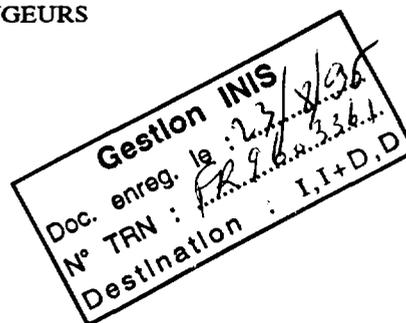# Production d'énergie (hydraulique, thermique et nucléaire)

AMORÇAGE DES DEFAUTS INTERGRANULAIRES A LA
SURFACE EXTERNE DES LIAISONS BIMETALLIQUES :
ETUDE DES MECANISMES DE CORROSION

*GRAIN BOUNDARY DEFECTS INITIATION AT THE OUTER
SURFACE OF DISSIMILAR WELDS : CORROSION
MECHANISM STUDIES*

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SYNTHÈSE :

Certaines liaisons soudées bimétalliques du circuit primaire principal des centrales REP présentent en première couche de beurrage des défauts de type décohésion intergranulaire. Parmi les hypothèses de mécanismes d'amorçage envisagées figurent la corrosion sous contrainte, la corrosion intercristalline et l'oxydation intergranulaire à chaud. En vue d'expliquer les défauts complexes observés, la structure métallurgique des liaisons présentant des défauts a été analysée ; les hypothèses concernant les mécanismes ont été étudiées aussi bien du point de vue du mécanisme proprement dit que du point de vue des conséquences qu'ils peuvent engendrer. L'objet de cette note est de présenter les études concernant les deux mécanismes de corrosion et de discuter leur possibilité d'existence.

Les défauts se présentent comme des décohésions intergranulaires affectant les premières couches de beurrage lorsque celles-ci sont purement austénitiques (fortement sensibilisées à la corrosion intercristalline). Les décohésions rejoignant l'interface forment des cavités dans le liseré martensitique. L'ensemble de ces défauts est rempli d'oxyde compact. L'acier ferritique présente par ailleurs des piqûres le long de l'interface.

Les essais de corrosion sous contrainte menés tout d'abord sur un matériau massif, représentatif de la première couche de beurrage des liaisons, ont montré qu'il est susceptible de subir une fissuration intergranulaire dans des milieux peu agressifs (milieu neutre contenant très peu de polluants). En revanche, le couplage galvanique entre l'acier ferritique et la première couche de beurrage protège cette dernière lors des essais sur des liaisons bimétalliques réelles. L'hypothèse de corrosion sous contrainte ne peut donc pas expliquer les défauts observés.

Les résultats des expertises et de différentes études de corrosion intercristalline ont conduit à ne garder que l'atmosphère comme milieu agressif possible. En accord avec cette hypothèse, les essais de corrosion accélérés, pratiqués en laboratoire en milieu SO_2, ont conduit à une corrosion intercristalline importante des matériaux purement austénitiques. Les essais menés en atmosphère naturelle confirment ces résultats.

Ainsi, les études des mécanismes de corrosion permettent d'éliminer la corrosion sous contrainte des trois hypothèses envisagées. Dans l'état actuel des études, elles ne permettent pas d'identifier avec certitude la cause de l'amorçage des défauts mais montrent que la corrosion atmosphérique affecte les premières couches purement austénitiques des liaisons bimétalliques.

EXECUTIVE SUMMARY :

Dissimilar welds located on the primary coolant system of the French PWR plants exhibit grain boundary defects in the true austenitic zones of the first buttering layer. If grain boundaries reach the interface, they can extend to the martensitic band. Those defects are filled with compact oxides. In addition, the ferritic base metal presents some pits along the interface. Nowadays, three mechanisms are proposed to explain the initiation of those defects : stress corrosion cracking, intergranular corrosion and high temperature intergranular oxidation. This paper is dealing with the study of the mechanisms involved in the corrosion phenomenon.

Intergranular corrosion tests performed on different materials show that only the first buttering layer, even with some δ ferrite, is sensitized.

The results of stress corrosion cracking tests in water solutions show that intergranular cracking is possible on a bulk material representative of the first buttering layer. It is unlikely on actual dissimilar welds where the ferritic base metal protects the first austenitic layer by galvanic coupling. Therefore, the stress corrosion cracking assumption cannot explain the initiation of the defects in aqueous environment.

The results of the investigations and of the corrosion studies led to the conclusion that the atmosphere could be the only possible aggressive environment. This conclusion is based on natural atmospheric exposure and accelerated corrosion tests carried out with SO_2 additions in controlled atmosphere. They both induce a severe intergranular corrosion on true sensitized austenitic materials.

This corrosion studies cannot conclude definitively on the causes of the defect initiation on field, but they show that the atmospheric corrosion could produce intergranular attacks in the pure austenitic zones of the first buttering layer of the dissimilar welds and that this corrosion is stress assisted.

Grain boundary defects initiation at the outer surface of dissimilar welds : corrosion mechanism studies

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Introduction

Dissimilar welds link the ferritic components and the stainless steel pipe of the reactor coolant system (RCS) of PWR plants. Following the detection, since 1990, of indications by dye penetrant test on the outer surface of these dissimilar welds, many field and laboratory investigations on removed samples have been performed. They showed two types of defects close to the dissimilar interface : pits in the ferritic steel nozzle along the interface and grain boundary decohesions in the 309L stainless steel first buttering layer[1]. Regarding the decohesions, the whole evaluation has led to select various assumptions about their origin. Nowadays, after elimination of the hot cracking hypothesis[1], three mechanisms were proposed to explain the initiation of those defects : stress corrosion cracking (SCC), intergranular corrosion and high temperature intergranular oxidation. In order to identify the most probable one, metallurgical examinations as well as corrosion tests have been carried out.

This paper deals with the mechanisms involved in the corrosion phenomenon. It first describes the dissimilar welds and their microstructures and gives the result of field and metallurgical laboratory examinations on the detected defects. Sensitization of these structures on stress corrosion cracking and atmospheric corrosion behaviour are described and the conclusions are discussed.

Metallurgy and field investigation of dissimilar welds

<u>Dissimilar weld description.</u>

The dissimilar welds affected were produced in the factory by manual shielded metal arc welding. The filler metals used were 309L steel in the initial buttering layer and 308L or 316L steels for other buttering layers and for filling. During fabrication or at the end of fabrication these welds also underwent several thermal treatments. Two fabrication stages are essential with regard to the microstructure of the initial layer and hence to its properties in service ; these are first of all, the deposit of the first layer which determines the constituent microstructures of the layer and, secondly, all the thermal treatments which induce in these structures a certain number of secondary changes.

   <u>Structure of the initial layer.</u> The initial buttering layer is a weld metal originating from dilution during welding of the filler metal with the base metal. It features fairly large columnar grains and segregation derived from solidification. The structure obtained in the initial layer depends on the welding conditions, in particular on dilution. In practice, several structures are possible. The matrix is austenitic and contains, as dilution increases, 6% to 0% of δ ferrite and 0% to 50% of martensite. In view of the manual welding method and process used, local dilution varies considerably and it is frequent to find in the same production run various structures with up to 3% of δ ferrite and/or 10% of martensite (fig. 1).

In addition to the structure in full pass, the welded area features a transition area with chemical composition and structure between the rest of the pass and the base metal : these are martensitic and austenic layers with typical widths of 25 μm and 100 μm respectively. The latter may appear locally in the form of strip of equiaxed grains. Consequently, in the initial buttering layer there is a majority of grain boundaries perpendicular to the interface ; locally there is also a grain boundary parallel and close to the interface.

   <u>Thermal treatments.</u> Thermal treatments have two consequences : the first is that the carbon of the ferritic steel continues to diffuse across the interface towards the stainless steel buttering layer. At the end of these treatments, a low-carbon area on the ferritic side and a high-carbon area on the austenitic side appear on either side of the interface (typically, 250 μm and 100 μm wide) (fig. 1). The second consequence is the precipitation of chromium carbides mainly in the martensitic layer and in the grain boundaries of the rest of weld metal. In term of properties during service, this may lead to a strong sensitivity to intergranular corrosion. In practice, this sensitivity is essentially determined by the δ ferrite content. The presence of the welding martensite also greatly reduced this sensitivity. Sensitization in the weld pass, controlled by the carbon and ferrite contents, will therefore be greater near the interface. On these steels, the final phase of such sensitivity may be the formation of tempered martensite. The latter is therefore located at the grain boundaries. Such martensite has already been observed in a dissimilar weld : it has a low chromium and nickel content (5% for each of these elements).

   <u>Residual stresses.</u> The outer surface of the dissimilar welds near the interface is the focus of residual stresses which have given rise to X-ray diffraction measurements and calculation. These studies have revealed that following thermal treatment, the values of stresses at the dissimilar welds were marginally impacted by the size of the different nozzles. The axial tensile stresses reached 450 MPa in the ferritic steel in the immediate proximity of the interface and became compression loads at a distance of some 2 mm from this same interface. The circumferential stresses were compressive in the ferritic steel and tensile stresses up to 100 MPa in the initial buttering layer[1]. The location of the tensile stresses was such that at the outer surface the two families of grain boundaries of the initial buttering layer were all subjected to them. All these stresses were very quickly absorbed in the thickness. Given their nature, these stresses were modified by the heat-up of the structure. Measurements by X-ray diffraction at temperatures up to 320°C and calculation of this heat-up revealed that the configuration of the residual stresses did not change but that their values decreased sharply with temperature. At 320°C the greatest axial tensile stress was only 100 MPa.

<u>Metallurgical features of defects.</u>

The tests conducted on site since 1990 include examinations on a broad range of components through the taking of replicas; the examinations under local microscope and in the laboratory on the basis of boat samples. The results of these examinations are presented below.

<u>Defects on the ferritic steel</u>. Defects at the outer surface observed on the ferritic steel comprise strings of small cavities along the interface and containing a little almost exclusively iron oxide. The main but not unique location of these defects is in the decarbonized area of the heat affected zone (HAZ) immediately along the fusion line. The martensitic layer, the rest of the HAZ and the base metal may also be affected. Most of these defects were observed during initial inspections. These appear to be either pit holes or the residue of imperfectly eliminated general corrosion.

<u>Defects in the initial buttering layer</u>. Many field examination of these defects have shown that there are surface defects and mainly comprises grain boundary decohesions. They are observed either after startup of the units for most of them or before startup for some of them. They are identical in all cases (in terms of their location, morphology, qualitative analysis of the pockets of oxide, nature of the structure). A typical description has been produced from the field examination :

- They only affect grain boundaries parallel or perpendicular to the interface of the initial buttering layer 309L in areas where its structure is 100% austenitic during metallographic observation and which occasionally reveals a few traces of martensite at the grain boundaries. The mean weighted concentrations of the matrix measured on samples in these areas are : 17% chromium, 8.5% nickel and 0.15% to 0.06% of carbon. They also affect all the martensitic areas crossed or encountered by decohesion : layer, irregular aspect of the fusion line, intragranular and intergranular ranges (fig. 2). Moreover, the adjoining ferritic steel does not suffer severe deterioration at the outer surface.
- Separations mostly emerge at the interface in the pockets filled with oxide. These pockets spread in the martensitic layer, occasionally a little in the decarbonized area of the base metal along the interface.
- The defects are filled with compact oxide containing mainly iron, chromium, a little nickel and occasionally silicon ; the micro-Raman examinations and quantitative electron probe microanalyses performed in the oxide of an grain boundary decohesion have revealed that the oxide contained iron (60%), chromium (8.4%) and a little nickel (3%) in the form of M_2O_3 and M_3O_4 without the presence of detected hydroxides.
- The density of these defects may sometimes be considerable and their dimensions along the length (max. 305 mm) and depth (max. 5.5 mm) vary greatly.
- The presence of chlorine and/or sulphur is frequently observed in both open or closed defects. The precautions taken during preparation and analysis confirm in some cases that these do not derive from contamination.
- The presence of superficial pit holes of many nozzles reveals corrosion of the ferritic steel and hence the presence at a given moment of an aggressive aqueous medium which may have affected the weld.
- Moreover, no propagation by fatigue was ever been observed.
- Monitoring under a site microscope of two cases left "as is" did not reveal any change in their surface after one and two operating cycles. However, this result does not prove that they do not evolve, if only in the depth.

The intergranular character of the defects, their multiple orientation, their presence solely on the surface, the presence of chlorine and/or sulphur and the presence of pit holes on the ferritic steel of the nozzles, all point to a corrosion mechanism. Under this assumption, the systematic and widespread presence of oxide in the defects suggests that the conditions in the medium prevailing at the time of corrosion did not remove the corrosion products: preference should therefore be given to wetting type conditions when assuming real media. We have verified that the absence of hydroxides is explained by the fact that components held under a given temperature before detection of the defects; at a temperature maintained at 300°C for several dozen hours, the hydroxides FeO(OH) created on these steels are totally converted into Fe_2O_3 and Fe_3O_4.

Experimental procedures

<u>Materials used</u>

The tests were carried out on homogeneous materials : A508/A533 steel representing the base metal of the dissimilar welds, 304 steel, used as reference material to compare the weld and wrought materials and a weld metal (modified 308 steel), representing the area with defects of the initial buttering layer. In the latter case, the test samples derived from a coated electrode arc welded deposit are drawn outside the dilution area. Tests were also performed on heterogeneous test lengths representing dissimilar welds (DW), either purely austenitic in the initial layers

(DW 0% δ) or containing δ ferrite (DW 3% δ) and are processed by means of a coated electrode arc welded deposit (309L) on a base metal in ferritic steel (A508/A533).

Table 1 includes typical chemical composition, the various thermal treatments conducted and the measurement of the concentration of δ ferrite in the weld metal or in the initial buttering layers of the dissimilar weld. Microscopic observation following attack by oxalic acid reveals the presence of a purely austenitic area without δ ferrite close to the martensitic layer between 150 μm and 250 μm for so-called "ferrite free" welds and less than 50 μm or totally non-existent for weld with ferrite.

Table 1 - Thermal treatments, yield stress, chemical composition (weight %) and δ ferrite content of studied materials.

Material	Thermal treatments	Yield stress	C	S	P	Si	Mn	Ni	Cr	Mo	N	δ ferrite
A 508	-	-	0.14	0.008	0.011	0.13	1.20	0.70	0.22	0.48	0.011	-
A 533			0.198	0.005	0.018	0.24	1.50	0.59	0.25	0.56	0.0136	-
304	30 min at 700°C	-	0.065	0.024	0.028	0.87	1.28	9.7	18	-	0.024	-
modified 308	5h at 610°C + 5h at 610°C	360 MPa	0.12	<0.002	-	0.8	6.7	7.8	17	0.08	0.05	<0.5
DW 0% δ A DW 0% δ B	18h at 550°C + 10h at 610°C 2.5h, 610°C + 3.5h, 610°C	370 MPa	0.08	0.01	-	0.5	2.1	10	16.5	0.2	0.045	<1
DW 3% δ	15h at 550°C + 7h at 600°C	-	0.059	0.014	0.11	0.424	1.02	9.05	17.4	0.168	0.045	2-5
defects area near the interface	-	0.15	-	-	0.50	0.65	8.5	17	-	-	0

Tests performed

Sensitization tests to intergranular corrosion were performed on all materials in accordance with the Standard ISO 3651/11 using sulfuric acid / copper sulphide medium (Strauss test) at boiling point during 24 hours.

The stress corrosion cracking tests were constant load tests performed at the same stress value (400 MPa) and at a temperature of 60°C. The medium was either representative of atmospheric pollution : neutral solution (pH varying between 5 and 7, prepared from buffer solutions containing dihydrogen-phosphate of potassium and caustic soda) or supposed to represent local media after for instance pit initiation : acid solution (pH 2, HCl). The chlorine content (1 ppm to 1000 ppm) was adjusted through the addition of NaCl. Tests were conducted on either weld metal or on test specimens containing an interface perpendicular to the axis of the test specimens. The latter were cylindrical (diameter of cylinder drum = 4 mm, working length = 40 mm) and were electropolished. The electrochemical potential of the test specimens was measured during the traction tests with a saturated calomel reference electrode (SCE) at room temperature.

For atmospheric corrosion phenomena, accelerated tests were conducted in a climatically controlled chambre in the laboratory (SO_2 atmosphere) and exposure tests were performed in a natural atmosphere. The former were conduced in accordance with Standard NF 30-055; they included two phases during a 24 hour cycle : 8 hours exposure in a SO_2 atmosphere at 37°C, then 16 hours at room temperature. The concentration of SO_2 was 660 ppm (0.2 litres of gaseous SO_2 in a 300 litre vessel containing 2 litres of water) or 10 ppm (0.2 litres of a gas with 1.5% SO_2 and 98.5% N_2 in the same vessel). The tests in a natural atmosphere were conducted at the Ponteau-Martigues test facility (site classified as highly corrosive according to Standard ISO 9223 for a carbon steel; mean value of deposit of SO_2: 35 mg/m²/day and chloride ions; 110 mg/m²/day; mean relative humidity over one year: 71% and of the temperature: 16°C).

The test specimens for these tests were in the form of plates (50 mm x 10 mm x 2 mm) polished with 8 μm diamond paste for tests conducted in a SO_2 atmosphere and with 4000 grade paper for tests in a natural atmosphere. Tests were conducted on unloaded specimens (Un-plate) and also on four-point bent specimens (4PB-plate) : the stress applied was slightly greater than the yield stress of the material. After exposure, the test specimens were pickled with a hydro-chloric acid solution containing a hexamethylene-tetramine inhibitor. The corrosion rate of the ferritic steel was deduced by weight loss. For the other materials, examinations using optical or scanning electron microscope were performed on the outer surface. The plates were then subjected to bending up to 90° (or 45°) in order to open any defects. The depth of the defects was estimated on the cross-sections of the test specimens and by measuring the surface extension of cracks. The cross-sectional plane was parallel to the interface.

Results

Sensitization to intergranular corrosion

The Strauss test has shown that the 304 stainless steel (after treatment for 30 mins at 700°C) and the modified 308 weld metal (after thermal treatment for 10 h at 610°C) were heavily sensitized to intergranular corrosion. They depth of attack is more than 1 mm after 24 h testing. Observation of a test specimen of the dissimilar weld containing ferrite (DW 3% δ) treated for 15 h at 550°C + 7 h at 600°C shows moreover a severe generalised corrosion attack of the A533 steel several particularities :

- on the first 500 microns of the first layer, the grain boundaries, most of which are oriented perpendicular to the interface, are corroded, while the second and subsequent layers show no visible signs of intergranular corrosion,
- the first 100 microns nearest to the interface are the most corroded, with some grains even being dislodged.

So, there is an intergranular corrosion sensitivity limited at the first buttering layer and, in addition, decreasing close to the interface.

Stress corrosion cracking

The tests results on the weld metal (table 2) show that under these conditions of temperature and stress, cracking occurs quickly and is always intergranular (fig. 3). They also show that almost neutral environments (pH ≥ 5) even with very low chlorine contents (< 1 ppm), are likely to cause cracking in a solid material representing the first layer of buttering of the dissimilar welds. The same test on a test specimen containing a dissimilar weld (DW 0% δ) does not cause cracking over a period neither of 500 h in a pH 7 environment with 1000 ppm of chlorine nor of 300 h in a pH 2 environment without chlorine.

Table 2 - Results of the SCC test at 60°C with constant load (400 MPa) of the weld metal (modified 308).

Cl⁻ content	pH			
(ppm)	2	5	6	7
résidual < 1	ti : 30min tf : 6h	ti : 30h tf : 125h		
10		ti : 20h tf : 75h		
50	ti : 45min tf : 8h30	ti : 6h tf : 81h	NC (200h)	
100		ti : 25h tf : 110h	NC (1100h)	NC (200h)
500	ti : 1h tf : 14h		ti : 10h NF (200h)	NC (280h)
1000	ti : 30min tf : 8h		ti : 10h tf : 72h	ti : 6h tf : 28h

ti : initiation time   tf : fracture time
NC : no cracking   NF : no failure

Table 3 - Free potential of the different materials measured in the SCC test solutions.

	E (V/SCE)		
pH	modified 308	DW 0% δ	A 533
2	-0.20	-0.46	-0.52
5	-0.49	-0.62	-0.65
6	-0.22	-0.52	-0.70
7	-0.16	-0.59	-0.58

The electrochemical potentials measured on the materials in the same environments are given in table 3. The potentials measured on a weld (DW 0% δ) as well as on the A533 steel are 300 mV to 400 mV less than those measured on weld metal (modified 308). This marked difference shows that there is a significant galvanic coupling on the dissimilar welds which puts the austenitic steel in a cathodic region, and protects it against SCC tests.

This results show that SCC cannot initiate on a dissimilar weld on environments representative of atmospheric pollution. It is unlikely on more acidic solutions supposed to represent local media after for instance pit initiation, but this point must be checked out further before definitive conclusion.

Atmospheric corrosion

Ferritic steel. Figure 4 shows the general corrosion obtained on the ferritic steel, in the SO_2 climatic chamber (one day representing one 24 h cycle) as well as at atmospheric corrosion station. It should be noted that the results of the station tests are very dependent on climatic conditions. Comparing the two exposure types, 1 month of exposure at the natural atmospheric corrosion station corresponds to 3 cycles in a 660 ppm SO_2 environment and 15 cycles in a 10 ppm SO_2 environment. For generalised corrosion of ferritic steel, the various tests may be classified in increasing order of severity, as a function of time, in the following order : natural atmosphere / 10 ppm SO_2 environment / 660 ppm SO_2 environment, with an acceleration factor, with respect to exposure in the natural atmosphere, of 2 for the 10 ppm SO_2 environment, and 8 to 10 for the 660 ppm SO_2 environment.

Austenitic materials - Tests in SO_2 climatic chamber. The tests in the 660 ppm SO_2 atmosphere lasted up to 15 cycles of 24 hours each, and those at 10 ppm up to 30 cycles. From the first cycles, in the more concentrated environment, the grain boundaries at the first layer of buttering of the dissimilar weld and the weld metal are marked while on the other hand, the sensitized stainless steel was not attacked at all for 7 cycles. After exposure of these plates for 15 cycles (fig. 5.a) attack was observed along the grain boundaries. Table 4 shows the depths of the attack on the cross-section, after bending the test pieces at 90°. In general, the depths of defects achieved on the test pieces subject to constant deformation strain by four-point bending are two to four times higher than those on the same pieces not subject to the stress. So, the stress speeds up corrosion but it is not absolutely necessary. Observations on cross-sections (fig. 5.b) confirm the intergranular nature of the cracking.

The uncertainty for the values listed in this table may be quite significant. On the one hand, the values recorded are only the lines of the defects at the intersection with the cutting plane ; on the other hand, the tests were only carried out on a single test piece (length of fusion line : 50 mm). However, the order of magnitude of the recorded values is precise.

All these observations allow the materials to be classified in decreasing order of sensitivity to the test: modified 308 / DW 0% δ B / DW 0% δ A / DW 3% δ / sensitized 304.

Table 4 - Defects depth measured on cross-section after exposure test in 660 ppm SO_2 atmosphere and in the natural atmospheric corrosion station.

Test type	Specimen type	Exposure time	DW 0% δ A	DW 0% δ B	DW 3% δ	modified 308	304 sensitized
10 ppm SO_2 atmosphere	Un-plate	30 cycles	40 µm	-	ND	350 µm	ND
	4BP-plate	30 cycles	80 µm	-	60 µm	450 µm	ND
660 ppm SO_2 atmosphere	Un-plate	3 cycles	130 µm	-	130 µm	50 µm	ND
		7 cycles	150 µm	70 µm	20 µm	150 µm	ND
		15 cycles	100 µm*	130 µm	160 µm	> 1 mm	ND
	4BP-plate	3 cycles	150 µm	-	150 µm	200 µm	ND
		7 cycles	300 µm	620 µm	70 µm	650 µm	ND
		15 cycles	-	1.4 mm	300 µm	> 1.5 mm	10 µm
natural atmosphere	Un-plate	1 month	100 µm	200 µm	ND	400 µm	-
		2 months	600 µm	450 µm	40 µm	650 µm	-
		7 months	1 - 2 mm	1,6 mm	100 µm	throughwall	320 µm
		9 months	throughwall	throughwall	450 µm	throughwall	520 µm
	4BP-plate	1 month	600 µm	-	-	600 µm	-
		8 months	> 1.5 mm	-	850 µm	throughwall	throughwall

Un-plate : Unloaded plate   ND : no significant defect observed
4BP-plate : four-point bent plate
* the depth could possibly be underestimated : the specimen has not been bent before cutting and examination

Austenitic materials - Tests in natural atmosphere. From the first month, all the specimens tested at the natural atmospheric corrosion station have been attacked, always excepting the 3% ferritic dissimilar weld, and the SEM examinations (fig. 6.a), after bending, already showed significant attack. The results, listed in table 4, show that after

about 6 months, the defects had reached a depth of more than one millimeter, and are of the same order of magnitude as those observed in service (cf. § investigation). In the same way as in the SO_2 atmosphere, application of stress increases the depth affected by the defects, but is not necessary for corrosion initiation. The micrographs on cross-section (fig. 6.b) show, as in the previous tests, that the defects are intergranular.

The same precautions need to be taken as before, in interpreting the values measured for the defect lines and it is important to note that climatic conditions are very influential on the kinetics of corrosion. However, it seems that these results are more reproductible than those for SO_2 atmosphere tests. So the classification of the materials, according to a decreasing order of sensitivity to atmospheric corrosion, is only slightly different to that defined above, with greater similarity between the behaviour of the two welds with A and B thermal treatments , and a worse behaviour from the sensitized 304 steel : modified 308 / DW 0% δ B - DW 0% δ A / sensitized 304 / DW 3% δ. These results may be explained by the heterogeneous nature of the specimens of the weld containing ferrite, with some cuts having a weak area with no ferrite along the length of the interface, and others not.

Discussion

Involved mechanism

Stress corrosion cracking tests showed that sensitized stainless steel can easily crack in sligthly polluted water solutions. Nevertheless, SCC mechanism was eliminated to explain the studied phenomenon. Indeed, although all necessary conditions for SCC are met :
- correspondence between the sites of the decohesions noted, and the residual stress field,
- neutral environments, with low intrinsic aggressivity for ferritic steel, reduced even more by the very low quantity of solution to be used,
- presence of chlorine and sulphur often detected in decohesions investigated,
it has been seen that SCC is unlikely on dissimilar welds because some coupling does exist between the two metals. On the contrary, the atmospheric corrosion tests have shown that :
- intergranular attack occurs on dissimilar welds or sensitized materials,
- stress is not a necessary condition for the appearance of defects, but only accelerates their propagation.

In this case, it appears that the more probable mechanism is atmospheric corrosion assisted by stress.

Effect of thermal treatment and structure

The results given in table 4 show no significant difference between either of the two thermal treatments (A or B) applied. This can be corelated to studies, carried out on a large number of welds in service that have shown no correlation between the appearance of defects and the thermal treatment applied to the affected material.

If there is a slight effect from the thermal treatment, it is always less than the effect of the metallurgical structure. All results actually show that a first buttering layer, containing δ ferrite, is much less sensitive than a true austenitic layer or weld metal without δ ferrite. These observations allow the materials to be classified in decreasing order of sensitivity to atmospheric corrosion : modified 308 / DW 0% δ / DW 3% δ / sensitized 304. This is a different order from that achieved with the intergranular corrosion test, and shows a greater sensitivity of weld materials (DW, 308) compared to that of wrought material (304). Two hypothesis can be examined to explain this effect : sensitivity to intergranular corrosion and galvanic coupling related to the grain size.

The first hypothesis is sensitivity due to the chromium carbide precipitation during thermal treatments and consequently to the dechromisation of the grain boundaries. Several parameters can play a part in this sensitivity to explain behaviour differences between the materials :
- The high carbon content of the weld materials (specially the modified 308 steel : 0.12% C) involves significant chromium carbide precipitation.
- The presence of δ ferrite (phase with highest chromium content) in weld materials supplies carbides with chromium during the precipitation and allows a lower dechromisation than with weld materials without δ ferrite.

- Grain size difference between weld materials (large grains) and wrought material (small grains) leads to a greater density of chromium carbides (then greater dechromisation) for the weld materials.

However intergranular corrosion test (Strauss test) results shows that this dechromisation is very high for all materials and that the chromium amount on grain boundaries is probably lower than 8%.

The second hypothesis is related to the grain size difference between weld and wrought materials. The very high difference between the grain boundary surface to grain surface ratio involves a coupling effect, the grain boundary is the anodic surface and the grain is the cathodic surface. For weld materials, this ratio is much lower than for wrought materials and the corrosion rate is consequently faster. This galvanic coupling does not happen in the Strauss test because the high solution acidity involves corrosion on all the grain boundaries (local chromium amount < 8%) and does not allow to make a difference between the dissimilar weld (DW 0% δ) and wrought metal (304).

Comparison with field defects

The defects obtained after atmospheric corrosion tests are mainly located in the area of the dissimilar welds close to the interface and along the length of the grain boundaries parallel or perpendicular to this interface. In addition, defects density is very high and their size is variable. These characteristics are close to those of the defects observed on actual components. Similarly, all the martensitic areas (layer, irregular aspects of fusion line) which may occur in the first buttering layer of the materials being investigated, or in the dissimilar welds of the real components, are similarly subject to generalised corrosion attack. When the intergranular defects have reached a size which matches the order of magnitude found in field (> 1 mm, 6 months of exposure in a natural atmosphere), the ferritic part of the dissimilar welds is corroded to a depth of about 50 μm, which is equivalent to that observed in field.

Contrary to the observations on real components, the first buttering layer with δ ferrite is corroded in all the corrosion tests. So the components undergo during their life a less aggressive atmosphere than in the corrosion tests. Additionaly, the atmospheric corrosion test conditions (in the laboratory and in a natural atmosphere) have not allowed observation of a systematic and massive presence of oxides in the defects, nor oxides pockets at the interface. It appears that the source of the difference in morphology between the observed defects and reality is the leaching by surface flow of the areas attacked during exposure, and the geometry of the test specimens (interface perpendicular to the exposed surface). Additional tests are presently being carried out to study these last points.

Conclusion

According to the corrosion hypothesis, stress corrosion cracking and atmospheric corrosion are the two considered mechanisms to explain the defects initiation on the outer surface in the first buttering layer of the dissimilar welds. The performed tests have shown that the SCC mechanism is unlikely on account of the galvanic coupling between the two materials constituting the dissimilar weld. Atmospheric corrosion tests have shown first a general corrosion of the ferritic steel and secondly, in the sensitized area of the dissimilar weld, an intergranular corrosion dependent on the first layer structure. This corrosion is accelerated by stress applied to the material. These characteristics are very similar to those observed on site. Then, an atmospheric corrosion mechanism can initiate some defects like those observed in service. However, the complete demonstration of a such mechanism will be only effective when oxides, similar to those analysed on site, will be displayed in the defects.

References

1. F. CATTANT, O. DE BOUVIER, J. ECONOMOU, A. TEISSIER, B. YRIEIX, "Examens et Etudes Métallurgiques de Liaisons Bimétalliques du Circuit Primaire Principal" Proceedings of the International Symposium Fontevraud III, Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors, Vol 1 (Fontevraud, France : French Nuclear Energy Society, 1994), p. 125.
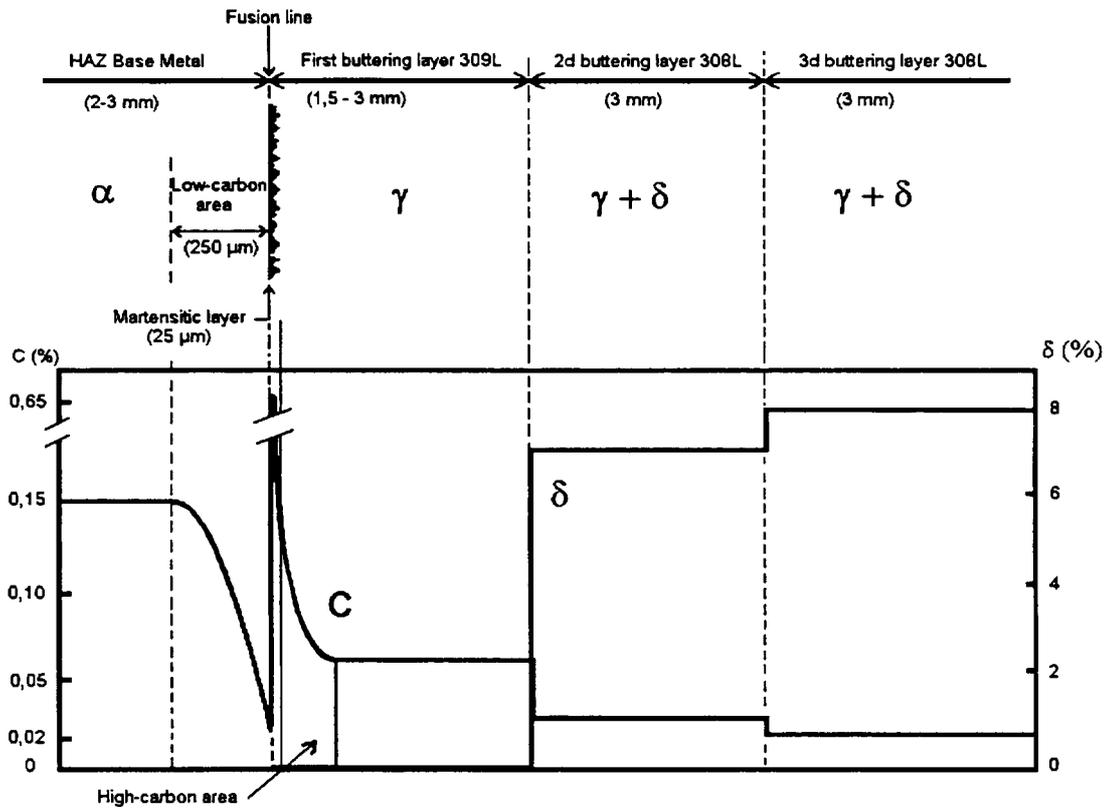
Figure 1 - Schematic view of structure, carbon and δ ferrite contents in a dissimilar weld with 100% austenitic first buttering layer.
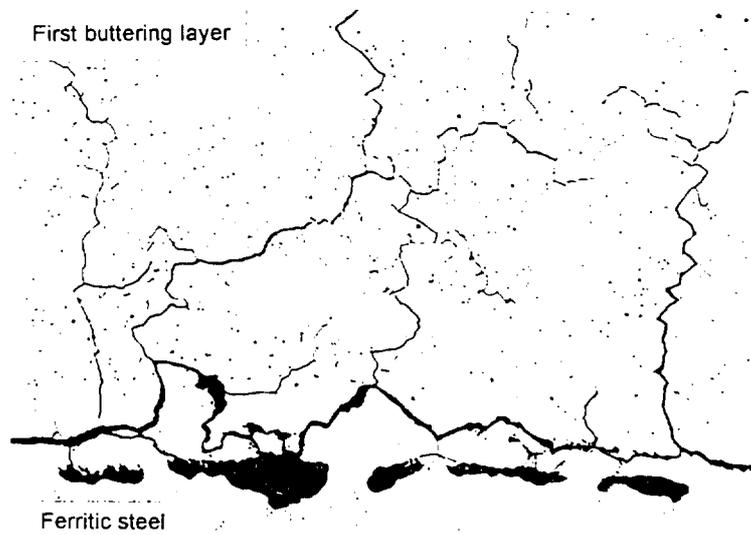

Figure 2 - Outer surface metallographic examination of a defects zone on dissimilar weld - decohesions at the interface with oxide pockets (after grinding, X350).
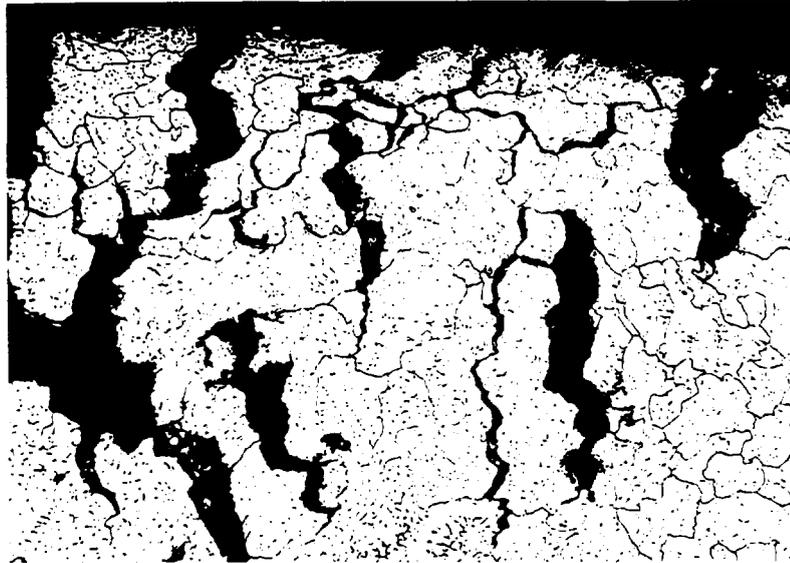
Figure 3 - Cross-section metallographic examination of the body specimen (modified 308) after SCC test (constant load : 400 MPa) in the solution at pH 6 with 1000 ppm of chloride ions - electrolytic etching in oxalic acid (X100).
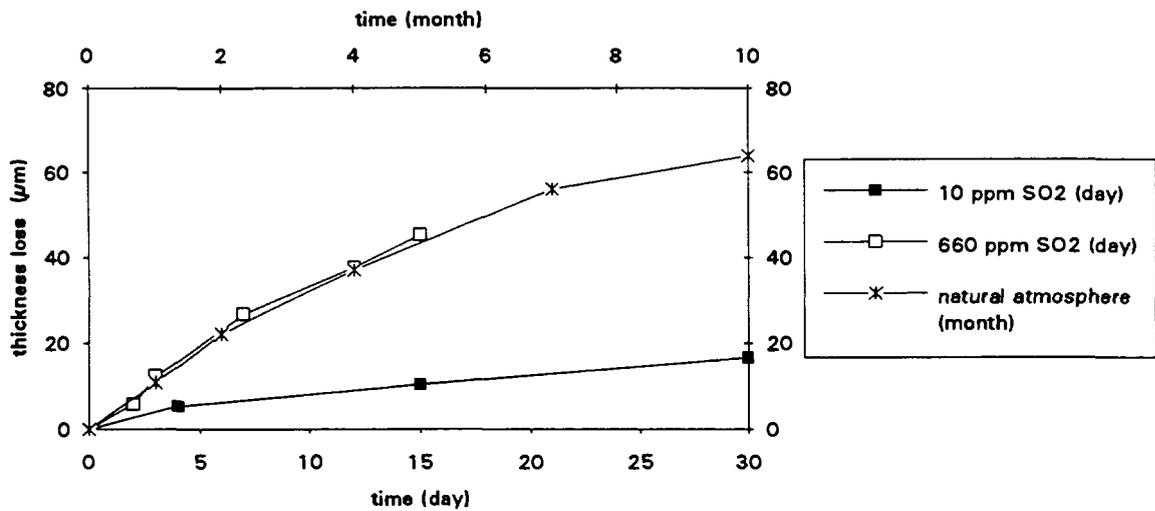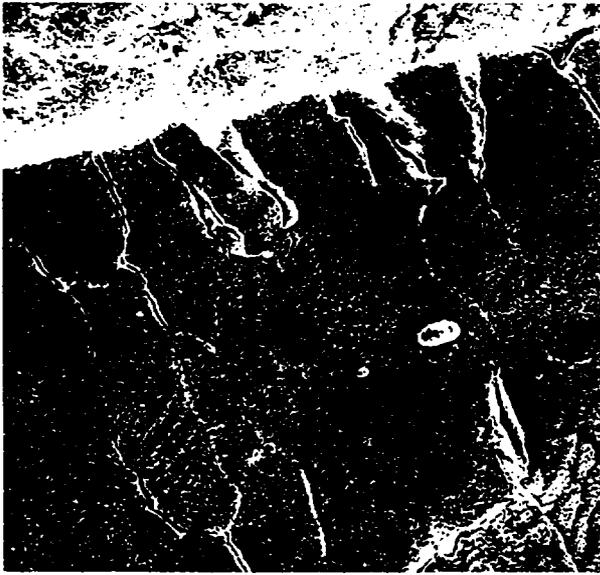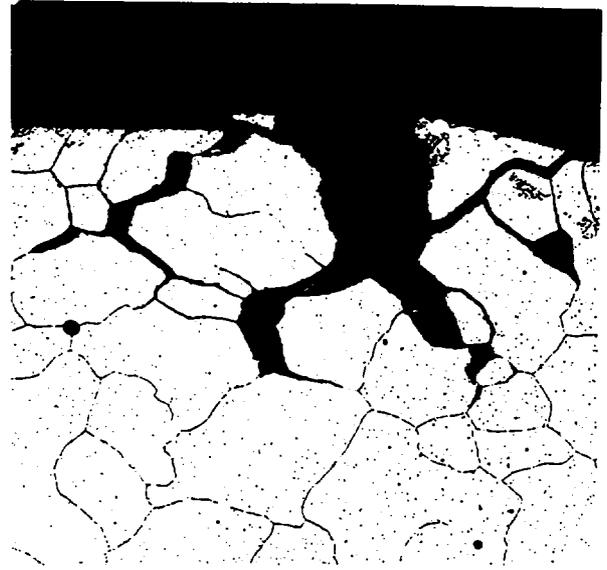

Figure 4 : General corrosion of the ferritic steel (A533) during exposure tests in SO_2 atmosphere and in natural atmospheric corrosion station.

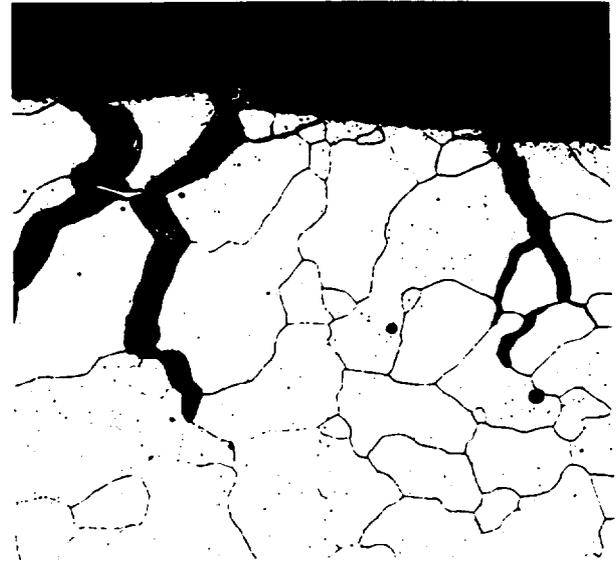a) plate specimen - exposure time : 15 cycles
(X300)

b) plate specimen - exposure time : 7 cycles
electrolytic etching in oxalic acid (X200)

Figure 5 - a) surface SEM and b) cross-section metallographic examination of the material DW 0% δ A after exposure test in 660 ppm SO_2 atmosphere and specimen bending at 90°.

a) four-point bent plate specimen - exposure time : 1 month
(X150)

b) plate specimen - exposure time : 2 months
electrolytic etching in oxalic acid (X100)

Figure 6 - a) surface SEM and b) cross-section metallographic examination of the material DW 0%δ A after exposure test in natural atmospheric corrosion station and specimen bending at 90°.