SHOT PEENING TO PREVENT INTERGRANULAR CORROSION OF FERRITIC STAINLESS STEEL

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ABSTRACT

Shot peening is usually considered as a sensible method to prevent cracking related to stress fatigue or stress corrosion. The prevention of intergranular corrosion (IGC) is not, up to now, a typical application of the process. The reason why is probably that IGC has no connection with mechanics. However, some authors have noted a beneficial effect for austenitic steels when shot peening is performed before sensitization (i.e. depletion of Cr by precipitation at the grain boundary). We provide in this paper a new insight by illustrating the effect of shot peening on a ferritic stainless steel when the treatment is applied after sensitization.

KEY WORDS : intergranular corrosion (IGC), ferritic stainless steel, shot peening, welding, residual stresses.

CONTEXT AND OBJECTIVES

Heat exchangers involving high steam-water velocity require material immune to erosion-corrosion. This is the reason why 1300 MW moisture separator reheaters used in nuclear power plants by EDF are protected by ferritic stainless steel plates. Feedback from plant experience on this vessel indicates that the behaviour of the parent metal sheet is satisfactory, but some degradation has been observed on welded fixing bearing pads (which assure the fixation of the parent sheet on the vessel, Fig. 1).

Cracking develops around the pad as an intergranular network with branching parallel to the plate. Damage is located in a narrow zone at the boundary between the heat affected zone and the base metal. The alloy matches with AFNOR norm Z6C13, which corresponds approximately to AISI 403 (Table I). Many hypotheses such as fatigue, embrittlement due to welding, and galvanic corrosion have been suggested to explain the phenomenon. They were considerated as improbable, due to the observed crack location and morphology (Fig. 2). A more probable explanation is intergranular corrosion after Cr depletion of grain boundaries by carbide precipitation. Suspecting that stresses could enhance the phenomenon (1), a mechanical analysis of the loading of fixed bearing pads has been performed, with a view to reducing stress levels (2). Shot peening was also suggested as a method to improve the resistance of the material (2).

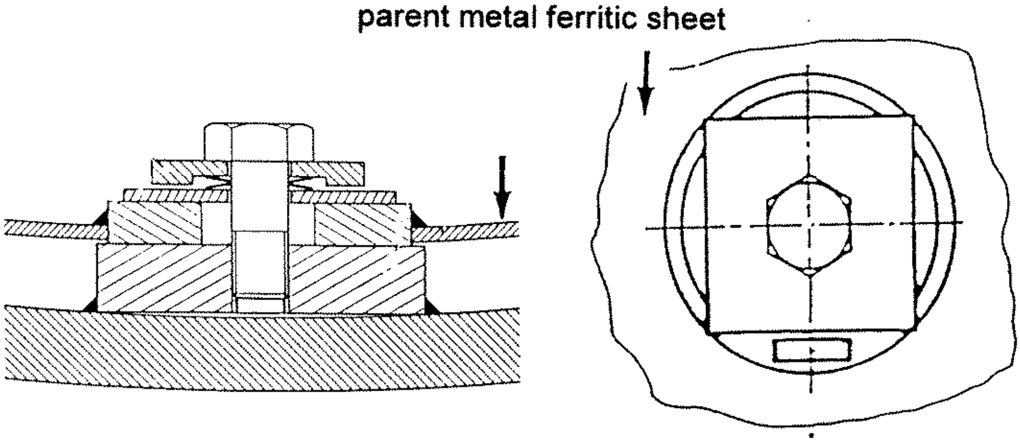

Fig. 1 Fixing bearing pad of 13 % Cr steel plates which protect against erosion-corrosion the inner part of vessels of moisture separator reheaters.

Intergranular corrosion may be attributed to Cr depletion adjacent to grain boundary Cr carbides (3). The occurrence of Cr depletion has not been proven in this case, but inferred from carbide precipitation. The present study was initiated to (i) prove that Cr depletion is actually operating (ii) provide metallurgical solutions. To reach these goals, the following points were studied, either on industrial specimens or representative laboratory mock-ups :

- microstructure and precipitation analysis by scanning electron microscopy (SEM) and transmission electron microscopy (TEM),
- damage simulation with an accelerated test appropriate to ferritic steels (in order to reproduce intergranular corrosion),
- determination of residual stresses,
- evaluation of the capabilities of heat treatment and shot peening.

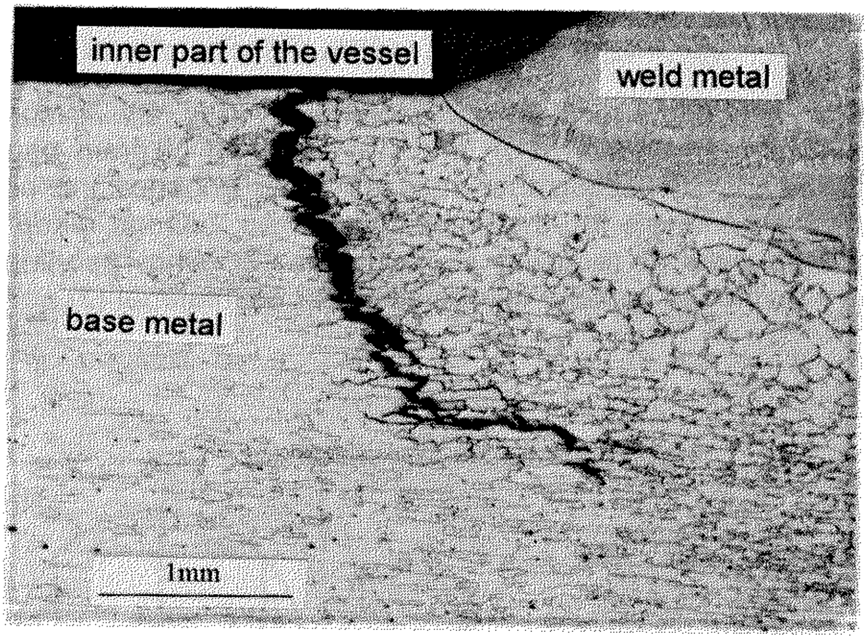

Fig. 2 Intergranular cracking is observed around the welded pad, at the boundary of heat affected zone and base metal.

Table I : Chemical composition of the ferritic stainless steel (wt %).

C	Si	Mn	S	P	Ni	Cr	Mo	Al	N
0.046	0.36	0.54	0.009	0.022	0.12	12.96	<0.01	0.08	0.031

CHROMIUM DEPLETION

Depletion of Cr at the grain boundary (or sensitization) occurs at a certain temperature well below the solution precipitation temperature for carbides (4). The reason why is that the Cr diffusion rate is much lower than that of carbon. This is true both for austenite and ferrite (5). However, the latter structure is more sensitive. In fact, precipitation could occur at higher cooling velocities due to the higher diffusion rate of Cr in the body centred structure than in the cubic face centred structure. Longer annealing times or higher temperatures - still below the solution temperature - permit the Cr to catch up and replete the Cr depleted areas (desensitization). If all the available carbon is precipitated, further depletion below the solubility temperature is not possible. This is theoretically the case for the plate under consideration : the only way to re sensitize is to exceed the carbide solubility curve.

To verify the depletion of Cr in the vicinity of precipitates, heat treatments were performed on the parent metal to sensitize and desensitize the material. The purpose was to distinguish depleted from non depleted grain boundaries by conventional metallographic etching. Nitric acid is a suitable etching agent, clearly revealing the sensitized zones (Fig. 3). It matches exactly the lateral extension of intergranular cracking as observed on the industrial component (Fig. 4).

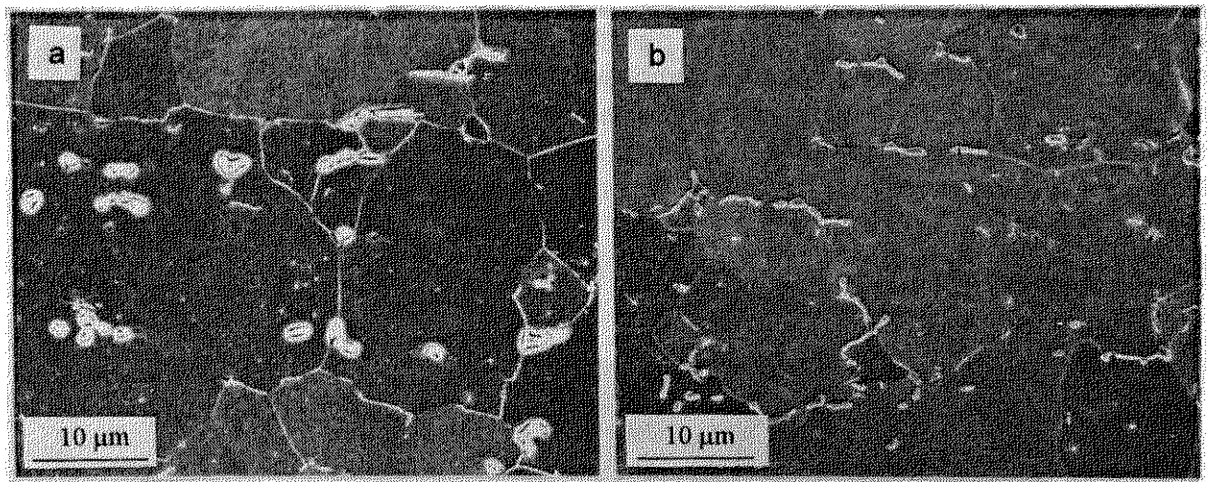

Fig. 3 Scanning electron micrography of the grain boundaries and carbide- matrix interface after nitric etching. (a) sensitized sample, (b) non sensitized sample.

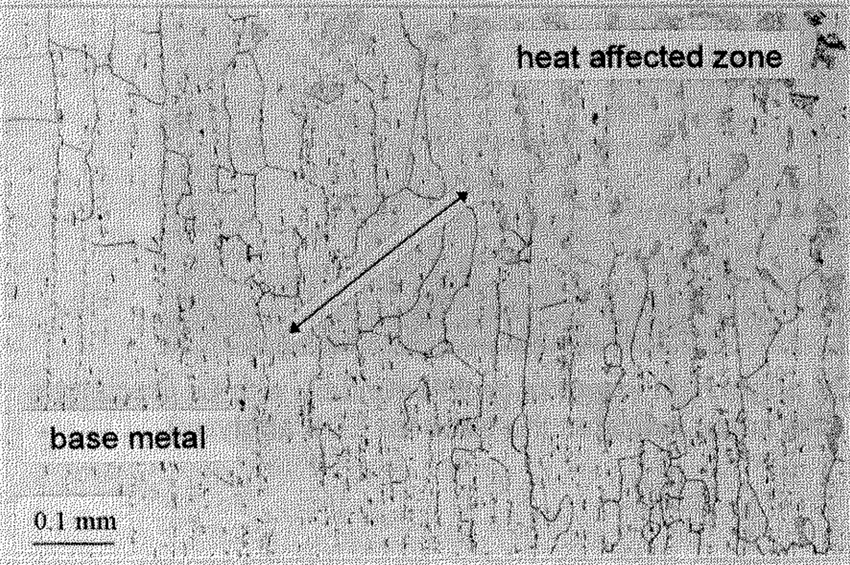

Fig. 4 Sensitized zone, as revealed by nitric acid etching.

Complementary investigations were made with TEM in order to determine the Cr profile at the grain boundaries. Energy dispersive X-ray spectra (EDX) were acquired on a Philips CM 200 FEG TEM equipped with a Kevex Quantum analyser. Planar specimens were prepared by dimple grinding followed by argon-ion milling, in order to reduce the possibility of preferential etching of Cr. The spectra were acquired on a pitch of 100 nm in the matrix, and 10 nm in the grain boundary region. The diameter of the electron probe was approximately 5 nm. Grain boundaries which appeared to be parallel with respect to the electron beam were chosen for the analysis, but no attempt was made at accurate alignment. The profile is flat for the so-called desensitized material, i.e. there is no depletion at the grain boundary. On the other hand, the profile exhibits a decrease in the Cr content at the grain boundaries close to Cr precipitates in the so-called sensitized material (Fig. 5). Depletion diminishes the Cr level down to 9.9 wt %, which is far below the accepted amount to guarantee passivity (Fig. 6).

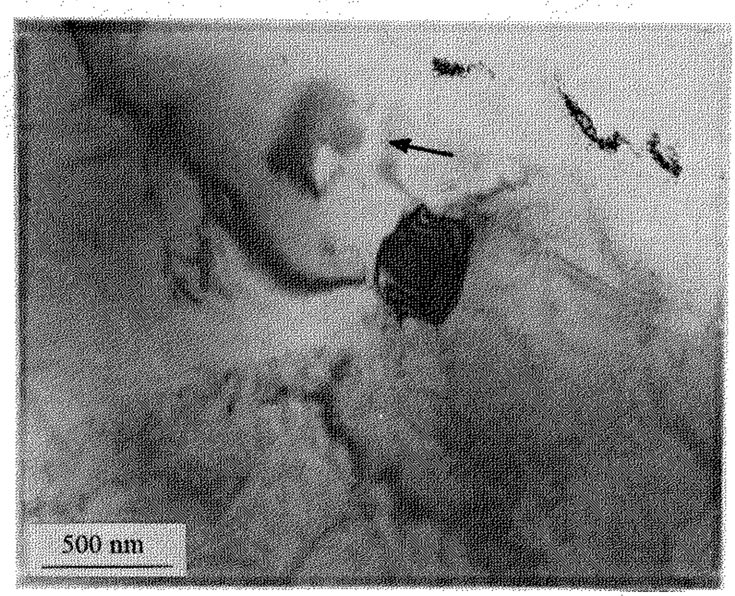

Fig. 5 TEM bright field image of grain boundary with Cr precipitate (the arrow indicates the trace for EDX analysis).

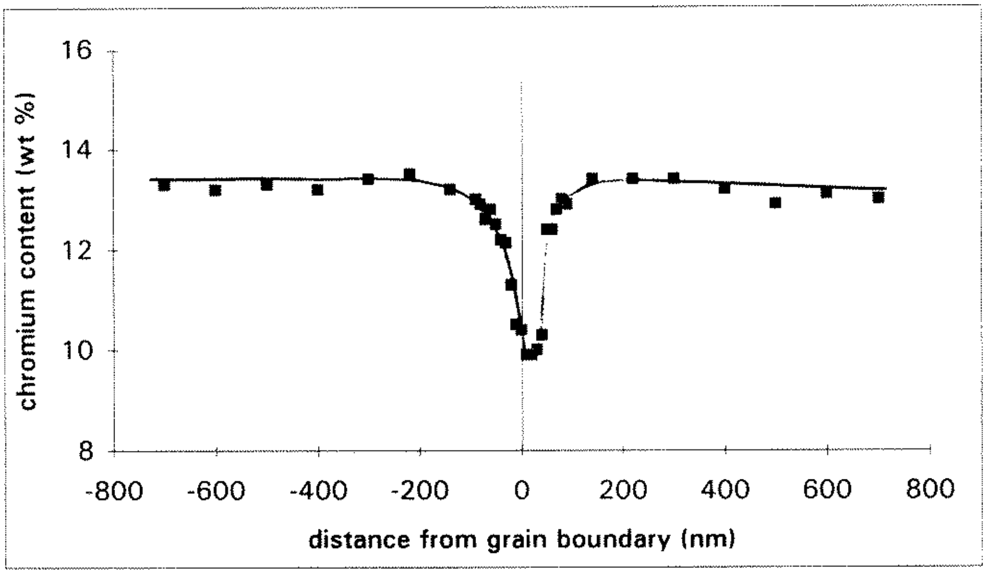

Fig. 6 Chromium profile obtained using EDX from a trace perpendicular to a grain boundary.

Comparisons between steels with different grain size leads to the conclusion that the higher the grain size, the higher the sensitivity. This, as is well known, is due to the fact that the high grain volume over grain boundary ratio produce significant precipitation.

Heating over 850 °C is necessary to reach depletion. It confirms that a prerequisite to re sensitize the steel is to exceed the solubility curve of Cr carbide. Such a condition, which explains the location and the narrowness of the observed sensitized zone, has probably occurred during welding.

EXPERIMENTAL SIMULATION OF THE DAMAGE

The well known Strauss test (as described in the norm ASTM A262E) is closely adapted for austenitic steels. When applying this conventional test to the ferritic steel, the result is not convincing. It leads to general corrosion (Fig. 7a). A more selective test is required to produce intergranular corrosion. One way to reduce the corrosion potential consists in decreasing the amount of sulphuric acid (6). Following Devine and Drummond (7), in a boiling solution containing 0.5 wt % H_2SO_4 + 6 wt % $CuSO_4$ + Cu chips, alloys with > 12 wt % Cr are passive and alloys with < 12 wt % Cr undergo general attack. For the steel under consideration, this results in intergranular corrosion (Fig. 7b) which matches closely with the phenomenon observed on the industrial specimen. When going from the outer to the inner part of the sheet, it is noticed that the cracking zone widens out similarly to the sensitive area. Following the previous paragraph, heat treatments of rehomogenization - if reheating over the solubility curve - would be a worthy solution. However, due to technological constraints - temperatures in between 600 and 800 °C have to be reached, without exceeding - another method would be preferable. Shot peening is a potential alternative solution (8).

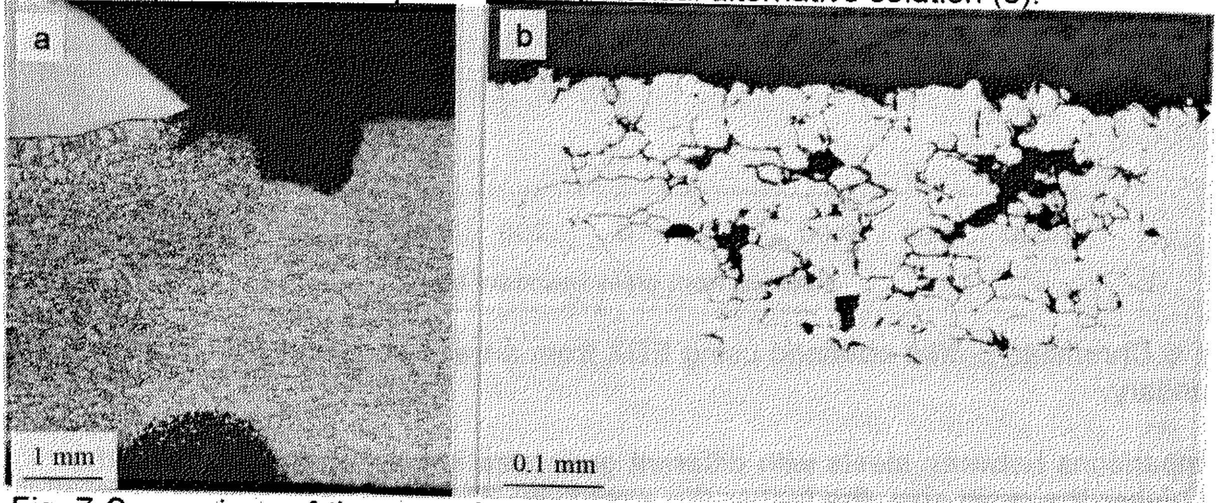

Fig. 7 Comparison of the corrosion obtained (a) by conventional Strauss test and (b) with lower amount of sulphuric acid.

SHOT PEENING EVALUATION

Shot peening is currently used in nuclear power plants, in particular for steam generator tubes made from alloy 600, to prevent stress corrosion cracking (9). Peening was carried out by the Metal Improvement Company using commercial peening equipment and procedures. The laboratory mock-up was treated manually over an angular sector corresponding to one third of the surface. The conventional material is BI 600 (eq. SS CWS 230) calibrated media. Intensity is fixed at F30/35A (eq. 12/14A) with a coverage of 300 % controlled by peenscan. Peening intensity is decreased near boundaries of the penned area to avoid tension. No peening parameters, no surface coverage and no alternate peening materials were investigated.

The effectiveness of the peening process was evaluated by applying the modified Strauss test to compare the behaviour of peened and non peened adjacent zones.

The efficacy is soon noticeable at the macroscopic scale : the peening surface is completely free from attack. In contrast, the unpeened surface is sensitive all along the welding ring. When examined at the microscopic scale, there is no doubt about the efficacy of the method (Fig. 8). If the peened surface is deeply mechanically deformed, it desensitizes locally. This confirms that it is the plastified skin generated by peening which protects the metal from corrosion. A way to go further in the study would be to investigate by etching at a constant potential (10).

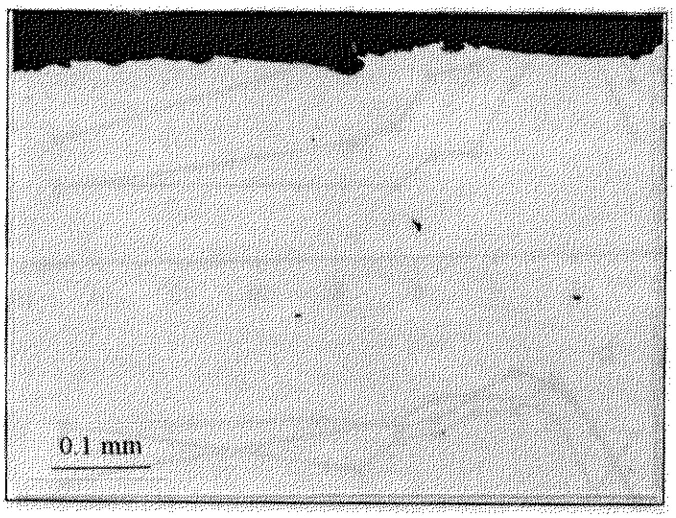

Fig. 8 Illustration of the beneficial effect of peening, as revealed by the modified Strauss test (to be compared to Fig. 7).

The reason why peening improves the corrosion resistance of the material could be due to the existence of stresses (11). Considering mock-up specimens, the stress origin could be only residual stresses. In order to verify if tensile stress is acting during laboratory experiments, a determination of residual stresses was made on the surface of the mock-up as a radial line from welding ring to base metal. Both circumferential and radial stresses were estimated by X-ray diffraction (12). Measurements were performed with a « Set-X » apparatus from Elphyse S.A. Experimental conditions were : K_α ray of Cr under 20 kV, 5mA with a vanadium filter ($\lambda = 0{,}229$ nm, planes {211}, $2\theta = 156{,}3°$). No correction of the residual stresses owing to material removal was performed. The measurement uncertainty is about ± 40 MPa and the analysis depth is about 5,5 µm. The results are displayed in Fig. 9. The important point is the absence of tensile stresses in the zone where the damage initiates. According to the welding conditions and the radial geometry of the specimen, tensile stresses are probably introduced into the welding ring. In conclusion, stresses are not acting during lab corrosion test. Even if external stresses have to be considered in service, stress free laboratory trials lead to a similar damage development to that observed on the industrial specimen.

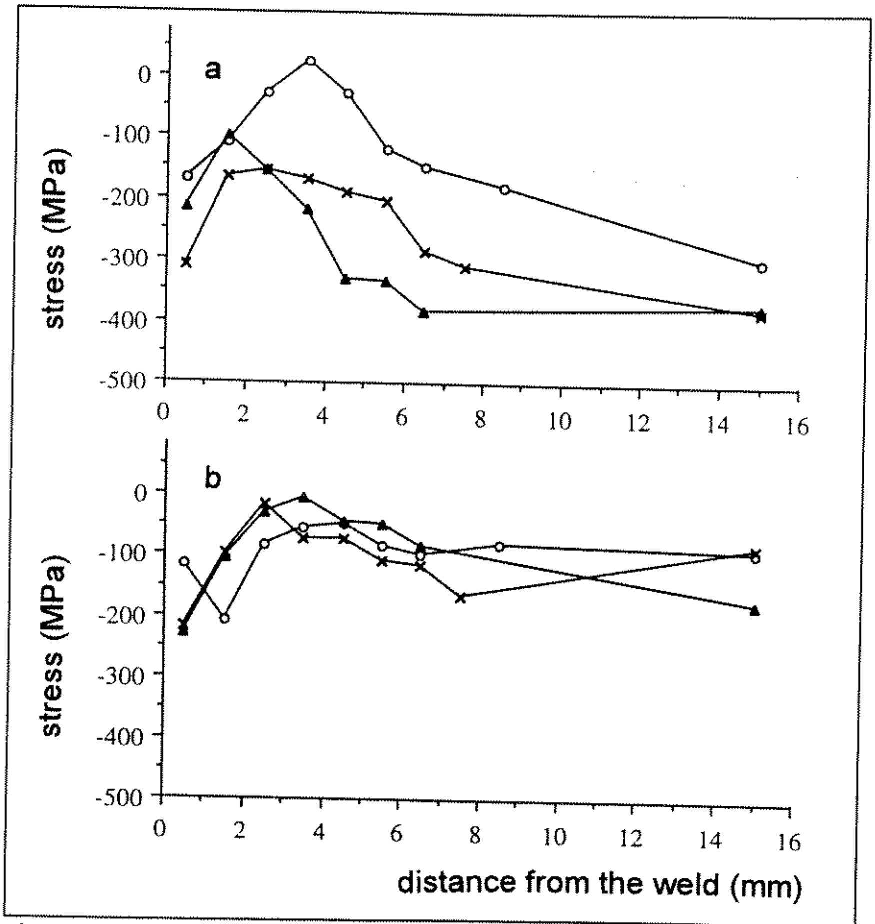

Fig. 9 Evolution of the residual stress level (a) in the circumferential direction (b) in the radial direction on three different mock ups.

Another possible to explanation for the success of peening is that plastic deformation has a strong effect on the grain structure near the surface. In order to investigate this, a TEM cross-section of a shot-peened sample was produced. The method of specimen preparation is described elsewhere (13). Fig. 11 shows the grain structure observed by cross-sectional TEM at a depth of approximately 30 µm from the surface. Peening causes the formation of dislocation cells and it is therefore impossible to distinguish grain boundaries from cell walls. Moreover, deformation bands are also present. Far from the surface, the original grain boundaries rest intact. These observations do not allow the unambiguous assertion that grain boundary structure is destroyed by peening, but at least it is strongly modified. In other words, the continuous sensitized network could be transformed into discontinuous isolated sensitized zones. Also, rehomogenization could occur after cold working.

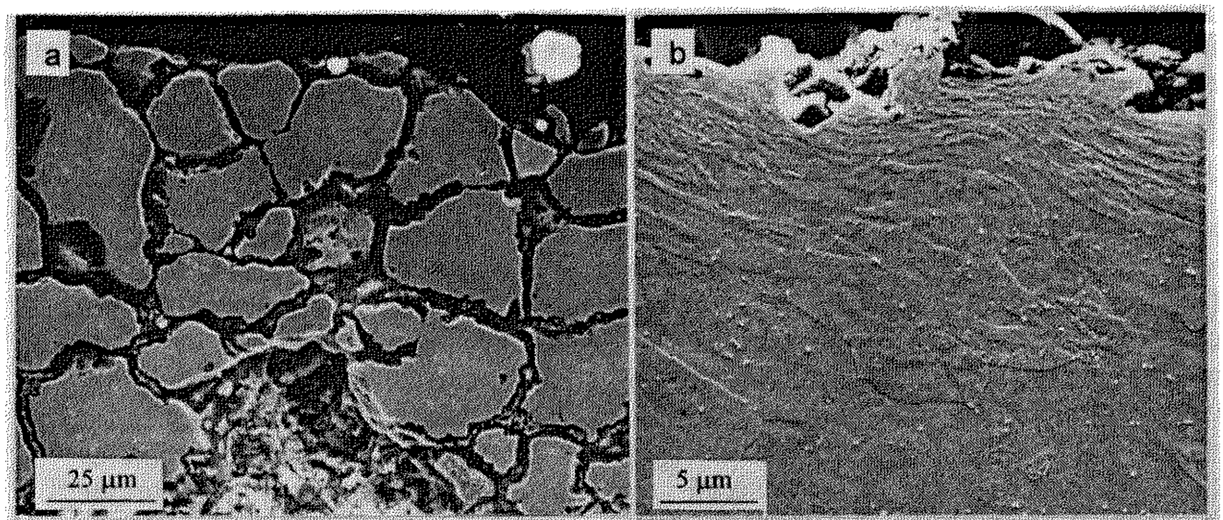

Fig. 10 Comparison of the behaviour of (a) unpeened and (b) peened specimens when exposed to the corrosion test.

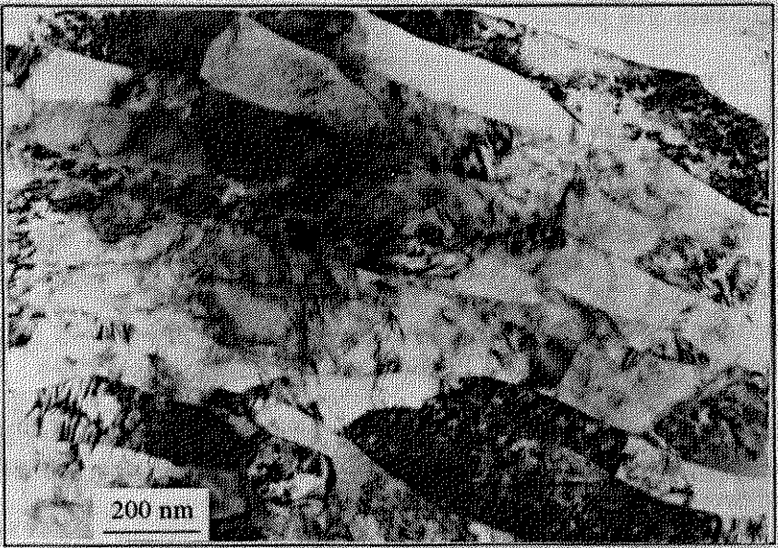

Fig. 11 TEM cross-section showing deformation structures approximately 30 μm below the surface of a shot-peened sample.

CONCLUSION

This study has established the manner in which only a narrow isothermal zone in the vicinity of the welding ring, is affected by IGC. Evidence of Cr depletion at grain boundaries in the vicinity of Cr precipitation was provided by metallographic examination after etching and TEM analysis. Also, the absence of stress contribution in the phenomenon was demonstrated.

Further, the utility of shot peening to protect ferritic stainless steel from intergranular corrosion has been demonstrated, even if shot peening is performed after sensitization. Special corrosion tests less aggressive than the usual Strauss test (which is pertinent for austenite) were developed for ferrite. When applied to laboratory mock-ups, they demonstrated the beneficial effect of shot peening. This quite unexpected result is probably due to modification of the grain boundary network during plastic deformation of the skin. Then, it seems shot peening could be an efficient method to prevent intergranular corrosion cracking initiation of ferritic stainless steel when sensitized by welding. Such a method is under consideration to improve industrial exploitation of heat exchangers in nuclear power plants. Nevertheless, industrial application and feed back evaluation are required to further validate the process.

REFERENCES

(1) Fujiwara K., Tomari H., Shimogori K., *Stress corrosion cracking behavior of weldments of ferritic stainless steels in high temperature pure water.* Trans. ISIJ, vol. 25, 333-339, 1985

(2) Gauchet J.P., Chatelain M., J. Marceau, *13 % internal hardware cracks of 1300 MW moisture separator reheater*, Fontevraud III, France, vol. 2, 12-16, Sept. 1994

(3) Pavlichko W., Hoke J.H., *Precipitates, intergranular attack and chromium depletion in ferritic stainless steel.* Microstructural Science, vol. 4, Proceedings of the 8th annual meeting of the International Metallographic Society, 3-12, 1975

(4) Sedricks A.J., *Corrosion of stainless steels*, John Wiley and Sons, New York, 1979

(5) Lula R.A., Davis J.A., *Intergranular corrosion in 12 percent chromium ferritic stainless steels*. In « Intergranular corrosion of stainless alloys »ASTM, Baltimore, 233-247, 1978

(6) Nichol T.J., Davis J.A., *Intergranular corrosion testing and sensitization of two high-chromium ferritic stainless steels*. In « Intergranular corrosion of stainless alloys »ASTM, Baltimore, 179-196, 1978

(7) Devine T.M., Drummond B.J., *An accelerated intergranular corrosion test for detecting sensitization in low chromium ferritic stainless steels*. Corrosion-NACE, vol. 38, n° 6 , 327-330, June 1982

(8) Friske W.H., *Shot peening to prevent the corrosion of austenitic stainless steels*. Rockwell International, California, 1-44, Sept. 1975

(9) De Keroulas F., *Mise au point d'un traitement de grenaillage des tubes de générateurs de vapeur de réacteurs à eau pressurisée en vue d'améliorer leur comportement à la corrosion sous tension*, First International Conference on Shot Peening, ICP1, Paris, Sept. 1981

(10) Qvarfort R., *Intergranular corrosion testing by etching at a constant potential*. Corrosion-NACE, vol. 51, n° 6 , 463-468, June 1995

(11) Wohlfahrt H., *Residual stresses as a consequence of welding* in « Advances in surface treatments ». Niku-Lari ed., vol. 4, Pergamon Press, 39-58, 1987

(12) Maeder G., Lebrun J.L., Diament A., *Caractérisation par diffraction X d'une couche grenaillée*. First International Conference on Shot Peening, ICP1, Paris, 263-270, Sept. 1981

(13) Scott C.P. et al., *TEM cross-section preparation with minimal ion-milling time*. Journal of Microscopy, vol. 182 (in press)