The Saga of Environmental Degradation of Welds – My Experiences

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1.0 INTRODUCTION

At the outset, I am grateful to the Indian Institute of Welding for selecting me to deliver the prestigious **Sri L. P. Misra Memorial Lecture**. I am doubly honoured since I am delivering this Lecture during the Golden Jubilee Year at the Home of the Institute.

It was July 1981, a couple of weeks before we, the trainees of the 24th Batch of the prestigious BARC Training School, were to be allotted our postings, that the legendary Dr. Placid Rodriguez, a technocrat of repute and a leader of men, was visiting BARC. I had opted to work at the Reactor Research Centre (RRC), Kalpakkam. The main reason being that the Metallurgy Programme there was being headed Dr. Placid Rodriguez. Dr Rodriguez met the four of us individually to know of our area of interest. During my meeting with him, I had expressed my interest to work in welding research. But he regretted since he wanted to take my co-trainee, a M.Tech in Welding, who had also opted for RRC, to work in the area. However, he promised to involve me in welding research through activities in environment sensitive cracking of welded joints. Thus began my foray into the fascinating world of research in welding and environmental degradation, to which I dedicated more than three and a half decades.

My interest in Welding was kindled by the silent inspirer of men, Prof. S. Sundaresan, who was an encyclopedia in welding. Prof. S. Sundaresan was the Head of Department of Metallurgical Engineering at the Regional Engineering College, Tiruchirapalli, during my tenure as an undergraduate student there. His simple and lucid style of conveying matters technical, left me in awe of the genius and had an impact on our impressionable minds. He was a "GURU" in the truest sense of the term.

My experiences in my research on environmental degradation of welds would not have been complete without the vibrant interactions which I had with my senior colleagues Dr. H. S. Khatak, Dr. R. K. Dayal, Dr. T. P. S. Gill, and with my juniors, Vinoy, Geogy George, Anita, Sivaibharasi, Poonguzhali, Zahida and many others. Their sense of total participation and cooperation helped me to carry out meaningful research in the topics of interest during the period.

India is struggling to increase its GDP by a few decimal points, but it can be shocking to know that 3% of the GDP is eroded in corrosion every year. The quantum of loss on account of corrosion is equal to the revenue contributed by the Indian Railways to the exchequer. The loss will be up to 6.5%, if indirect cost of corrosion, in the form of loss of functioning of the plants, accidents, material discarded prematurely, and the various human liabilities are taken in to account. Therefore, it is important that environmental degradation, particularly of the weak weld links, is taken seriously by each and every industry, and efforts are taken to combat it. It is in this context that this year's Sir L. P. Misra Memorial Lecture assumes significance, since I am probably the first person who has dedicated a life time in the area of environmental degradation of welds to receive this honour.

In this Lecture, I would present results from some of the important works carried out by me in the areas of environmental degradation and tensile properties of welds, monitoring techniques for sensitization in HAZ of austenitic stainless steels, and consultancy services.

2.0 ENVIRONMENTAL DEGRADATION

In the 80s and 90s, stress corrosion cracking (SCC), as a mode of failure was not very well understood, more so in austenitic stainless steels and their welds. I forayed into my association with SCC of welds with my first study on SCC of weld joints of

type 316 stainless steel [1]. Weld joints with a sensitised heat affected zone (HAZ) and a non-sensitised HAZ were made using the MMA and TIG welding processes. The welds were tested in an acidified Nacl solution using the constant load testing technique. The results are shown in **Fig. 1**. Weld joint with sensitised HAZ showed higher susceptibility to SCC and a more negative critical cracking potential (CCP). Failure occurred in the HAZ of sensitised weldment, and in the weld metal of non-sensitised weldment. This showed that a sensitized HAZ was the most susceptible zone for SCC in an austenitic stainless steel weld joint. Tests with applied potential indicated that SCC occurred in a narrow range of potentials anodic to CCP in both the sensitized and non-sensitised weldments. SCC susceptibility increased with increasing anodic polarization. Slight cathodic polarization to CCP inhibited cracking. This suggested that dissolution mechanism of SCC was operative in these weld joints.

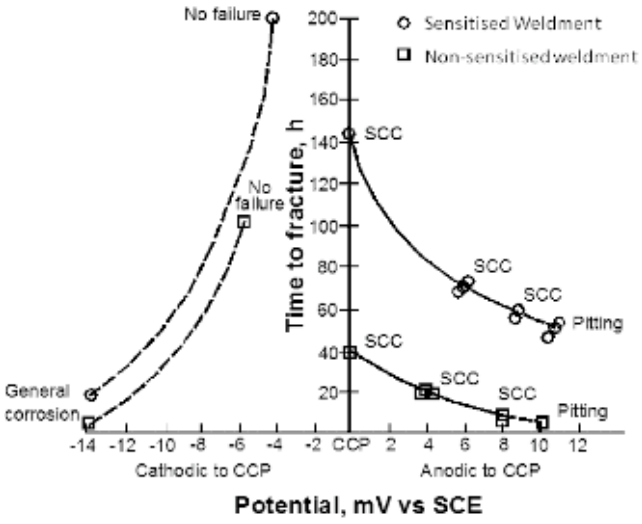

Fig. 1 : SCC of sensitized and non-sensitised weld joints

It was believed that increasing heat input always increased the susceptibility of weld metal to SCC and pitting corrosion. This was based on studies carried out on autogenous welds. However, no report was available on effect of increasing heat input on the SCC susceptibility of multi-pass welds. We undertook this study to, assess the pitting and SCC behavior in multi-pass weld joints of type 316N stainless steel [2,3]. MMA weld metal (C=0.061 wt.%, N=0.14 wt.%). Round tension specimens of MMA welds made with four different heat inputs ranging from 3.07 to 7.41 kJ/cm, were subjected to SCC tests using the constant load testing technique in boiling NaCl solution at an initial stress level of 250 MPa. The results showed an increase in resistance to SCC and pitting corrosion with increasing heat input **(Fig. 2)**. Lack of secondary phase precipitation, breaking up of the δ-ferrite network, and softening of the austenite matrix, due to reheating of the previous passes, caused the improvement in SCC and pitting corrosion resistance. However, the same may not be true in case secondary phase precipitation occurs during reheating of previous passes, as is likely in the case of types 304 and 316 stainless steels. Studies need to be carried out on multi-pass weld metals of types 304 and 316 stainless steels to know the exact behavior.

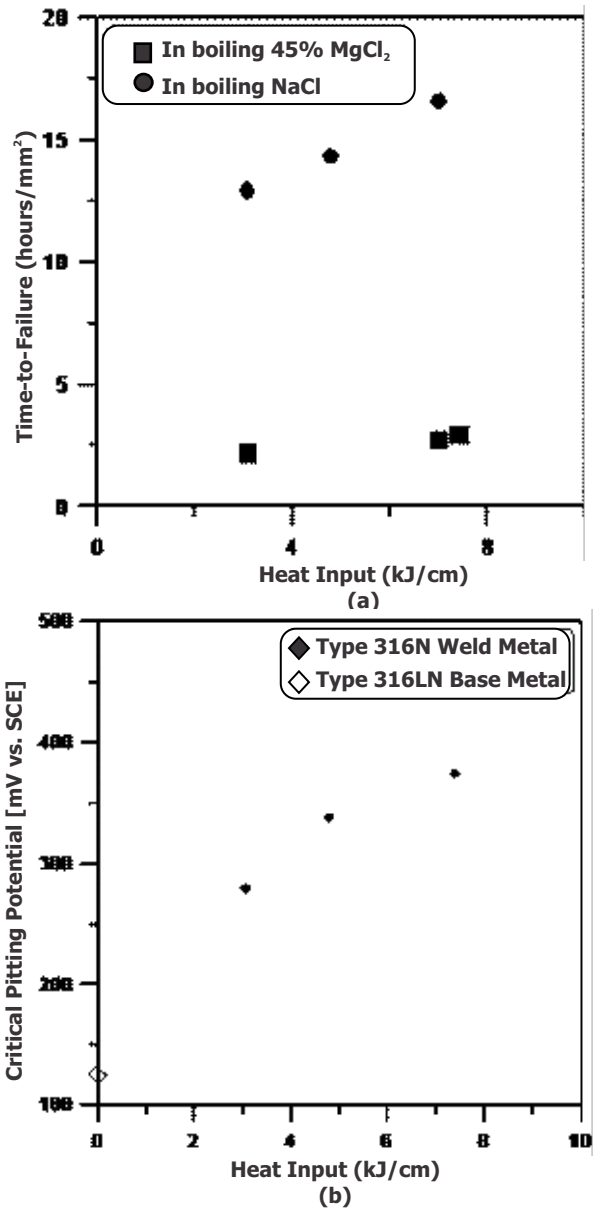

Fig. 2: Effect of Heat Input on (a) SCC behavior, and (b) pitting corrosion behavior

Pitting corrosion studies on weld metal of AISI type 316N stainless steel, aged at 923, 973 and 1023 K for various times, in deaerated acidified chloride solution indicated a decrease in critical pitting potential (E_{pit}) on aging **(Fig. 3)** [3]. The extent of decrease in E_{pit} increased with increasing temperature in the weld metal. The decrease in E_{pit} on aging the weld metal was attributed to any of or a combination of the following reasons: (i) depletion of Cr+Mo from the matrix consequent to formation of C/CN and σ phases, (ii) decrease in the nitrogen content of the matrix, and (iii) creation of additional interfaces. However, at 1023 K, a significant increase in E_{pit} was observed on aging the weld metal for 1000 hours, despite the presence of a large amount of σ phase in the microstructure. This was attributed to the more complete self healing of Mo for weld metal aged at 1023 K for 1000 hours rather than to globularisation of σ phase.

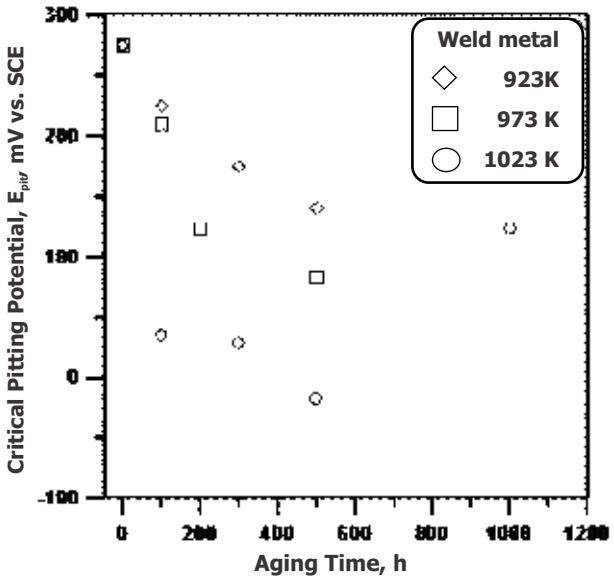

Fig. 3: Variation in critical pitting potential of Weld metal with aging time at different temperatures

Quantification of SCC data, which would be useful to the designers, is possible using the Fracture Mechanics Approach. We were the first laboratory in the country to use the fracture mechanics approach to study SCC of austenitic stainless steel welds. Our involvement with fracture mechanics approach dates back to the late eighties onwards. Initially, we studied the stress corrosion crack growth behavior on type 316 stainless steel, and subsequently on types 304N and 316LN stainless steels and their weld metals in acidified chloride solution. The results of our study are shown in **Table 1** [4,5]. It is seen that sensitisation decreased K_{ISCC} and J_{ISCC} and increased plateau crack growth rate (PCGR) of types 304N and 316 stainless steel, while weld metal of type 304N stainless steel possessed lower K_{ISCC} and J_{ISCC}, and increased PCGR vis-à-vis type 316LN stainless steel base metal.

Another interesting study initiated in our laboratory was on corrosion fatigue behavior of austenitic stainless steels [3,6,7]. Besides studying the base metals of various austenitic stainless steels, we also investigated the effect of sensitization on corrosion fatigue behavior of type 316LN stainless steel in

Table 1 : SCC growth data for the three stainless steels in different metallurgical conditions in 5M NaCl + 0.15M Na_2SO_4 + 2.5 ml/l HCl

Parameters	Annealed 304N SS	Sensitised 304N SS	SA 316 SS	Sensitised 316 SS	316 LN BM	316 N WM
K_{ISCC} ($MPa.m^{0.5}$)	17.0	11.0	13.0	10.5	22.38	14.5
J_{ISCC} (kPa.m)	0.9	0.5	1.0	0.6	2.601	0.583
PCGR (m/s)	1.3E-8	2.3E-8	4.0E-9	1.0E-8	1.75E-9	2.8E-8
K_Q ($MPa.m^{0.5}$)	18.0	17.0	11.2	13.28	18.0	24.0
J_Q (kPa.m)	240.0	230.0	74.8	84.0	112.0	122.0

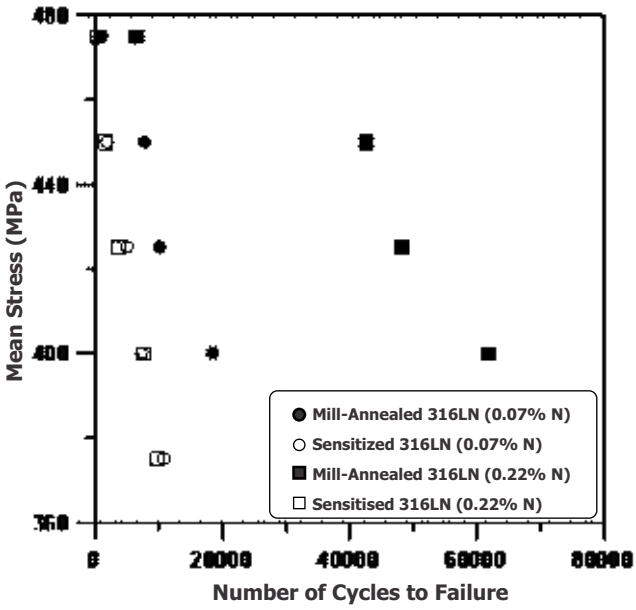

Fig. 4 : Corrosion fatigue behaviour of type 316LN stainless steel with 0.07 and 0.22 wt. % nitrogen in boiling acidified NaCl solution, in mill annealed and sensitised conditions

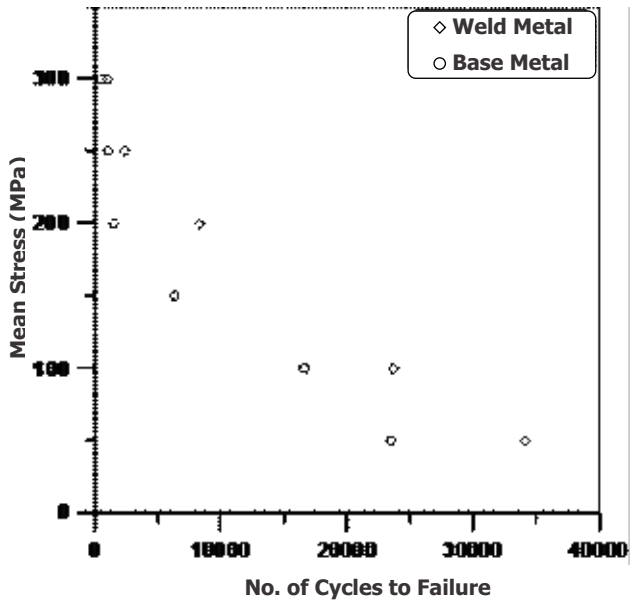

Fig. 5 : Corrosion fatigue behaviour of type 316LN stainless steel base metal and type 316N stainless steel weld metal

acidifed chloride solution. **Fig. 4** shows that mill-annealed type 316LN stainless steel with 0.22 wt. % nitrogen showed far better corrosion fatigue resistance (as measured by the number of cycles to failure) than type 316LN stainless steel with 0.07 wt. % nitrogen at all values of mean stress for the mill-annealed condition. It is also seen that aging reduced the corrosion fatigue resistance drastically, the reduction being more in type 316LN stainless steel with 0.22 wt. % nitrogen. No fatigue limit was observed.

Studies on the corrosion fatigue resistance of base and weld metals in acidified chloride media showed a higher resistance to corrosion fatigue for the weld metal vis-à-vis the base metal **(Fig. 5)**. This was due to the higher YS and UTS of the weld metal and the presence of higher defect density in it. The fatigue resistance of a material is directly proportional to its tensile strength. The weld metal possessed higher tensile strength than the base metal, thus accounting for its higher resistance to fatigue in the chloride environment. Also, for a similar mean stress, the higher YS of the weld metal would reduce the crack-tip opening for the weld metal as compared to the base metal. This would restrict the supply of chlorides to the crack tip and reduce the interaction of the environment with the material. No fatigue limit was observed for both the base and weld metals.

3.0 TENSILE BEHAVIOUR

It was mandatory for me to study the tensile behavior of weld metals of austenitic stainless steels to carry out SCC studies and, also, to understand SCC behaviour. In the early 90s, I carried out a study on the effect of the amount of and physical parameters of σ phase on the tensile properties of austenitic stainless steel weld metal [8]. σ phase precipitated on aging type 316L stainless steel weld metal was estimated by an electrochemical extraction technique, which was performed at a potential of 1.5 V (with respect to the platinum electrode) in a methanol solution containing 10 vol.% HCl. **Fig. 6 (a)** shows approximately 20% rise in ultimate trnsile strength (UTS), and **Fig. 6 (b)** shows a nearly 35% drop in ductility, when about 12 wt.% σ phase is precipitated in the weld metal. This is quite a significant change considering that the weld metal was aged for only about 2000 hours. However, yield strength (YS) dropped on aging vis-à-vis as-deposited weld metal (ADWM) **(Fig. 6 (c))**. This indicated that matrix softening, which occurred due to σ phase precipitation, caused the changes in YS and not the σ phase.

It has been reported in literature that the higher YS and UTS and lower ductility of an as-deposited austenitic stainless steel weld metal is higher than its base metal due to the presence of δ-ferrite in it. I was left wondering if 3-8 wt% of δ-ferrite could bring about such changes (sometimes by a factor of 2 or more)

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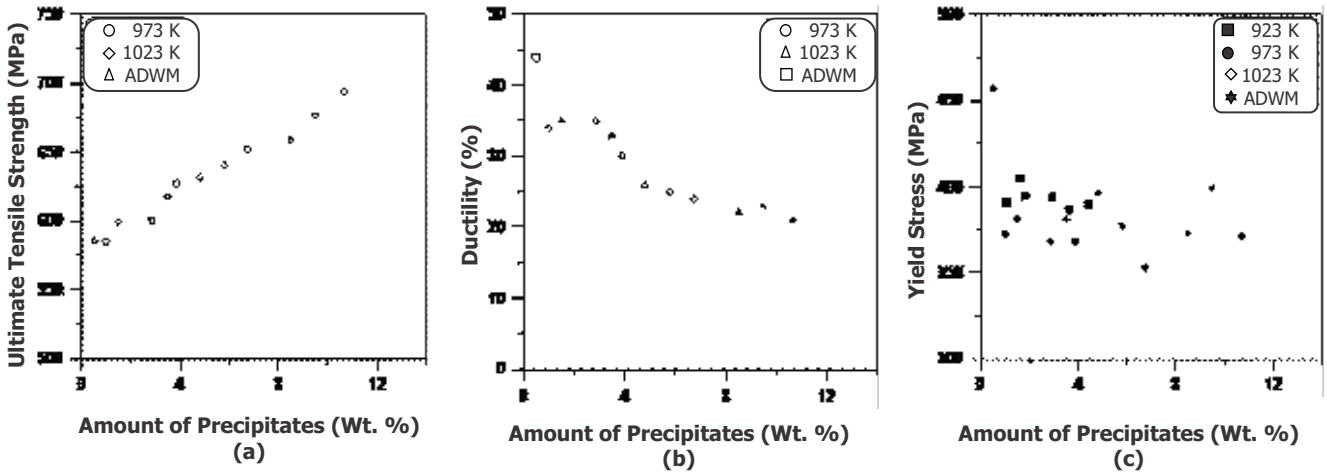
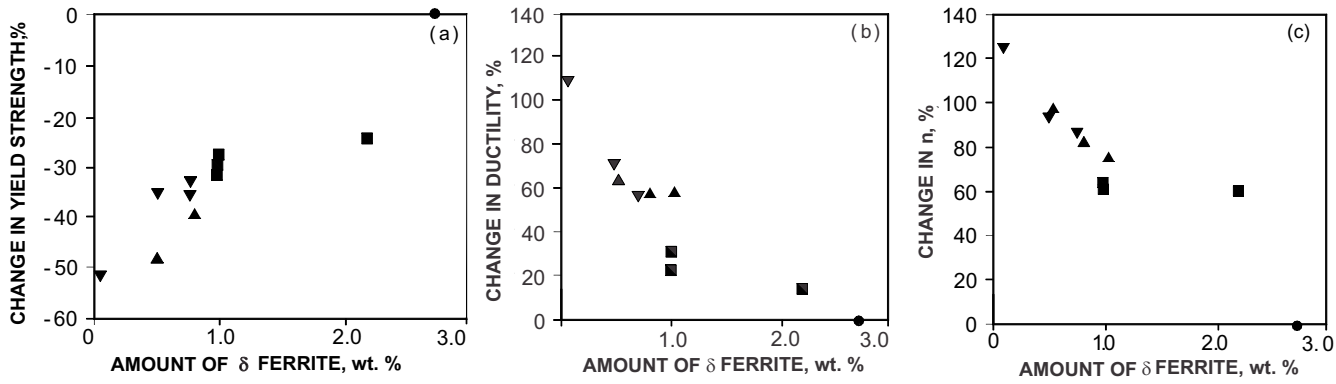


Fig.6 : Effect of amount of phase on the (a) UTS, (b) ductility, and (c) YS of weld metal of AISI type 316L stainless steel

in the tensile behavior of the weld metal, particularly considering that both austenite and δ-ferrite are deformable phases. My doubts deepened, as my earlier studies on effect of phase on the tensile behavior of weld metal showed only about 20% increase in UTS and a 35% reduction in YS with increase in the amount of undeformable σ to ≅ 10 wt%.

We undertook an investigation to study the effect of δ-ferrite on the tensile behavior of the weld metal [9]. Round tensile specimens were machined from undiluted weld deposits and mill annealed type 316 stainless steel base plate (wt. % C = 0.05). The weld metal tensile specimens were aged at 1323, 1373, and 1423 K for various durations up to 80 min. δ ferrite content in the weld was measured before and after aging with a Magne- Gage. The secondary phases present in the weld metal were identified by X-ray diffraction (XRD) technique, after extraction by electrochemically dissolving the austenite in a 10 vol.% HCl in methanol electrolyte at a potential of 1.5 V with respect to the platinum electrode. Optical microscopic examinations were carried out after etching the weld metals in boiling Murakami reagent. Ferrite distribution (number of δ ferrite particles/mm^2 of specimen), shape factor (diameter to length ratio, d/l), and degree of interconnectivity (DOI, ratio of number of interconnected particles to total number of particles) of δ ferrite were determined. The changes occurring in the austenite were studied after electrolytically etching the weld metals in a 10 wt -% ammonium persulphate solution. Tensile tests were carried out on as deposited weld metal, aged weld metals, and on mill annealed base metal to determine YS, UTS, percentage total elongation, and work hardening exponent (n).

The YS of weld metal was 397 MPa, and that of base metal was 186 MPa; while ductility values were 28% and 78% respectively. The UTS values did not vary significantly (about 580 MPa). The YS of weld metal corresponded to nearly 30% cold worked base metal. **Fig. 7** shows that on annealing the weld metal, YS was found to decrease while ductility and 'n' increased with decrease in the amount of δ-ferrite. **Fig. 7 (a)** shows that the YS of the weld metal aged at 1423 K for 10 min was higher than that of the weld metal aged at 1373 K for 40 min, despite the amount of ferrite being the same (0.5 wt-%). **Fig. 7 (b)** shows that the ductility of the weld metal was higher when aged at 1373 K for 10 min rather than at 1323 K for 10 min, in spite of a similar δ ferrite content (1.05 wt-%). **Fig. 7 (c)** shows that the percentage change in n, however, was the same (60%) despite variation in the ferrite content on aging the weld metal at 1323 K for 5, 10, 20 min. This clearly indicated that the amount of δ-ferrite did not influence the properties of the weld metal. Similarly, ferrite distribution, shape factor and degree of interconnectivity of δ ferrite did not show any systematic correlation with the tensile behavior of the weld metal. This suggested that the tensile properties of the weld metal do not depend on the amount, DOI, shape factor, and distribution of ferrite. Hence, it is inferred that the changes in weld metal tensile properties to values of mill annealed base metal, with increasing aging temperatures, are caused by thermally activated processes which lead to microstructural changes in the austenite. **Fig. 8** shows that on aging the weld metal between 1323 and 1373 K, recovery and recrsytallisation processes cause microstructural changes in the austenite. The process of recovery in the austenite does not cause substantial changes in the tensile properties of the as



●as deposited; ■weld metal aged at 1323 K; ▲weld metal aged at 1373 K;▼ weld metal aged at 1423 K; a YS; b ductility; c n

Fig. 7 : Effect of amount of δ ferrite on given properties of weld metal

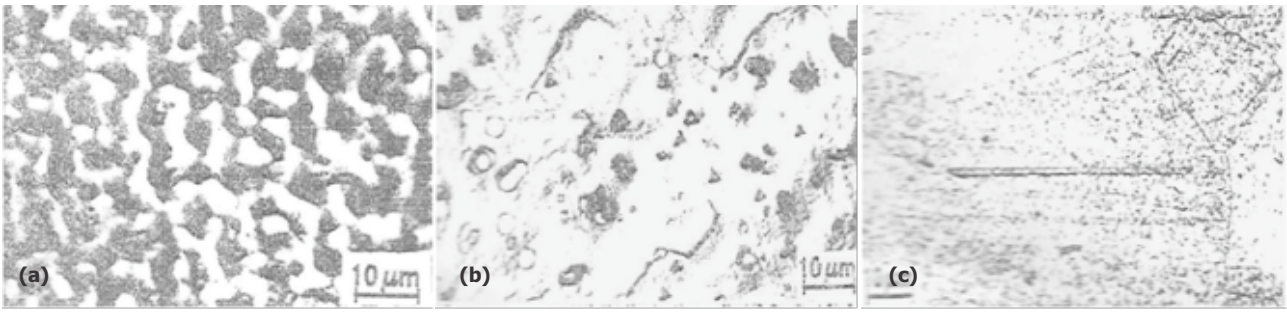
deposited weld metal. As evidenced by X (X is the ratio weld metal YS/ base metal YS) reducing from 2.14 to 1.56; while Y (Y is the ratio weld metal ductility/base metal ductility) improved from 0.37 to 0.52 on aging the weld metal at 1323 K for 20 min. Corresponding to the stage of onset of recrystallisation of the austenite, on aging the weld metal at 1373 K for 40 min, X reduced to 1.11 and Y improved to 0.59. When substantial recrystallisation occurred on aging the weld metal at 1423 K for 80 min, X considerably reduced to 1.02 while Y significantly improved to 0.85. This suggests that the weld metal nearly acquires the base metal properties upon recrystallisation of its austenite, thus implying that it is the deformation of the austenite, which is induced during solidification, that dictates the tensile behavior of the as-deposited weld metal.

4.0 NON DESTRUCTIVE EVALUATION

With the dawn of the 21st Century, my interests also branched off to application of non-destructive testing (NDT) to evaluate sensitisation and to mechanistic studies of SCC. One of my first attempts was to find an alternative method to electro potentiokinetic reactivation (EPR) technique, which is standardised by ASTM G108, to evaluate sensitization. I felt the need to develop an existing technique to detect and quantify sensitization, despite EPR being a NDT technique, because EPR technique suffered from some inherent drawbacks. The threshold EPR charge value above which a stainless steel is susceptible to intergranular corrosion (IGC) in ASTM A262E is not a unique number, but depends on temperature at which the material was sensitised. Also, EPR tests have an inherent disadvantage in that they are very sensitive to changes in Cr depletion anywhere in the alloy and cannot easily differentiate between matrix and grain boundary depletion.

After discussions with my colleagues, it was decided to use eddy current testing (ECT) as an alternate method to detect and quantify sensitization in austenitic stainless steels [10-12]. AISI type 316 stainless steel plates of 3 mm thickness were heat treated at 873, 973 and 1073 K for different time durations in the range of 15 min to 25 h. Rectangular specimens of dimensions 100 x 10 x 3 mm were then machined from the as-received and aged material. Optical microscopic examination of the as-received and aged base metals was carried out after etching electrolytically in 10% (by weight) ammonium persulphate solution at a current density of 1 A/cm^2 for 1.5 min to detect intergranular carbide precipitation. The as-received and aged specimens were tested for IGC resistance by the ASTM A262 Practice E test (modified Strauss test). EPR tests were carried out on the as-received and aged specimens in a solution containing 0.5M H_2SO_4 + 0.01M NH_4SCN at room temperature, using the double loop technique. The degree of sensitisation (DOS) in the as-received and aged specimens was also measured using the ECT technique. The measurements were made on as-aged specimens and after exposure to Strauss test solution.

Low magnification optical microscopic examination of the bent region was used to classify the Practice E exposed aged specimens into four categories viz. unaffected base metal **(Fig. 9 (a))**, base metal containing fissures **(Fig. 9 (b))**, base metal containing cracks **(Fig. 9 (c))** and broken base metal **(Fig.9(d))**. Microstructures are also affixed to these classifications. Based on these classifications, the results of the EPR and EC tests were analysed.



(a) as deposited; (b) aged a5t 1323 K for 20 min; (c) aged at 1373 K for 40 min

Fig. 8 : Representative optical micrographs showing evolution of austenite matrix in weld metal after given heat treatment

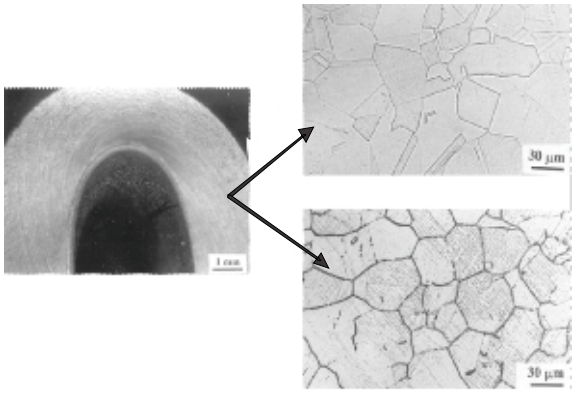


Fig. 9 (a)

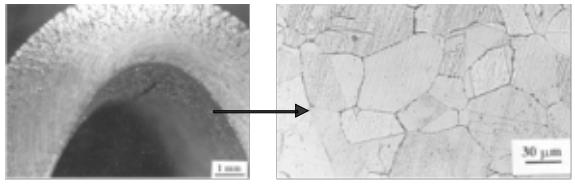


Fig. 9 (b)

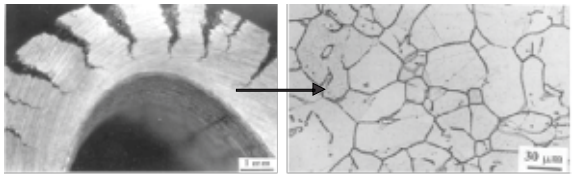


Fig. 9 (c)

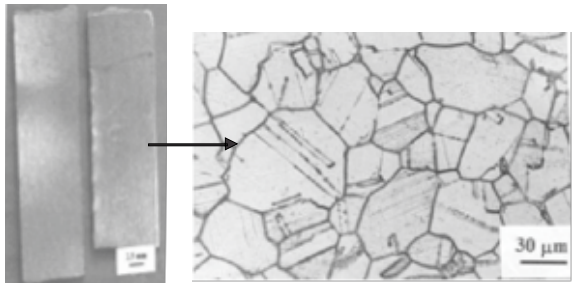


Fig. 9 (d)

Fig. 9 : Correlation of results of ASTM Practices A 262 A and E

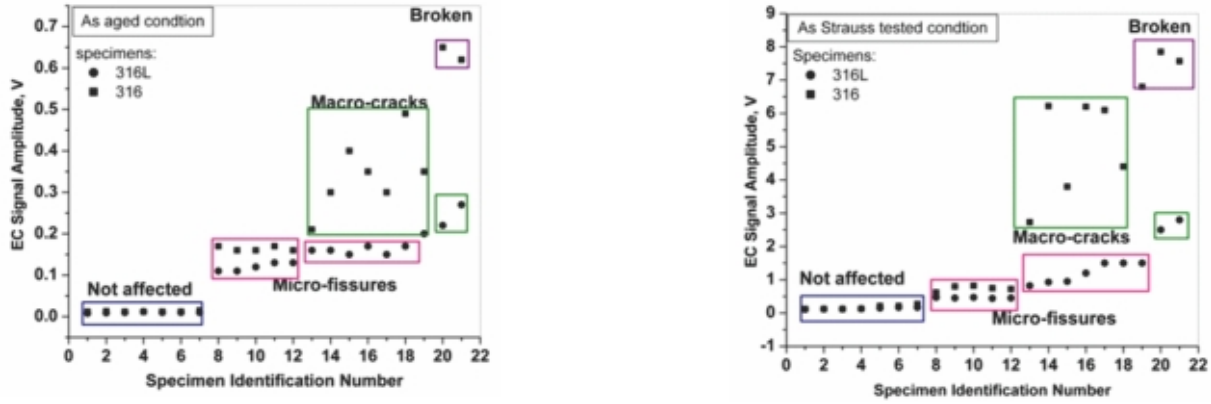


Fig. 10 : ECT amplitude response of types 316 and 316L stainless steels in (a) as aged condition, and (b) Strauss tested condition

The EC signal amplitudes from various specimens in the as-aged condition (prior to Strauss test) are shown in **Fig. 10 (a)**. It can be seen that the overall change in the amplitude among all the specimens was small i.e. about 0.75 V for type 316 stainless steel and about 0.25V for type 316L stainless steel. This was attributed to a small change in conductivity/ permeability due to depletion of chromium adjacent to grain boundaries which could cause local increase in the nickel content that could result in increased magnetic permeability of the material there. A Cr-depleted zone becomes ferromagnetic and its spontaneous magnetization can be detected.

Fig. 10 (b) clearly shows that in the case of aged specimen exposed to Strauss test, the EC amplitude of the unaffected and fissured specimens in types 316 and 316L stainless steel did not vary significantly. However, in case of specimens that showed cracking or were broken, type 316 stainless steel showed higher values of EC amplitude as compared to type 316L stainless steel. Repeated measurements at various locations on these specimen found that the scatter was within the range of ±0.005 V.

The fact that unaffected specimens also included those with continuous grain boundary carbide precipitation but self-healed indicated that carbide precipitation per se had little or no role in affecting the conductivity/permeability of the steel. This indicated that the changes in the conductivity/ permeability of the as-aged specimens were related to depletion of alloying elements, and those exposed to Strauss tests were a consequence of grain boundary grooving. The slight difference in ECT response between types 316L and 316 stainless steels, in the unaffected and fissured categories, was attributed to lesser amount of carbide formation and the consequent lesser depletion of chromium and lesser grooving. However, in the cracked and broken categories, higjer amount of depletion of Cr and Mo in type 316 stainless steel due to higher carbon content vis-à-vis type 316L stainless steel, caused more extensive grooving during Strauss test, thus producing a higher change in the conductivity. This implies that more reliable detection and assessment of DOS and the propensity for IGC is possible with increasing carbon content in the stainless steel using ECT technique.

A very important application arising from this work is that by knowing the EC signal amplitude for different category specimens, the propensity to and extent of IGC could be assessed without subjecting the specimens to bend test. The impact of this would be felt during monitoring of the stainless steel components in service by providing vital information on the initiation and progress of IGC/IGSCC in service. Also, eddy current testing could be used as a very reliable tool to ensure quality of fabrication against sensitization. This would help fabricators and the users to guard against sensitization, particularly in applications where fabrication costs are linked to DOS.

5.0 CONSULTANCY SERVICES

During my three decades at Kalpakkam, I carried out metallurgical analysis of a number of component failures. I was associated with nearly twenty failure analyses involving a vast number of industries, such as fertilizers, pharmaceuticals, wind energy and our own nuclear industry. Of these consultancy services, the one I enjoyed most was retrieving the steam generators (SG) tubes of our Prototype Fast Breeder Reactor coming up at Kalpakkam [13]. This experience was particularly satisfying since I could contribute to retrieving fabricated SG tubes equivalent of two steam generators, which were damaged due to a fire in a dehumidifier at a private fabrication company. **Fig. 11** shows the damaged tubes after the fire. Before starting the retrieval operation, trial tests were carried out to determine the chemical products of the deposits, develop a cleaning procedure and check the effectiveness of the cleaning by carrying out various tests.

The possibility of not carrying out any cleaning operation was checked by subjecting the cut pieces from the affected tubes to a heat treatment of 760± 10 °C for three hours. This heat treatment was chosen since the fabricated steam generators are to be subjected to a post weld heat treatment at this temperature-time combination. The heat treatment was carried out both in air and in argon. **Fig. 12** shows that the appearance of the heat treated sample was much worse than the sample from the as–received affected tubes. The heat treated tubes showed a number of pits which were wide and deep.

Failure of the heat treatment of the as-affected tubes to yield the desired result led us to devise a cleaning operation on the SG modules. This was achieved by characterizing the surface before and after cleaning by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDAX) techniques. The residue which was collected from the SG tubes at the private firm was analysed for its chemical composition. The results of the chemical composition analysis are shown in **Table 3**. It is seen

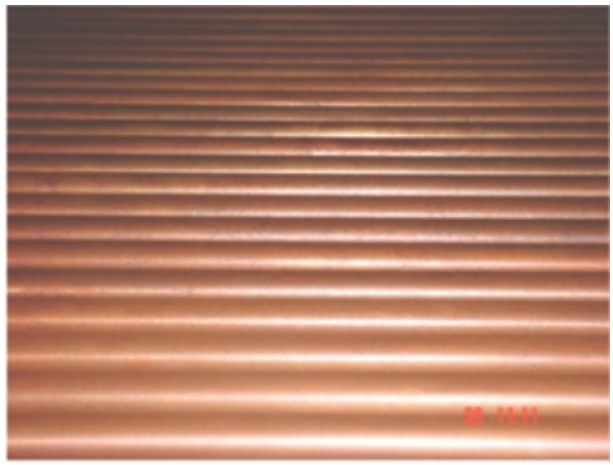


Fig. 11 : The damaged SG tubes after deposition of the byproducts of the burnt dehumidifier

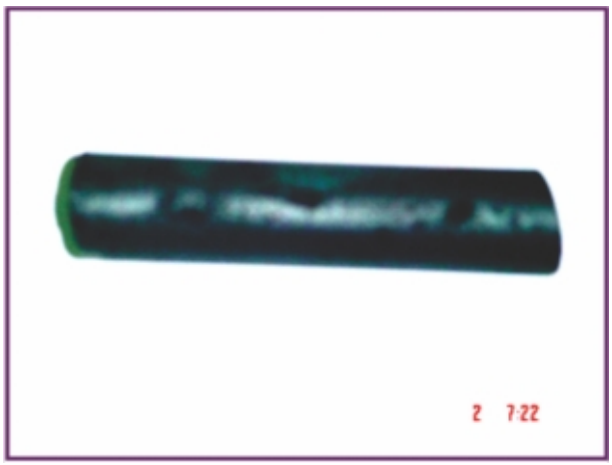


Fig. 12 : As-affected tubes after the heat treatment at 760 ± 10°C for 3 hours

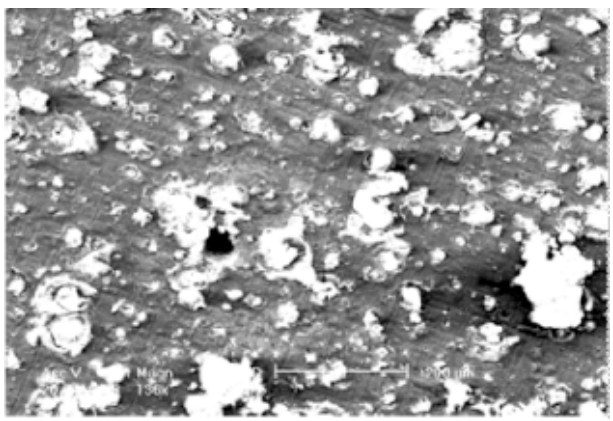


Fig. 13 : SEM photo of the affected tube showing the deposits and pitting attack

that the deposits on the tubes contained significant amount of chlorides and fluorides, which were dangerous for the chemical compatibility of the tubes.

Table 3 : Chemical composition of the deposits collected from the SG tubes

Element	Content
Cr	8.6 wt.%
Mo	0.94 wt. %
Cr	1.54 wt. %
F	229 ppm
Fe	74 Wt. %

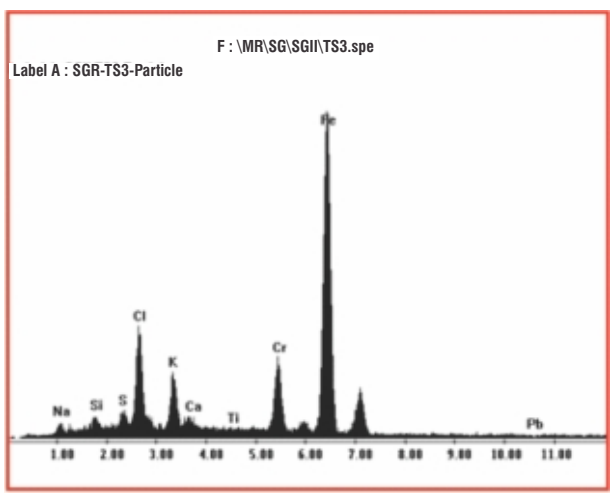


Fig. 14 : EDAX analysis of the as-affected tubes showing the presence of chlorides on the surface

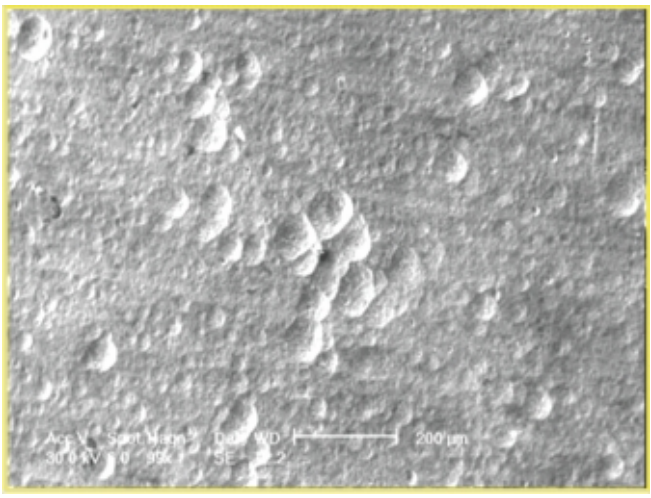


Fig. 15 : SEM picture of cleaned tube

The results of the chemical analysis were further validated by EDAX analysis. **Fig. 13** shows the SEM micrograph of as-affected tubes. It was found that the deposits were non-conducting particles sticking to the surface of the steel. Pits can also been seen on the surface of the steel. EDAX analysis of these affected tubes showed presence of significant amount of chloride ions **(Fig. 14)**. A chemical cleaning procedure was envisaged since mechanical cleaning of the tubes was difficult due to inaccessibility of the inner layer of tubes. Also, it was felt that chemical cleaning with HNO_3 and /or HNO_3 + HF solutions was desirable since these solutions were to be used for pickling and passivation of the fabricated SG. Use of any other chemical for cleaning would bring about additional uncertainties.

Choice of degreasing agent was an important step. Trials were conducted by degreasing with acetione, a chloro hydro carbon, and a Nonyl Phenol Polyoxyethylene Ether. Attempts were made to clean before and after the PWHT. Heat treatment of as-received affected tubes (with the deposits) at 760 ± 10 °C in nitrogen followed by (a) air cooling and (ii) cooling in nitrogen. This was followed by cleaning in (i) 20% HNO_3 (by weight) solution, and (ii) 15% HNO_3 (by weight) + 0.05% HF (by weight) solution. Cleaning in the two different solutions after the heat treatment did not show much improvement in the surface condition. The pits formed after the heat treatment remained though the products were removed. Cleaning of the affected tube for 90 minutes in (i) 20% HNO_3 (by weight) solution, and (ii) 15% HNO_3 (by weight) + 0.05% HF (by weight) solution was carried out. Cleaning before the heat treatment gave a clean bright surface. The surface finish was brighter when cleaning was done with 20% HNO_3 (by weight) solution than with 15% HNO_3 (by weight) + 0.05% HF (by weight) solution. SEM micrograph shows clean bright surface with no pit marks **(Fig. 15)**. Depth of corrosion attack was measured to be around 10 µm. **Fig. 16** shows the EDAX analysis of the cleaned surface. The reduction in chlorides is very clearly visible.

The cleaning was achieved by degreasing for 30 minutes in a Nonyl Phenol Polyoxyethylene Ether followed by rinsing the tubes immediately by immersing in DM water. Cleaning was achieved by immersing the tubes in agitated 20% by volume HNO_3 solution for 90 minutes. This was followed by rinsing the tubes with DM water till the pH of the drained water equals that of DM water being used. The tubes were then dried using hot nitrogen gas. **Fig. 17** shows the cleaned SG tubes.

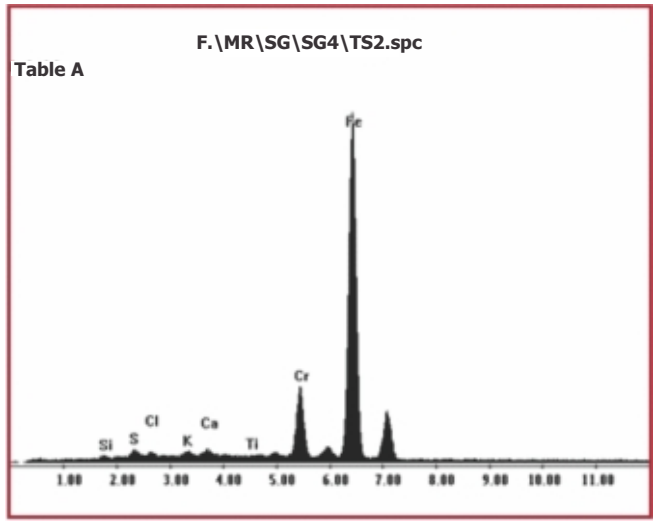


Fig. 16 : EDAX analysis for the cleaned surface

Fig. 17 : Appearance of the cleaned tubes

6.0 RESEARCH POST-IGCAR

After taking my voluntary retirement from IGCAR, I joined Mohamed Sathak A. J. College of Engineering, Chennai, as its Dean (Research). In this capacity, I was involved in research, though not as actively as at IGCAR. I carried out a project for IGCAR by funding from BRNS, Mumbai, on determining appropriate preheating and post heating conditions to avoid hydrogen embrittlement in as-welded conditions in modified

9cr-1mo steel welds, during welding of grade 91 steel [14]. Preheating is necessary to avoid hydrogen assisted cracking (HAC) and also post weld heat treatment (PWHT) is mandatory to improve the mechanical properties and relieve the internal stresses etc. In the case of steam generators, made of mod. 9Cr-1Mo steel, which comprise of thousands of welds, it is cumbersome and costly to carry out the PWHT on each of the weld joints. It would be much easier to carry out PWHT on the whole component after all the welding is over. However, it is not clear if absence of PWHT or long delay between the welding and PWHT, would cause environment-induced hydrogen embrittlement due to the presence of martensitic micro-structure, high hardness and tensile residual stress in the weld metal and Heat Affected Zone (HAZ). The study under the BRNS project was to determine the effect pre-heating and post heating on the microstructure, residual stresses, tensile and corrosion behavior of modified 9Cr-1Mo steel weld joints. Weld joints made by multi-pass TIG welding process with different combinations of preheating and post heating conditions, were tested for tensile, corrosion and hydrogen embrittlement (HE) properties to determine the appropriate combination of pre-heating and post-heating temperature and time **(Table 4)** which would ensure immunity from environment-induced HE of the weld metal and HAZ even if the PWHT is delayed indefinitely.

Table 4 : Preheating and Post heating conditions

Specimen Identification	Pre-heating temperature (°C)	Inter-pass temperature (°C)	Post heating temperature (°C) & Time
WJ 1	Nil	100	Nil
WJ 2	150	150	Nil
WJ 3	200	200	Nil
WJ 4	250	250	Nil
WJ 5	300	300	Nil
WJ 6	150	150	150 & 30 min
WJ 7	200	200	200 & 30 min
WJ 8	250	250	250 & 30 min
WJ 9	300	300	300 & 30 min
WJ 10	150	150	150 & 120 min
WJ 11	200	200	200 & 120 min
WJ 12	250	250	250 & 120 min
WJ 13	300	300	300 & 120 min

Fig. 18 shows that the hardness varied between 300 to 375 VHN. No systematic trend was observed based on preheat and post heat temperatures and times. In all the thirteen fabricated conditions, the weld final pass showed higher hardness as compared to that of weld center (mid thickness of weld). This was due to the presence of untempered fresh needle like martensite lath in the weld final pass and tempered martensite in the mid thickness of the weld.

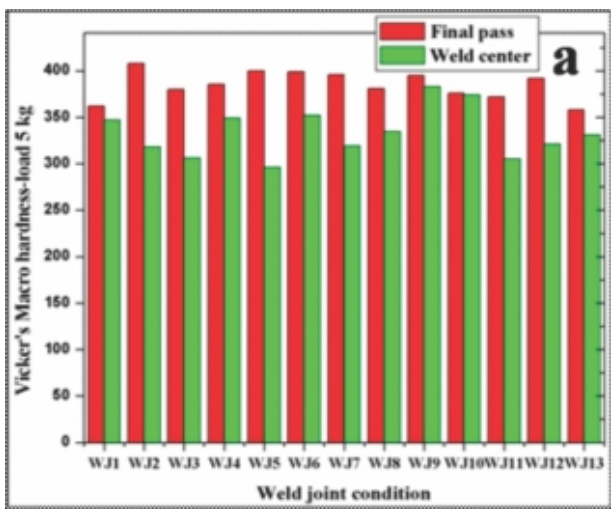


Fig. 18 : Bar charts showing macrohardenss of the weld metal

Residual stress measurements were carried out on the weld centre as well as base metal (5mm away from the fusion line). The relieved strain pattern obtained from the incremental depth of drilling up to 2 mm is shown in **Table 5**. The negative sign of the relieved strains indicates that the residual stresses are tensile in nature. The residual stresses in the weld metal without preheating and post heating (WJ1), shows a tensile residual stresses of 80 MPa in the longitudinal direction and 258 MPa in the transverse direction. But these tensile residual stresses in longitudinal direction in the case of no preheating and no post-heating condition, changed to compressive, and significant amount of stresses were reduced in the transverse direction by employing preheating and post-heating. The cooling rate of the weld is reduced by preheating and post-heating, compressive residual stresses were found in the longitudinal direction. However, the base metal residual stress measurements showed tensile residual stresses in both transverse and longitudinal directions. The tensile residual stresses were found to increase on preheating and post heating.

Table 5 : Calculated residual stresses

Sample ID	Measured location	σ max (MPa)	σ min (MPa)	β (orientation angle)
No preheat; No postheat	Weld metal	258	80	-79.46°
	Base metal	234	65	4.26°
Preheat at 300°C/postheat 300°C-30 m	Weld metal	92	-98	85.7°
	Base metal	321.64	12.57	2.66°
Preheat at 300°C/postheat 300°C-2 h	Weld metal	117	-97	84°
	Base metal	324.28	49.22	7.24°

Table 6 : Tensile & Corrosion Tests Results

Fabricated Condition	YS (MPa)	UTS (MPa)	% elongation	% R in A	Corrosion Rate (mpy)	HE Results
No PrH-No PoH	498	643	16.4	71.4	3.601	No failure
Preheat:150°C , No post heat	501	658	15.65	64.24	2.053	No failure
PrH:150°C PoH:150°C/30 m	506	641	15.83	69.9	2.403	---
PrH:150°C PoH:150°C/2 h	504	654	16.77	69.72	1.156	No failure
PrH:200°C, No PoH	498	651	15.16	70.1	1.698	No failure
PrH:200°C PoH:200°C/30 m	491	639	16.3	71.56	1.217	---
PrH:200°C PoH:200°C/2 h	487	645	18.63	71.18	1.536	No failure
PrH:250°C, No PoH	496	661	13.78	66.69	1.817	No failure
PrH:250°C PoH:250°C/30 m	521	665	14.08	70.67	1.795	---
PrH:250°C PoH:250°C/2 h	484	644	16.49	68.11	1.075	No failure
PrH:300°C ,No PoH	494	654	14.24	69.22	2.253	No failure
PrH:300°C PoH:300°C/30 m	493	648	14.74	68.76	1.981	---
PrH:300°C PoH:300°C/2 h	505	654	13.3	67.39	1.008	No failure

Results of the tensile, corrosion, and HE studies indicated minimal changes in properties with variations in pre and post heat temperature and time (Table 6).

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REFERENCES

1. H. Shaikh, H. S. Khatak and J. B. Gnanamoorthy, 'Stress Corrosion Cracking of Weldments of AISI Type 316 Stainless Steel', Werkstoffe und Korrosion, 38 (1987) 183-187.
2. T. Anita, H. Shaikh, H. S. Khatak and G. Amarendra, 'Effect of Heat Input on the Stress Corrosion Cracking Behaviour of Weld Metal of Nitrogen-Added AISI Type 316 Stainless Steel', Corrosion, 60 (2004) 873-880.
3. Hasan Shaikh, 'Studies on the Stress Corrosion Cracking, Corrosion Fatigue and Pitting Corrosion Behaviour of Austenitic Stainless Steels Used For Nuclear Reactor Applications', PhD Desertation, University of Madras, 2007.
4. T. V. Vinoy, H. Shaikh, H. S. Khatak, N. Sivaibharasi, and J. B. Gnanamoorthy, 'Stress Corrosion Crack Growth Studies on AISI Type 316 Stainless Steel in Boiling Acidified Sodium Chloride Solution', Journal of Nuclear Materials, 238 (1996) 278-284.
5. H. Shaikh, G. George, F. Schneider, K. Mummert and H. S. Khatak, 'Stress Corrosion Crack Growth Studies on Nitrogen-Added AISI Type 316 Stainless Steel and its Weld Metal in Boiling Acidified Sodium Chloride Solution Using the Fracture Mechanics Approach', Werkstoffe und Korrosion, 51 (2000) 719-727.
6. H. Shaikh, A. Poonguzhali, R. K. Dayal and H. S. Khatak, 'Corrosion Fatigue of AISI Type 316LN Stainless Steel and its Weld Metal', Corrosion, 65 (2009) 37-48.
7. Zahida Begum, A. Poonguzhali, Ranita Paul, H. Shaikh, R. V. Subba Rao, Awani Kumar Patil and R. K. Dayal, 'Corrosion Fatigue Behaviour of Different Austenitic Stainless Steels', Corrosion Science, 53 (2011) 1424-1432.
8. H. Shaikh, M. G. Pujar, N. Sivaibarasi, P. V. Sivaprasad and H. S. Khatak, 'Effect of High Temperature Aging on Ferrite Trans-formation Kinetics and Tensile Properties of Type 316L Stainless Steel Weld Metal', Materials Science and Technology, 10 (1994) 1096-1103.
9. H. Shaikh, T. V. Vinoy, H. S. Khatak, 'Correlation of Microstucture and Tensile Properties of 316 Stainless Steel Weld Metal Solution Annealed at High Temperatures', Materials Science and Technology, 14 (1998) 129-135.
10. H. Shaikh, B. P. C. Rao, S. Gupta, R. P. George, S. Venugopal, B. Sasi, T. Jayakumar and H. S. Khatak, 'Assessment of Intergranular Corrosion in AISI Type 316L Stainless Steel Weldments', British Corrosion Journal, 37 (2002) 129 - 140.
11. H. Shaikh, N. Sivaibharasi, B. Sasi, T. Anita, R. Amirthalingam, B. P. C. Rao, T. Jayakumar, H. S. Khatak and Baldev Raj, 'Use of Eddy Current Testing Method in Detection and Evaluation of Sensitisation and Inter-granular Corrosion in Austenitic Stainless Steels', Corrosion Science, 48 (2006) 1462-1482.
12. Hasan Shaikh, N. Sivaibharasi, B. Sasi, T. Anita, B. Poorna Chandra Rao, Ravin Kumar Dayal, T. Jayakumar and Baldev Raj, 'Effect of Carbon Content on Eddy Current Response to Sensitisation and Integranular Corrosion in Simulated Heat Affected Zone of Austenitic Stainless Steel ', Welding in the World, 56 (2012) 44-53.
13. T. Anita, R. V. Subba Rao, H. Shaikh, R. K. Dayal, 'Report on the Cleaning Procedure Developed for the Affected Steam Generator Tubes of Prototype Fast Breeder Reactor', IGCAR/CSTD/2008/34 dated 30 July, 2008.
14. H. Shaikh, S. K. Albert, H. C. Dey and D. Sunil Kumar, Unpublished Work.