45%; and Cr 20%, Ni 45%, Mn 5% do not show any cracking whatsoever after 10 months of testing. Other researchers[5,6] have also produced stress cracking in Inconel 600 in pure water at high temperatures. (2)

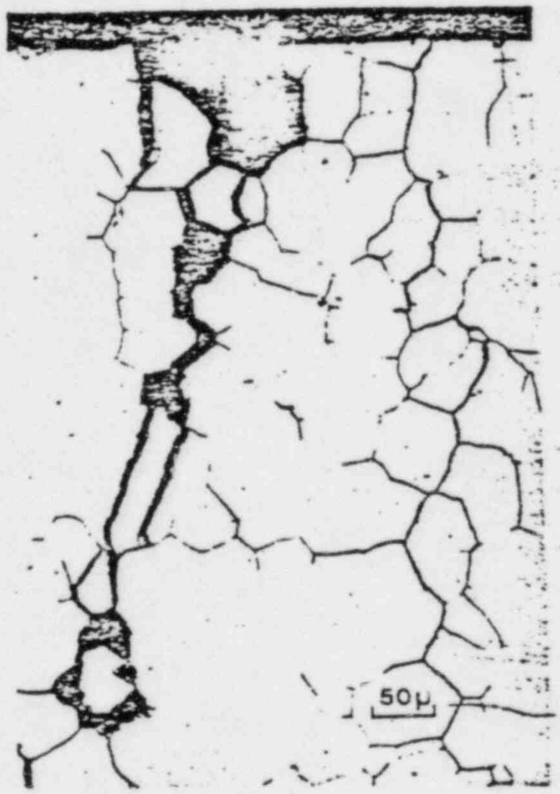


**FIGURE 1 – Alloy Cr 17%, Ni 77% cracked after six months of testing in 350 C water.**

It is noted that cracking as shown in Figure 1 occurs in an alloy whose composition is similar to that of Inconel 600 but which has been specially prepared by vacuum melting and has a very low carbon content, C = 0.002% (commercial alloys contain 10 to 20 times as much carbon). This extra low carbon alloy behaves almost the same as the commercial alloys. Also, tests made under dynamic conditions (resistivity of the water maintained constantly at 1 M Ω/cm, $O_2 \leq 3\ \mu g \cdot kg^{-1}$, temperature 350 C) have led to the same results.[7] Electron micrographs reveal carbide precipitation in commercial Inconel 600, whereas the grain

(1)Translated from the French by R. D. McCright.

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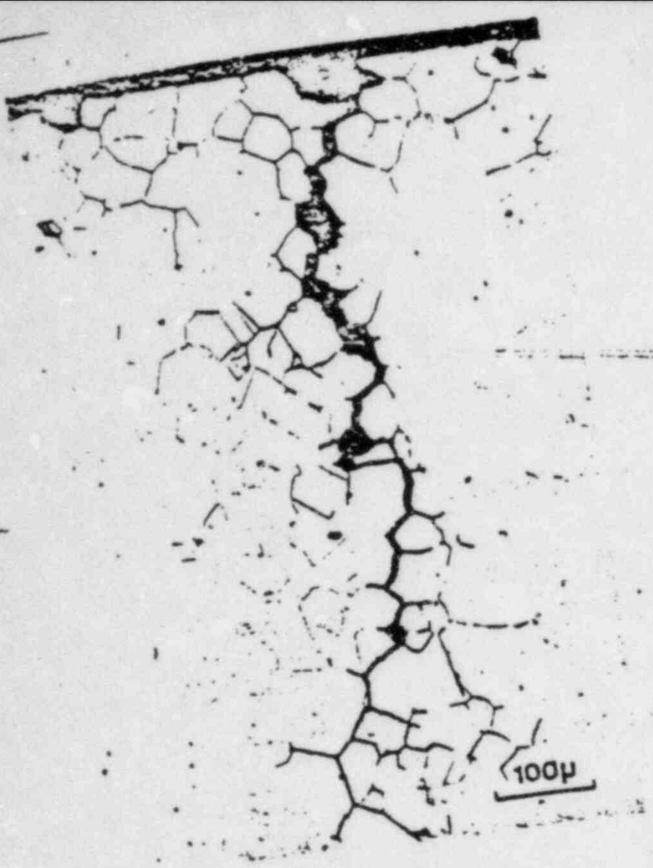

FIGURE 2 — Alloy Inconel 600 cracked after nine months of testing in 350 C water.

boundaries of the extra low carbon alloy are practically free of precipitate. In the second part of this article, the influence of heat treatments will be discussed.

Our research on stress corrosion cracking (SCC) of high nickel alloys is the subject of our other papers.[8,9]

*Water Containing Chloride*

It appeared useful to effect some stress corrosion test in deoxygenated water at high temperature (350 C), with chloride additions [1 $g \cdot \ell^{-1}$ $Cl^{-}$(1) as NaCl]. Consequently, a series of austenitic alloys (chromium-nickel-iron) with 17% chromium and a nickel content varying from 10 to 77% (Table 1) was tested. After 6 months of corrosion under stress applied by flexure (0.5% permanent deformation), cracks appeared in the alloys with 10% and with 77% nickel. The cracks are *transgranular* (Figures 3 and 4) in the 10% nickel alloy and *intergranular* (Figure 5) in the 77% Nickel alloy and in commercial Inconel 600 (Cr 15%, Ni 78%). Transgranular striations were revealed in the 15% nickel alloy. The alloys with 25, 35, 45, and 65% nickel do not show any cracking.[7]

Tests performed in pure or chloride containing water at high temperature, therefore, show that the nickel content is the predominant factor in determining the occurrence and the mode of stress corrosion in these alloys.

From the practical point of view, the totality of our results points out the interest in austenitic alloys (chromium-nickel-iron) with intermediate nickel contents (Ni 35 to 45%).

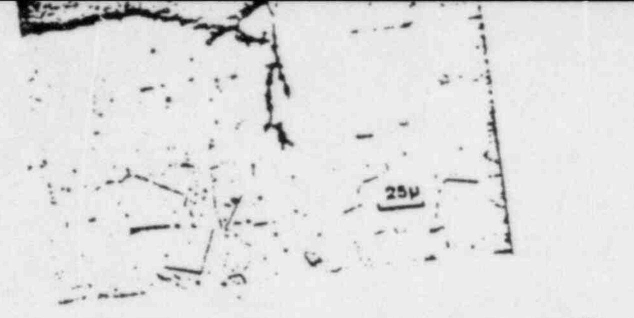

FIGURE 4 — Transgranular cracking of a Cr 17%, Ni 10% steel in water containing 1 $g \cdot \ell^{-1}$ $Cl^{-}$ (NaCl), at 350 C after six months of testing ($O_2 \leq 3$ $\mu g \cdot kg^{-1}$).

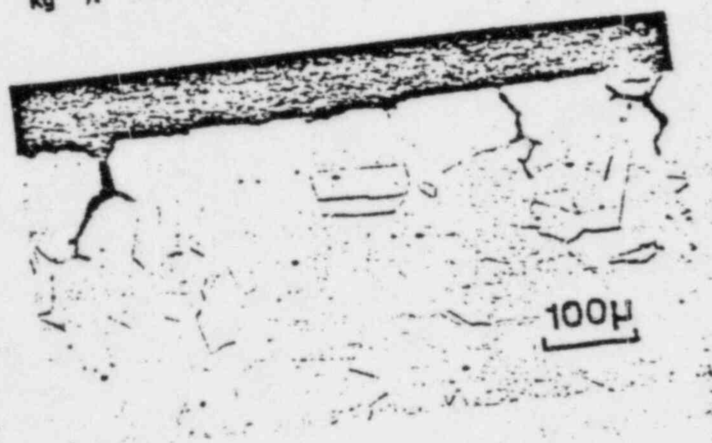

FIGURE 5 — Intergranular cracking of a Cr 17%, Ni 77% alloy in water containing 1 $g \cdot \ell^{-1}$ $Cl^{-}$ (NaCl), after six months of testing (experimental conditions same as those in Figures 3 and 4).

FIGURE 3 — Transgranular cracking of a Cr 17%, Ni 10% steel in water containing 1 $g \cdot \ell^{-1}$ $Cl^{-}$ (NaCl), at 350 C after six months of testing ($O_2 \leq 3$ $\mu g \cdot kg^{-1}$).

## Role of Various Parameters

The service conditions of austenitic alloys with high nickel content in pressurized water reactors involve several parameters. It is important to define the influence of these from the practical point of view as well as that of understanding the phenomenon.

During recent studies, we have determined the role played by the following parameters: stress (extremely variable in the installations), heat treatment (for example those involving intergranular sensitization), coupling with other materials (often encountered in steam generators), grain size, and structure.

(1) Concentration extrapolated to 350 C.

Except as otherwise indicated, these studies have been performed at 350 C in water with a very low oxygen content ($O_2 \leq 3\ \mu g \cdot kg^{-1}$) and whose initial resistivity is greater than 1 MΩ-cm.(2) The autoclaves are made of 18/10 stainless steel.

*Relationship Between the Stress and the Time to Failure*

This relationship has been studied on Inconel X 750, which has the same basic composition as Inconel 600, but with additions of elements for structural hardening (Al, Ti, Nb). Cylindrical test specimens ($\phi$ 2.2 to 4.0 mm) have been machined from a bar that the fabricator had heat treated in such a way to obtain a yield stress $E_{0.2}^{350}$ C(3) = 80 $kg \cdot mm^{-2}$. The composition of the alloy expressed in percent is given in Table 2.

**TABLE 2**
(Compositions Expressed in Percent)

| C | Cr | Ni | Mn | Si | S | Fe | Al | Ti | Nb |
|---|---|---|---|---|---|---|---|---|---|
| 0.04 | 15.2 | 72.5 | 0.12 | 0.39 | 0.004 | 6.4 | 1.00 | 1.86 | 0.87 |

**Experimental Method.** The stress is applied in tension by means of the apparatus shown in Figure 6 and constructed entirely of 18/10 stainless steel. This apparatus consisted principally of a calibrated piston, provided with a cooled toric joint, and upon which the pressure from the saturated steam at the test temperature acts. An assembly of eitht specimens, fastened together with anchoring pieces and electrically insulated by oxidized Zircaloy 2 rings, is

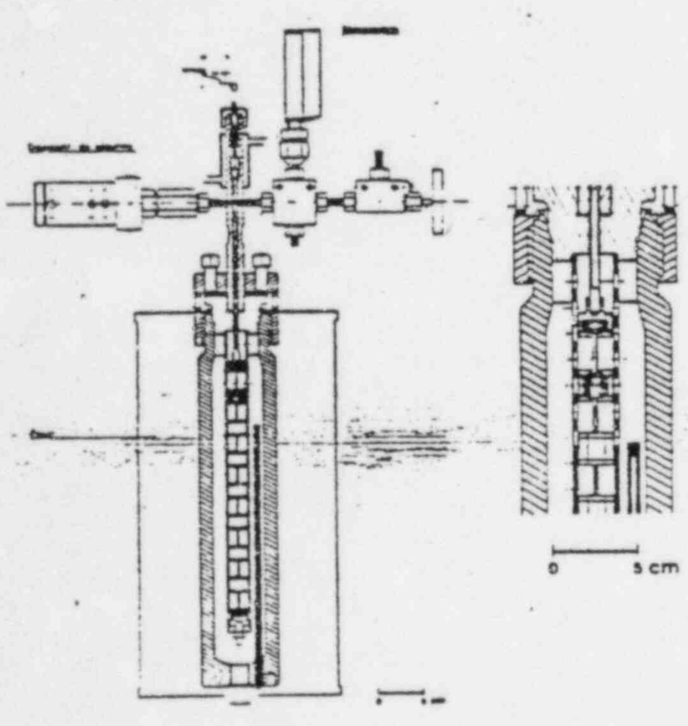


FIGURE 6 – Autoclave with tensile stressing apparatus. Detail of specimen arrangement.

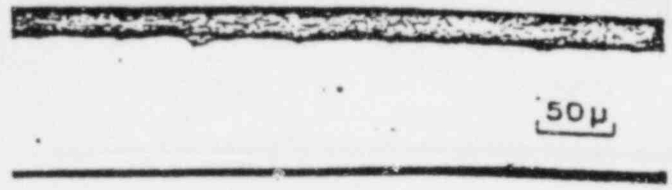


FIGURE 7 – Initial surface condition: longitudinal section of a specimen before test.

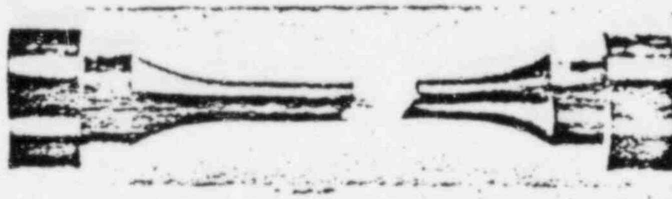

FIGURE 8 – Specimen of Inconel X 750 broken after 210 hours in 350 C water under tensile stress: $\sigma = 1.2E_{0.2}^{350\ C}$.

attached at one end to the piston and at the other to a fixed point situated at the end of a thick perforated tube which leads to the bottom of the autoclave. By action of the saturated steam, the piston exerts a tensile force which is known by previous calibration. The diameter of the exposed part of each of the test specimens is chosen in such a way that the test specimen undergoes the desired uniaxial stress.

When a specimen fractures, a solitary finger of the piston activates a microswitch which cuts off the heat to the furnace of the autoclave. The recording of the temperature curve allows the determination of the exact time to failure of the specimen. After the autoclave is opened, all of the samples are examined by optical microscopy. The cracked specimens, as well as the broken ones, are withdrawn and replaced.

This method of tensile straining with constant load is severe. In effect, when a crack starts to form, the uniaxial stress increases and this tends to accelerate the cracking.

The surface preparation of the specimens involved a finish machining (Figure 7) followed by ultrasonic cleaning in a ternary mixture of acetone-alcohol-toluene. Diameters of the test specimens have been chosen in order to obtain the following applied stresses: 0.4, 0.6, 0.8, 1.0, 1.2 $E_{0.2}$ 350 C. (The precision of the diameter of the exposed part of the specimens involves an error of the calculated stress less than or equal to 1%.)

Results. Fractures of the specimen (Figure 8) result from a characteristic intergranular cracking (Figure 9). For each stress level, the result has been obtained from 10 to 20 test speicmens and the results are expressed as the length of time necessary to cause rupture or cracking of a given percentage of the specimens (Table 3).

We can, thus, draw a curve for each alloy, $\sigma = f(t)$, $\sigma$ being the applied stress and t being the length of time necessary to crack 50% of the specimens (Figure 10).

The time of failure increases significantly when the stress level is lower, this factor being much more important for small applied stresses. For the range of stresses studied, the shape of the curve $\sigma = f(t)$ does not indicate the existence of a threshold stress level below which cracking would not occur for each given alloy.

(2)The resistivity measured after opening the autoclaves when the specimens have fractured was always on the order of 0.2 MΩ-cm.

(3)Editor's note – This shorthand nomenclature indicates the respective 0.2% offset yield stress at the indicated temperature.

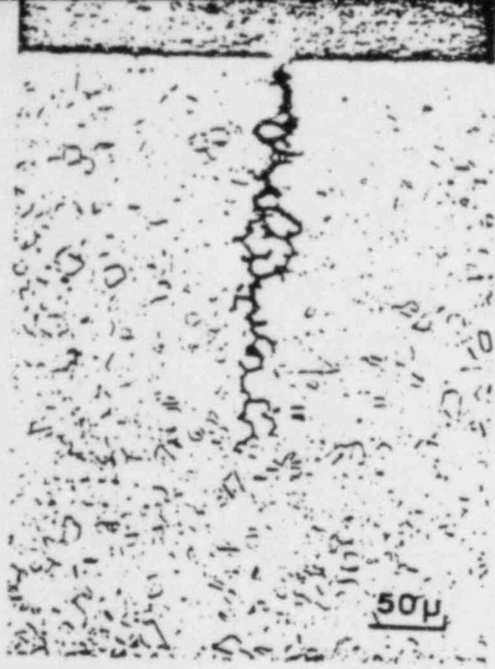


FIGURE 9 — Intergranular aspect of cracking in Inconel X 750 tensile stressed ($\sigma$ = 1.0 E 0.2 350 C) after 510 hours in 350 C watar.

TABLE 3

| Applied Stress | Number of Samples (Percent of Samples that Cracked) | Elapsed Time Until Fracture or Cracking 100% | 80% | 60% | 30% | 10% |
|---|---|---|---|---|---|---|
| 1.2 E 0.2 350 C | 10 | 260 | 220 | 210 | 200 | 160 |
| 1.0 E 0.2 350 C | 19 | 1860 | 410 | 320 | 230 | 220 |
| 0.8 E 0.2 350 C | 18 | | 1700 | 910 | 510 | 350 |
| 0.8 E 0.2 350 C | 20 | | | 3860 | 1800 | 410 |
| 0.4 E 0.2 350 C | 10 | | | | | 4170 |

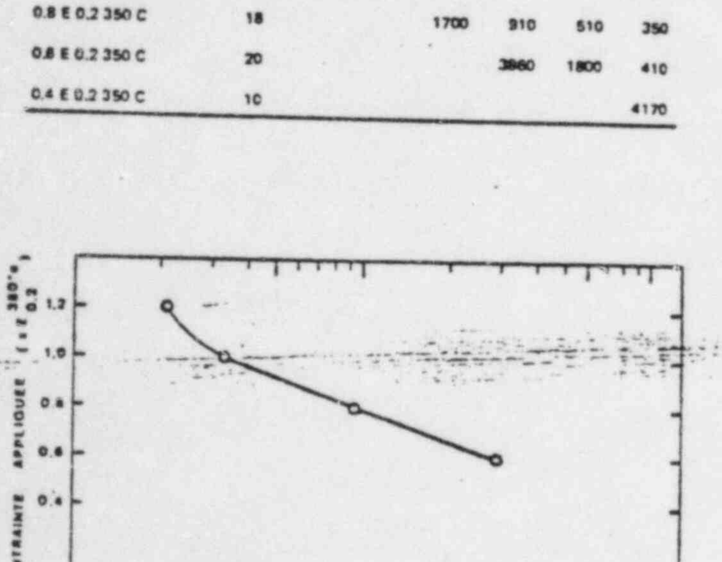


FIGURE 10 — Relationship between the applied stress and time until 50% of the specimens failed in water at 350 C. (Note: X-axis = time, in hours, before fracture or cracking: Y-axis = applied stress).

*Influence of Heat Treatment*

Nickel base, nickel-chromium-iron alloys differ from 18/10 stainless steels by a smaller solubility of carbon in the austenitic matrix; thus, carbides are frequently observed in industrial alloys.[10] It has been previously shown[7] that an Inconel 600 type alloy, with a very low carbon content (C = 0.002%), in pure water at 350 C shows a susceptibility to stress cracking practically identical to that of commercial Inconel 600 alloy in the quench-annealed state. Electron microscopic examinations show intergranular precipitations in the commercial alloys, whereas the grain boundaries of the low carbon alloy are free of carbide precipitates. As a complement to this study, it appeared interesting to us to examine the occasional influence of certain heat treatments, such as those of sensitization.

**Operating Conditions.** The materials studied include two industrial grades of Inconel 600 and an alloy of the type Cr 17%, Ni 77% with a particularly low carbon content. The compositions, expressed as percent, of these different alloys are given in Table 4.

TABLE 4
(Compositions Expressed in Percent)

| | C | Cr | Ni | Mn | Si | Ti | S | Fe |
|---|---|---|---|---|---|---|---|---|
| A = Inconel 600 | 0.053 | 15.9 | 73.8 | 0.18 | 0.40 | 0.22 | 0.0096 | Remainder |
| B = Inconel 600 | 0.040 | 14.9 | 78.4 | 0.12 | 0.21 | 0.24 | 0.0067 | Remainder |
| C = Alloy 17/77 | 0.002 | 18.0 | 77.3 | 1.06 | 0.51 | 0.00 | 0.0070 | Remainder |

Test specimens (50 x 10 x 1.0 or 1.3 mm) were descaled in a hydrofluoric-nitric acid mixture in a manner to regularly eliminate about 10 μm of metal from each face. This descaling is performed either after water quenching or before the sensitization treatment, when this is applied.

All of the test specimens then undergo an activation treatment in dilute hydrochloric acid followed by a passivation treatment in nitric acid. A photomicrograph taken of each lot after descaling indicated the absence of intergranular indentations on specimens so prepared.

The specimens are stressed in a horseshoe by cold forming with the aid of a mandrel and a mold. The specimens are then inserted in a stirrup and mounted on supports of the same grade of material. These assemblies, which are analogous to those in Figure 9 but without galvanic coupling, are electrically insulated from the support assembly and from the autoclave by fritted alumina pieces for tests performed in water and by oxidized Zircaloy for tests performed in lithium hydroxide.

The maximum stress of the external fiber at 20 C, evaluated by strength of material calculations and by micro-hardness measurements, is estimated at 180 ± 15% of the yield stress of the alloy before bending.

The starting values of the yield stress $E_{0.2}$ for the various grades are given in Table 5.

TABLE 5

| | $E_{0.2}$ at 20 C in kg · mm$^{-2}$ |
|---|---|
| A = Inconel 600 | 40 |
| B = Inconel 600 | 24 |
| C = Alloy 17/77 | 23 |

corresponds to an industrial treatment of *incomplete* solubility of the carbides; (2) the quenched condition which is obtained by a *complete* solubility of carbides with the appropriate heat treatment, holding from one to two hours at 1100 C followed by water quench; and (3) sensitized condition characterized by precipitation of carbides principally at grain boundaries after a treatment of one hour at 700 C followed by quenching in helium gas.

For the specimens treated above, tensile tests and electron microscope examinations were performed. Table 6 summarizes the characteristics of the studied alloys.

Results. The proportion of cracked specimens, as well as the elapsed time before cracking, are gathered in Table 7.

TABLE 6

| [illegible] | [illegible] Condition | Yield Strength [illegible] at 20 C (kg · mm⁻²) | [illegible] A% at 20 C | [illegible] | [illegible] | Figure |
|---|---|---|---|---|---|---|
| | A1 = [illegible] | 40 | [illegible] | [illegible] | [illegible] | 11 |
| Alloy A [illegible] C = [illegible] | A2 = [illegible] | [illegible] | 47 | [illegible] | [illegible] | 12 |
| | A3 = [illegible] | [illegible] | [illegible] | [illegible] | similar to A1 + [illegible] | 13 |
| | B1 = [illegible] | [illegible] | 47 | [illegible] | [illegible] | 14 |
| Alloy B [illegible] C = [illegible] | B2 = [illegible] | [illegible] | 47 | 75 | [illegible] | 15 |
| | B3 = [illegible] | [illegible] | [illegible] | [illegible] | similar to B1 + [illegible] | 16 |
| Alloy C Cr 17%, Ni 77% C = [illegible] | C2 = [illegible] | [illegible] | [illegible] | 75 | [illegible] | 17 |
| | C3 = [illegible] | [illegible] | [illegible] | 75 | [illegible] | 18 |

TABLE 7

| [illegible] Condition | Alloy A [illegible] C = [illegible] As-Received | As-Quenched | Sensitized | Alloy B [illegible] C = [illegible] As-Received | As-Quenched | Sensitized | Alloy C Cr 17%, Ni 77%, C = [illegible] As-Received | Sensitized |
|---|---|---|---|---|---|---|---|---|
| [illegible] at 20 C (kg/mm⁻²) [illegible] | 72 | [illegible] | 72 | 40 | [illegible] | 40 | 41 | 41 |
| [illegible] |  |  |  |  |  |  |  |  |
| 750 hours | 0/6 | 0/3 | 0/3 | 0/3 | 0/7 | 0/7 | 4/7 | 0/5 |
| 1500 hours | 0/6 | 0/3 | 0/3 | 0/3 | 0/7 | 0/7 | 7/7 | 3/5 |
| 2750 hours | | 0/3 | 0/3 | 1/3 | 0/7 | 0/7 | | 0/5 |
| 3000 hours | | 0/3 | 0/3 | 2/3 | 0/7 | 0/7 | | |
| 4500 hours | | 1/3 | 0/3 | 2/3 | 0/7 | 0/7 | | |
| 5750 hours | | 1/3 | 0/3 | 3/3 | 0/7 | 0/7 | | |
| 10000 hours | | 2/3 | 0/3 | | 1/7 | 0/7 | | |

The following points are concluded from these tests: (a) All of the alloys tested in the as-received state were susceptible to intergranular cracking, although the appearance and distribution of carbides were very different from one alloy to another; (b) the same alloys tested in the as-quenched state also were susceptible to intergranular cracking. This treatment resulted in the complete solution of carbides and the absence of carbides in grain boundaries; and (c) a sensitization treatment effected from the as-received state for the two grades of Inconel 600 retarded stress cracking. In effect, under our operating conditions and after 10,000 hours of testing, no cracking was observed at all in these specimens.

This behavioral difference is especially remarkable for specimen A (Inconel 600). Cracks of samples in the as-received condition were repeatedly observed after 1500 hours of testing whereas in the sensitized condition no intergranular cracking at all was observed.

On the other hand, for alloy C: Cr 17%/Ni 77%, with a particularly low carbon content, (0.002%), and with a sensitization treatment of 700 C, no carbides were precipitated in the grain boundaries as is shown in Figure 18. The susceptibility of this alloy to stress corrosion is, therefore, practically the same whatever its heat treatment.

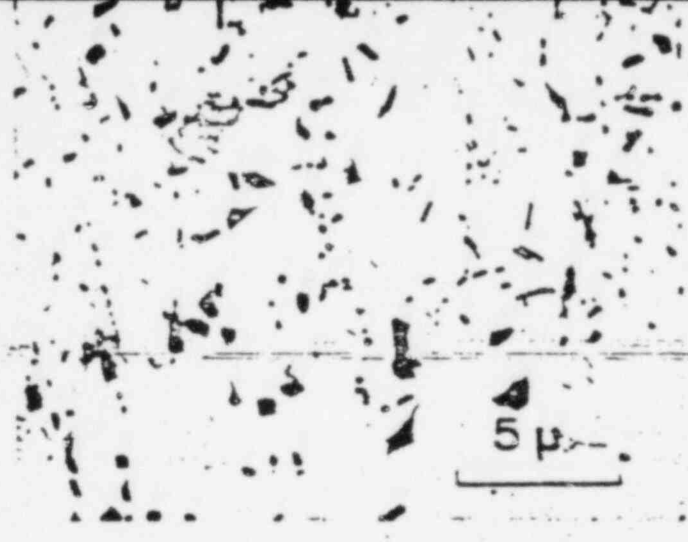


FIGURE 11 — Alloy A (Inconel 600) electron microscopic examinations. A1 = as received condition.

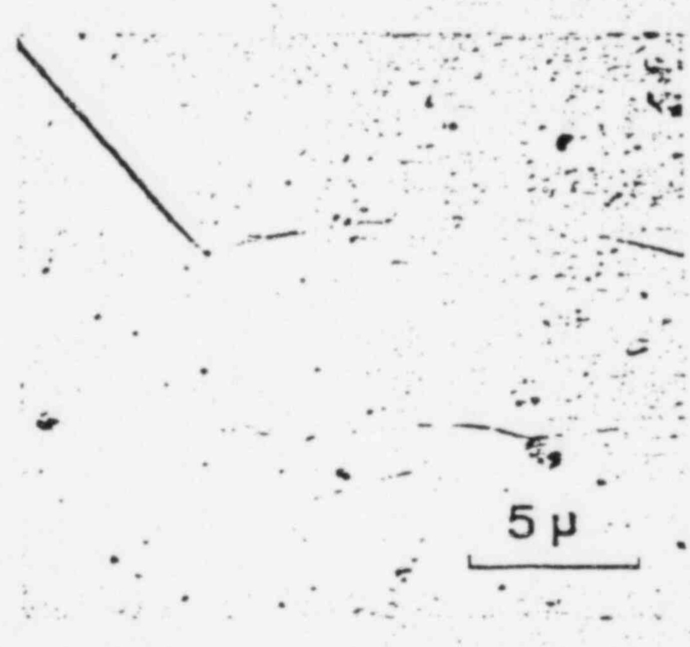


FIGURE 12 — Alloy A (Inconel 600) electron microscopic examinations. A2 = Quenched in water after 2 hour treatment at 1100 C.

*Influence of Coupling with Other Metals*

A study has been made on the influence of coupling with mild steel, with stainless steel (Cr 18%/Ni 10%/C < 0.03%), with gold and with platinum, on the stress corrosion of Inconel 600 alloys (grades A and B) and Inconel X 750 whose composition expressed in percent is given in Table 8. This alloy has a yield stress $E_{0.2}$ 20 C = 84 kg · mm$^{-2}$.

The specimens were tested in the as-received condition (see Table 6) and descaled in a hydrofluoric-nitric medium (thickness removed: 10 µm).


FIGURE 13 – Alloy A (Inconel 600) electron microscopic examinations. A3 = Sensitized condition (one hour at 700 C).

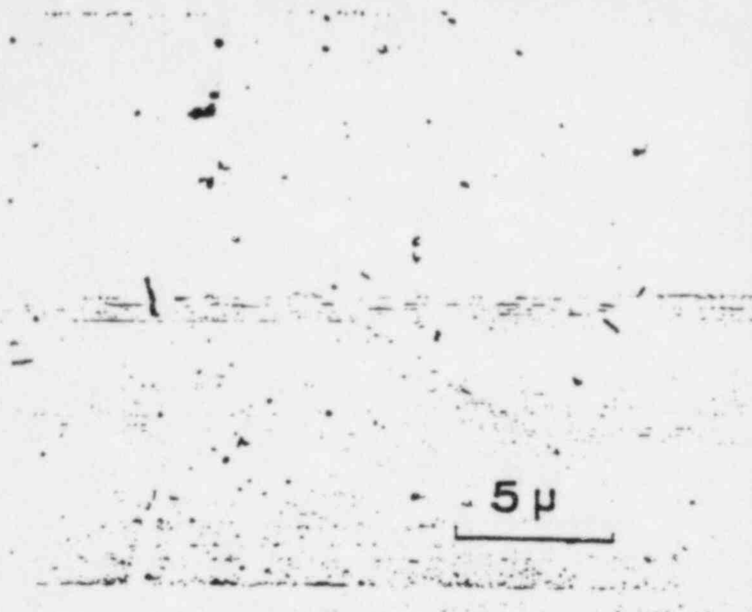


FIGURE 15 – Alloy B (Inconel 600) electron microscopic examinations. B2 = Quenched in water after 2 hour treatment at 1100 C.

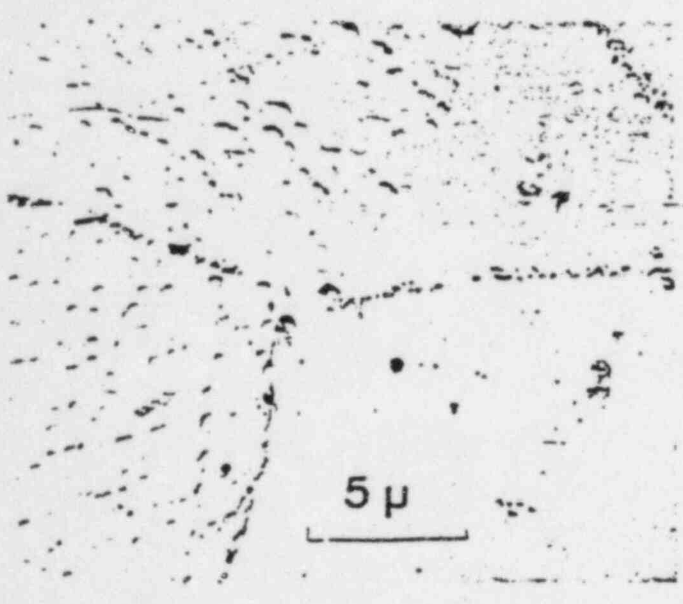


FIGURE 14 – Alloy B (Inconel 600) electron microscopic examinations. B1 = as received condition.

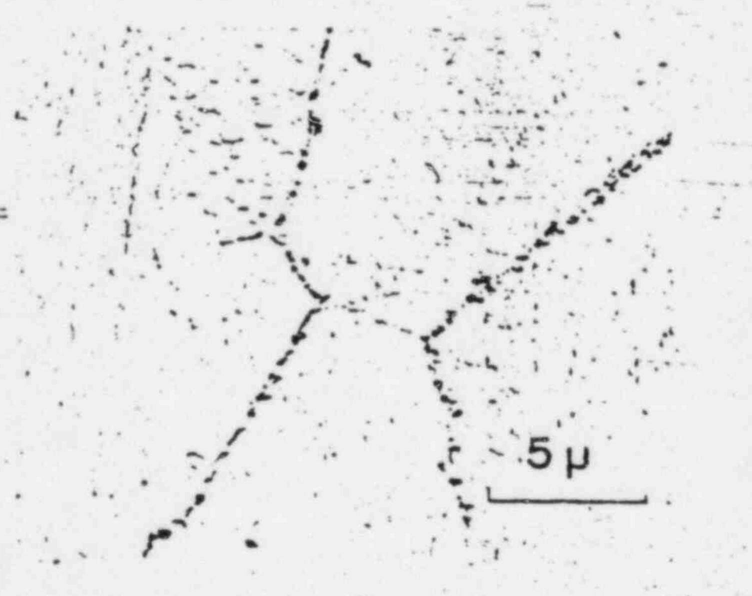


FIGURE 16 – Alloy B (Inconel 600) electron microscopic examinations. B3 = Sensitized condition (one hour at 700 C).

The couplings were made in the apparatus previously described, avoiding all crevice effects between the materials as illustrated in Figure 19. The stirrup and the holding screw are, moreover, made of Inconel 600 in order to eliminate all parasitic effects.

These tests were carried out in demineralized water, whose initial resistivity was greater than 1 MΩ-cm, and in solutions of lithium hydroxide whose pH was 10.5 and 11.5. These various solutions were deoxygenated ($O_2 \leqslant 3$ $\mu g \cdot kg^{-1}$).

At each opening of the autoclaves for examining the specimens, the resistivity of the water was on the order of 0.2 MΩ-cm. The variation of pH in the lithium hydroxide solutions never went beyond 0.5 pH units.

The results are summarized in Tables 9 and 10.

In water, the test performed with cold-worked Inconel 600 ($E_{0.2}^{20\,C}$ = 40 kg·mm$^{-2}$) indicates that coupling with gold leads to the absence of cracking for the conditions and for the time considered.

Coupling of this alloy with stainless steel seems to have a slightly unfavorable influence, but this is not very clear under our conditions.

In lithium hydroxide at pH = 11.5, the effect due to coupling does not seem to be detectable. This medium exercises a retarding action on cracking.

After 12,000 hours of testing in water 350 C, we note a ~~negligible~~ major influence of coupling grade B Inconel 600 and Inconel X 750 with mild steel. The same conclusion cannot

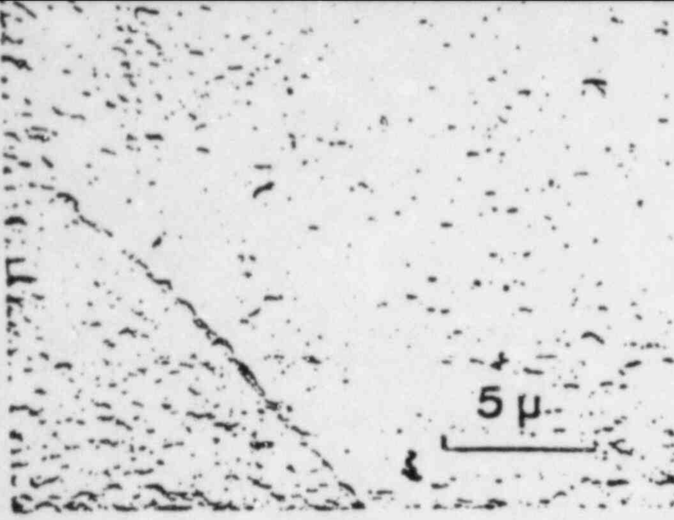


FIGURE 17 – Alloy C (Cr 17%, Ni 77%, C 0.002%) electron microscopic examinations. C2 = as received condition.

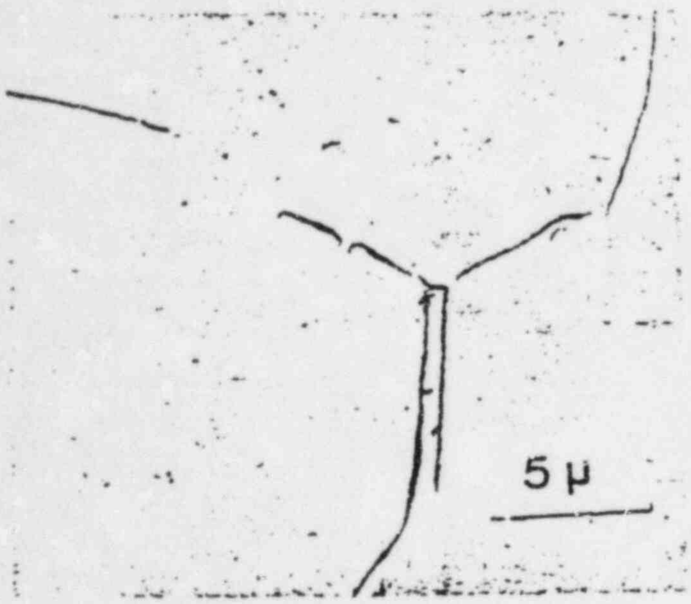


FIGURE 18 – Alloy C (Cr 17%, Ni 77%, C 0.002%) electron microscopic examinations. C3 = Sensitized condition (one hour at 700 C).

TABLE 8

(Compositions Expressed in Percent)

| C | Cr | Ni | Mn | S | Fe | Al | Ti |
|---|---|---|---|---|---|---|---|
| 0.05 | 14.7 | 70.9 | 0.10 | 0.05 | 6.20 | 0.66 | 1.96 |

be made from Inconel 600 coupled with 18/10 stainless steel.

*Influence of Grain Size*

Some tests were performed on Inconel 600 specimens with a relatively large grain size (between 200 and 300 µm). These specimens were descaled in the hydrofluoric nitric acid medium (thickness removed: 10 µm).

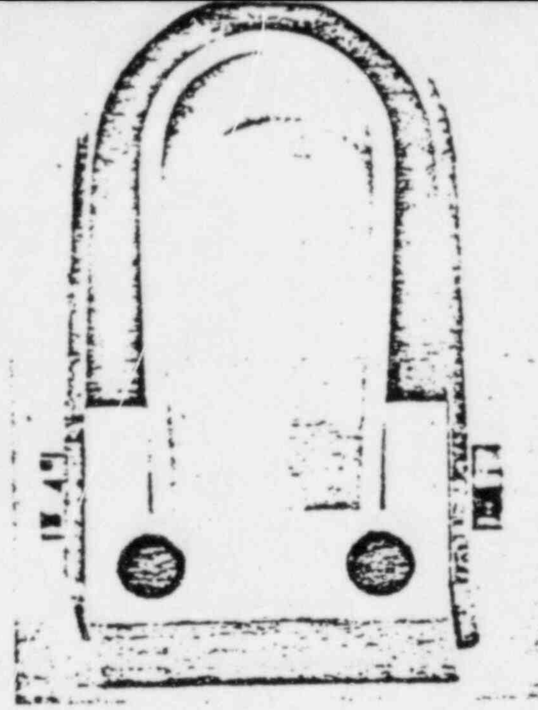

FIGURE 19 – Horseshoe apparatus. Sample of Inconel 600 (interior) coupled to gold (exterior) without crevice effect.

TABLE 9

| Alloy A Inconel 600 | Number of Samples that Cracked | | | |
|---|---|---|---|---|
| | Water at 350 C | | LiOH at 350 C, pH = 11.5 | |
| | After 850 hours | After 1500 hours | After 850 hours | After 1500 hours |
| Uncoupled samples | 1/20 | 20/20 | 0/20 | 0/20 |
| Samples coupled to 18/10 stainless steel | 3/10 | 10/10 | 0/10 | 1/10 |
| Samples coupled to gold | 0/7 | 0/7 | 0/10 | 0/10 |

TABLE 10

(Inconel 600 Corresponds to Alloy B in Table 14)

| | | Number of Samples Cracked After 12,000 Hours (examined by optical microscopy) | |
|---|---|---|---|
| | | Water | LiOH at pH = 10.5 |
| Inconel 600 | uncoupled | 0/9 | 0/9 |
| Inconel X 750 | | 0/9 | 0/9 |
| Inconel 600 | coupled to gold | 0/9 | 0/9 |
| Inconel X 750 | | 0/9 | 0/9 |
| Inconel 600 | coupled to platinum | 0/9 | 0/9 |
| Inconel X 750 | | 0/9 | 0/9 |
| Inconel 600 | coupled to 18/10 stainless steel | 1/10 | 0/9 |
| Inconel X 750 | | 0/9 | 0/9 |
| Inconel 600 | coupled to mild steel | 4/10 | 2/10 |
| Inconel X 750 | | 6/10 | 0/9 |

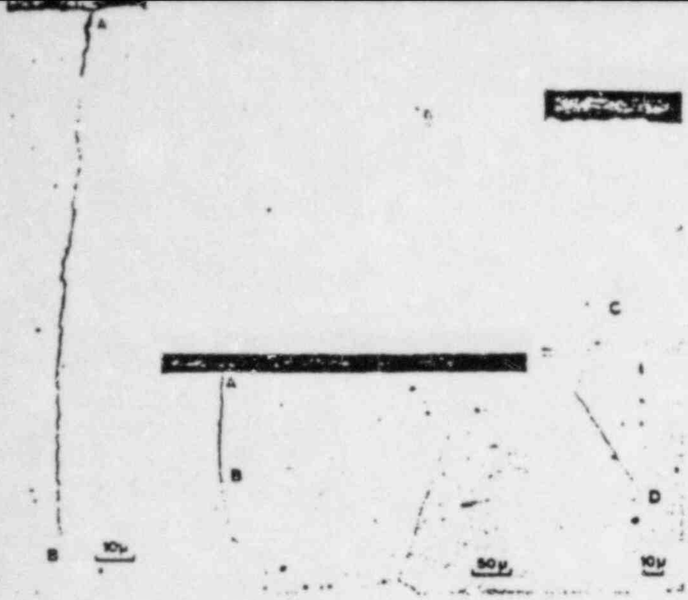


FIGURE 20 — Intergranular cracks (paths AB and CD) obtained in Inconel 600 with very large grains. AB polish with diamond paste; micrographic attack (aqua regia and glycerin); CD polish with diamond paste.

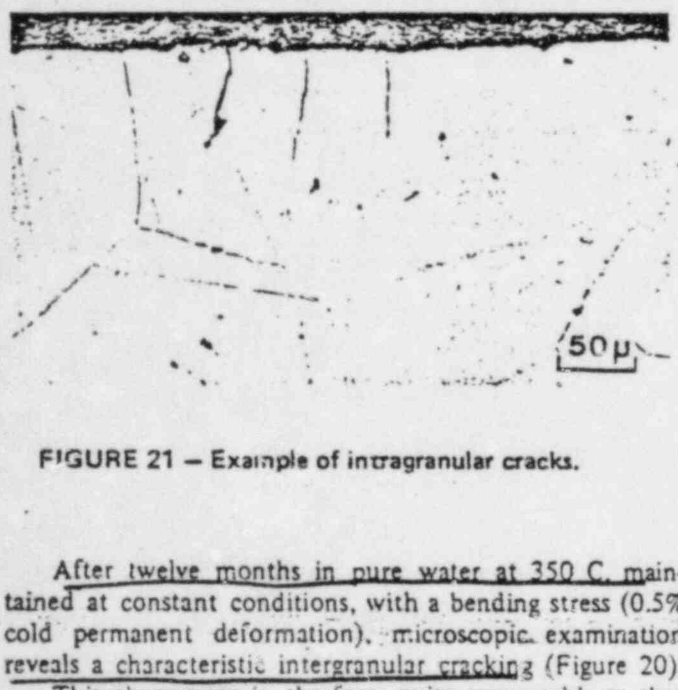


FIGURE 21 — Example of intragranular cracks.

After twelve months in pure water at 350 C, maintained at constant conditions, with a bending stress (0.5% cold permanent deformation), microscopic examination reveals a characteristic intergranular cracking (Figure 20).

This phenomena is, therfore, quite comparable to that observed for the usual alloy whose grain size is generally on the order of 20 to 40 $\mu m$.

However, under our particular conditions, we note the appearance of a few rare cracks of an intragranular nature but which do not go beyond the perimeter of the grain for the time of our test (Figure 21).

*Influence of the Structure*[11]

After a complete aging heat treatment, Inconel X 750 attains a yield stress of about 80 to 90 $kg \cdot mm^{-2}$ by precipitation of intermetallic compounds. It is, therefore, possible to vary the structure and the resulting mechanical properties from the solution treated condition (yield stress 35 $kg \cdot mm^{-2}$) to complete precipitation (maximum hardness).

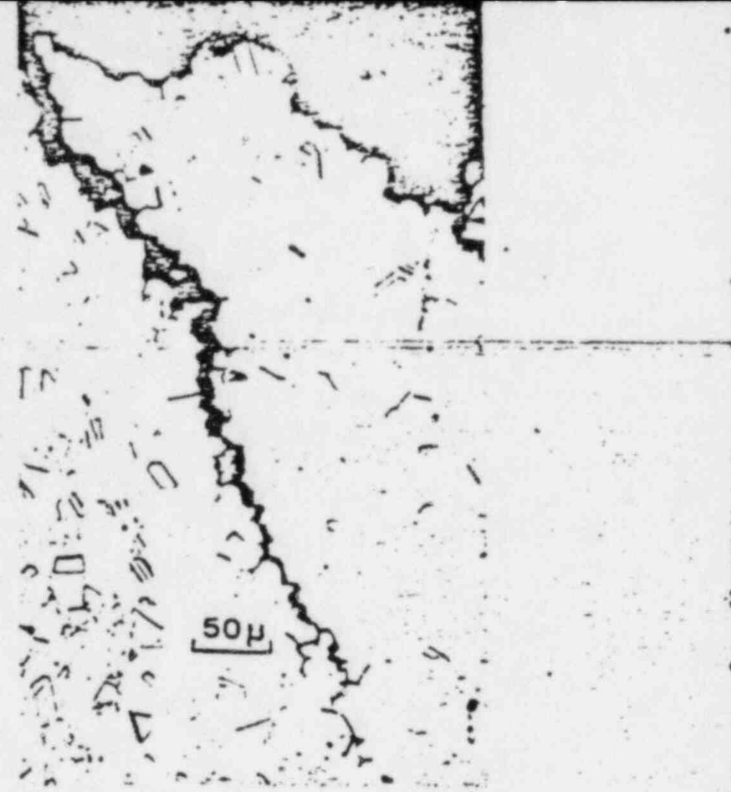


FIGURE 22 — Tensile specimen ($\alpha = 2/3\ E_{0.2}$ 300 C) after 2,000 hours in 350 C deoxygenated water. Intergranular nature of the crack.

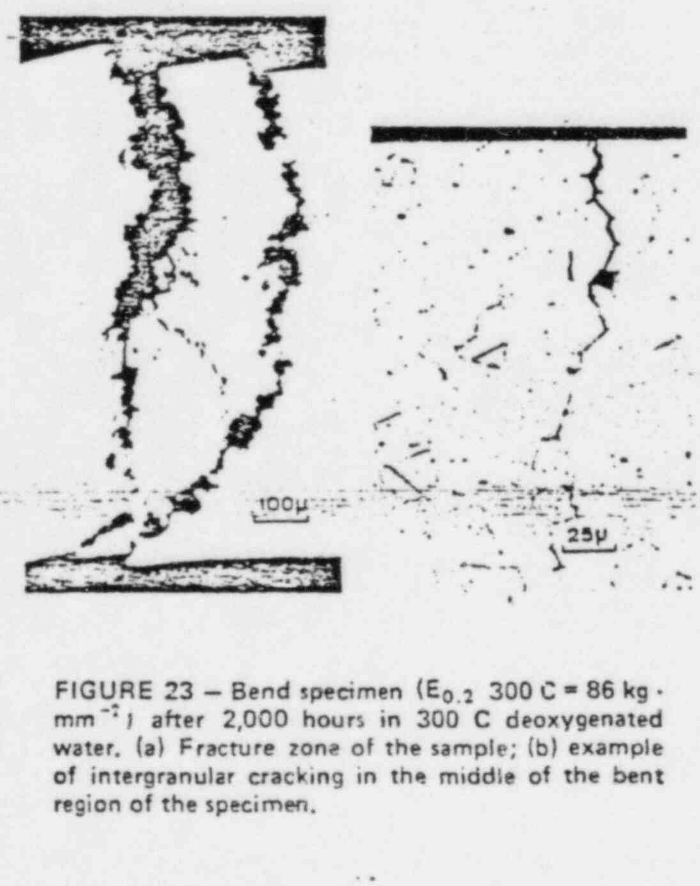


FIGURE 23 — Bend specimen ($E_{0.2}$ 300 C = 86 $kg \cdot mm^{-2}$) after 2,000 hours in 300 C deoxygenated water. (a) Fracture zone of the sample; (b) example of intergranular cracking in the middle of the bent region of the specimen.

Some specimens of this alloy have been tested under the same conditions as before, either in flexure or in tension, in deoxygenated water at 300 and 350 C. The surfaces preparations are identical to those used for the other cases described above.


FIGURE 24 – Intergranular cracking of a bend specimen ($E_{0.2}$ 300 C = 68 kg · mm$^{-2}$) after 2,000 hours of testing in 300 C deoxygenated water.

The following resulted: (a) Tensile specimens stressed to 2/3, 3/4, and 1 $E_{0.2}$ 300 C, with or without notches, were all broken by an intergranular process after 2,000 hours of testing at 300 C for the alloy heat treated to the strength of 86 kg · mm$^{-2}$ (Figure 22). Specimens with lower mechanical properties (68 kg · mm$^{-2}$) did not crack after 6,000 hours of testing; (b) Bend specimens (0.5% cold permanent deformation) underwent intergranular cracking after 2,000 hours at 300 and 350 C, whether the metal was heat treated to 86 or 68 kg · mm$^{-2}$). However, this cracking was clearly more severe for the alloy with higher mechanical properties (Figures 23 and 24); and (c) Some bend specimens, made from sheet material which was quenched after solution treatment (yield stress 35 kg · mm$^{-2}$), did not show any cracking. These tests went beyond 8,000 hours at 350 C.

These results confirm that Inconel X 750, in the hardened state, has a susceptibility to intergranular stress cracking much more severe than the homogeneous Inconel 600 alloy. Furthermore, the role of the structure factor is noted since the susceptibility is greatly lowered when the intermetallic precipitates are decreased in number and the resulting mechanical properties decreased. In the extreme case, Inconel X 750, in the quench after solution annealing condition, seems to behave similarly to Inconel 600.

## Observations on the Cracking Process— Role of Sulfur

Scanning electron microscopic examination and analysis of the emitted X-rays bear on the intergranular cracking process for the alloys studied.

The samples examined were cracked under stress at 350 C in demineralized water ($O_2 \leq 3$ μg · kg$^{-1}$). Inconel 600 in sheet form was bent (0.5% cold permanent deformation). Cracks were produced between six and nine months of testing. Inconel X 750 in bar form was tensile tested (0.6 E 0.2 350 C). Fracture occurred after 800 hours of testing.

The following points are made from the test: (a) Microfractography confirms the microscopic observation that the cracking is intergranular in nature (Figure 25). This cracking is then transformed into an aspect of brutal fracture of a ductile transgranular type (Figure 26); (b) in the propagation zone of the intergranular crack, the presence of numerous crystalline precipitates at the grain surface is noted. These precipitates are dispersed or in aggregates in platelet or rod-like form (Figures 27 and 28); (c) these precipitates have a tendency to be more abundant


FIGURE 25 – Intergranular aspect of cracking (Inconel 600 type alloy).


FIGURE 26 – Transition between intergranular cracking and brutal ductile transgranular fracture. (Inconel 600 type alloy).


FIGURE 27 — Precipitates at grain surfaces on flanks of the crack (Inconel X 750).


FIGURE 28 — Precipitates at grain surfaces on flanks of the crack (Inconel X 750).

in the zones near the lip of the crack. They become rare in the neighborhood of the propagation zone and are nonexistent in the zone of brutal fracture. They are not observed except in a few rare cases on the external surfaces of the samples; and (d) analysis by emitted X-rays of the

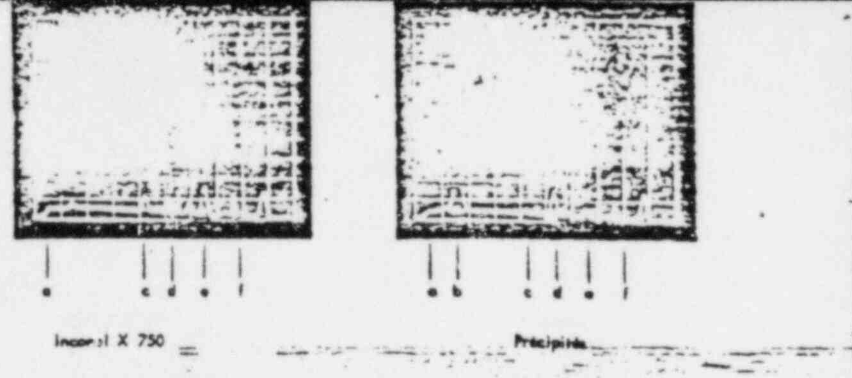


FIGURE 29 — X-ray emission spectrographs. Precipitates: a = aluminum; b = sulfur; c = titanium; d = chromium; e = iron; f = nickel.

precipitates reveal that they are very rich in sulfur, frequently in nickel (Figure 29), and that they can also contain some iron. The X-ray image, compared to the electronic image, confirms this point very well (Figure 30).

According to our observations, it seems possible that intergranular cracking of the alloys rich in nickel, such as Inconel 600 or Inconel X 750, is related to the presence of sulfur containing compounds in the metal. We can make the comparison with the properties of nickel, even high purity nickel, that is embrittled at grain boundaries by segregation of manganese and nickel sulfides, this occurring for a sulfur content as low as 0.0009%.[12] In the alloys containing 75 to 77% nickel such a segregation is thought to occur. These compounds, which are probably unstable in water at 350 C, lead to the formation of a strongly sulfurous medium in the small metal volume at the bottom of the crack. This region would then be favorable to a rapid point by point dissolution of the nickel rich alloy. Precipitates found on the flanks of the crack would be products of this reaction.

This mechanism would explain that the observed phenomenon is rather specific to alloys with a high nickel content; therefore, if the concentration of this element was lowered, the process would not occur.

Furthermore, since the nature of the sulfur compounds and their distribution in the alloys are not controlled, great differences should be produced by different melting and fabrication techniques. This would explain the apparent divergencies observed between different batches with the same nominal composition.

## Conclusions

Different service conditions for "nickel-chromium-iron" austenitic alloys with high nickel content, such as Inconel 600 and X 750 type alloys, exert an important influence on the susceptibility to intergranular fracture of these materials in water at 350 C. The following points are made:

1. The time to failure of Inconel X 750 increases sharply when the stress decreases. However, it does not appear from our tests that there is a threshold stress below which the phenomenon is not produced. Cracking has been observed for a value as low as 0.4 $E_{0.2}$ 350 C.

2. Certain heat treatments can strongly influence the behavior of Inconel 600. We have shown that a sensitiz tion at 700 C, although producing an intergranular precipitation of carbide, notably slows down the cracking process.

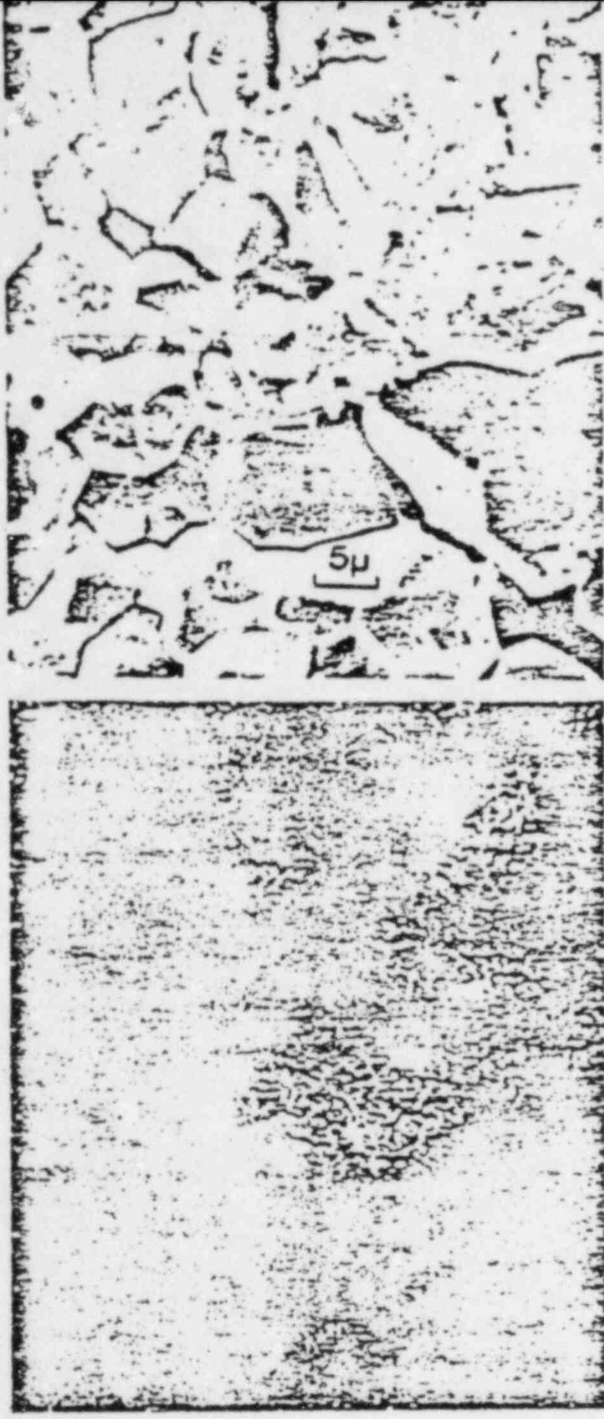


FIGURE 30 — Electronic images (above) and X-rays (below) from the same zone of the crack, showing the association of sulfur with the precipitates (Inconel X 750).

3. The important role played by certain galvanic effects have likewise been shown. Contact with a noble metal, such as gold, exerts a protective effect; contact with carbon steel leads to a strong acceleration of the cracking process, on the contrary. 18/10 stainless steel may have a slightly unfavorable influence. However, it is recalled that the influence of these various couplings has been determined in the absence of crevice effects. These effects can perturb the cracking phenomenon, occasionally accelerating it.

water at 350 C; however, the appearance of some intragranular cracks was noted on certain large grains.

5. The influence of the structure has been shown on alloy Inconel X 750. The susceptibility to stress corrosion decreases greatly if the intermetallic precipitates become less numerous and the resulting mechanical properties decrease.

6. A mechanism is proposed and related to the presence of sulfur containing compounds in the metal. This can explain certain of the observed phenomena.

Thus, the complexity of industrial installations inevitably leads to the simultaneous intervention of numerous parameters whose interactions can be contradictory. Consequently, the real service behavior of Inconel 600 and X 750 type alloy will be apparently quite variable; it is, therefore, wise to adopt the greatest prudence in their application.


## Acknowledgments

We would like to thank Madame Meny and Mr. Olivier for the scanning electron microscopic examinations.


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## DISCUSSIONS

**J. H. Westbrook, General Electric Corp.:**

At the Montreal grain boundary meeting next month,[1] Dr. Floreen and I will report some results on highly pure Ni-S binary alloys which I believe are very complementary to and confirmatory of the very interesting studies you have just described to us. Our alloys ranged from about 20 ppm S to *less than 1 ppm S* (!) and we were monitoring the grain boundary interaction with S by the microhardness technique we have previously reported (Acta Met., Vol. 17, p. 1175 (1969)). Quenching from 900 C shows no grain boundary hardening for all compositions; slow cooling from that temperature shows an amount of hardening decreasing with decreasing S but still sensible at <1 ppm S. Reheating, after quenching, to modest temperatures (100 to 700 C) brings all alloys to a steady state grain boundary hardness whose value is a function of sulfur content. The kinetics of this grain boundary hardening are such that it is impossible to maintain a soft grain boundary at *room temperature* for more than a few minutes following a 900 C quench. Therefore to examine the possible effects of sulfur-grain boundary interaction on a *bulk* property, it is necessary to make measurements at sub-normal temperatures. Accordingly, tensile specimens were tested at liquid $N_2$ temperature for two conditions: (1) slow cooled from 900 C, and (2) quenched from 900 C to ice water and immediately to liquid $N_2$. All alloys for condition (2) showed 80-90% RA and predominantly transgranular fracture. *All* alloys for condition (1) showed much reduced RA figures in the range 30-40% (the more so the greater the S content), and with accompanying increase in the proportion of IG failure. Although these experiments are purely mechanical and not electrochemical, they do show quite directly the powerful role of even very tiny amounts of S and its interaction with the grain boundary. Whether the latter phenomenon is properly to be regarded as equilibrium segregation, vacancy promoted nonequilibrium segregation, or conventional precipitation is yet to be determined. Perhaps each plays a role in its proper concentration range.

**Authors' Reply:**

These results are very interesting. Thank you for reporting them. They show that sulfur undoubtedly plays an important role in the intergranular processes in nickel and presumably in high nickel alloys.

[1]Now published, Canadian Met Quarterly, Jan/Mar (1974).

Our comments will include a very brief review of our test results on Inconel 600 and then we wish to raise a question on the SCC behavior of Inconel 600.

In our laboratories, investigations are in progress to determine the long-term SCC characteristics of Inconel 600 in the boiling water reactor environment. For purposes of this review, only the long-term test data will be presented.

Test Data
Specimen Type: Uniaxial Tensile
Load: 125% of 550 F Yield Strength

| No. Spec. | Metallurgical Condition | Test Time (hrs) | Environment |
|---|---|---|---|
| 2 | Mill annealed, machined | 28,000 (NF)[1] | 550 F |
| 2 | Mill annealed, furnace sensitized | 28,000 (NF) | 0.2 ppm $O_2$ |
| 2 | Mill annealed, machined, furnace sensitized | 28,000 (NF) | 0.5 ppm Cl |
| 2 | Mill annealed, welded, furnace sensitized | 28,000 (NF) | water |
| 2 | Mill annealed, furnace sensitized, welded | 28,000 (NF) | 550 F |
| 2 | Mill annealed, machined | 24,250 (NF) | 0.2 ppm $O_2$ |
| 2 | Mill annealed, furnace sensitized, machined | 24,250 (NF) | water |

[1]NF = No Failure – all tests are continuing.

In the test program, a uniaxial tensile specimen of Inconel 600 failed by intergranular stress corrosion in 550 F water (0.2 ppm $O_2$, 0.5 ppm $Cl^-$). This specimen was tested at 125% of the 550 F yield strength. The specimen was of a crevice configuration, *i.e.*, a foil band of Inconel 600 was wrapped around the gage length and the failure occurred after 6633 hours in the crevice region. Duplicate companion specimens have not failed after 11,477 hours of testing. Other creviced specimens in triplicate have not failed after 11,477 hours of exposure at stress levels of 125, 150, and 200% of the 550 F yield strength in simulated BWR water (0.2 ppm $O_2$). These tests are continuing.

These test data form the basis for our question on the SCC behavior of Inconel 600 which is related to the effect of temperature on the SCC of Inconel 600. M. Grall presented test results on specimens exposed at 300 C (572 F) and 350 C (662 F) while our tests were performed at 288 C (550 F). We would like to ask Mr. Grall to comment on the possible existence of a temperature threshold below which SCC will not occur?

**Authors' Reply:**

As a matter of fact, we never performed experiments on Inconel 600 at temperatures below 300 C; most of our work was performed at 350 C.

Taking into account the general scatter observed, the incubation time, for example, we do not consider that there is a significant difference between the results obtained at these two temperatures (300 and 350 C) in high-resistivity, deoxygenated water.

For lower temperatures, and in different environments, the possibility exists for a lower susceptibility to cracking, but we have no data to support this.

UNITED STATES OF AMERICA
NUCLEAR REGULATORY COMMISSION

BEFORE THE ATOMIC SAFETY AND LICENSING BOARD



In the Matter of

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