Bull. Mater. Sci., Vol. 17, No. 6, November 1994, pp. 671–684. © Printed in India.

Metallurgical aspects of corrosion

K BALAKRISHNAN
Central Electrochemical Research Institute, Karaikudi 623 006, India

Abstract. Metallurgical properties have strong effects on corrosion. The paper discusses and reviews the work done at CECRI on the metallurgical aspects of corrosion of some industrially important alloys like steel and aluminium alloy weldments, stainless maraging steel and prestressing steel. The corrosion control methods for the above materials are also reviewed.

Keywords. Weldments; corrosion; maraging steel; heat treatment; prestressing steel; shot peening.

1. Introduction

Metallurgical properties have strong effects on corrosion. The strength of the materials is increased by addition of alloying elements, heat treatments and other techniques. A major constraint for these techniques is increased susceptibility to stress corrosion cracking above certain strength levels. Many unexpected catastrophic failures have occurred due to stress–environment interactions. Knowledge of the relation between stress, mechanical properties, environments and stress corrosion resistance is critical to the proper application of many materials in various industrial sectors. Many of the mechanical properties and the corrosion resistance of a material can be related to its heat treatment. Welding affects the metallurgical properties and corrosion of the weldment. Metallurgical aspects of some important alloys are carried out at the Central Electrochemical Research Institute (CECRI), Karaikudi and this paper discusses and reviews the following metallurgical aspects of corrosion: (i) corrosion of steel and aluminium alloy weldments, (ii) effect of heat treatment on the corrosion behaviour of stainless maraging steel and (iii) effect of shot peening on the stress corrosion resistance of prestressing steel.

2. Corrosion of steel weldments

Welding causes inhomogeneities. Weld metal may not have the same composition and microstructure as the parent metal and the surface of the weld metal is generally rough. Residual stresses will be introduced in the weld because welding involves localized heating and cooling. Weld metal also has higher hardness and strength levels than the parent metal.

The difference in chemical composition, surface conditions, microstructure and mechanical stresses in the weldments make the corrosion behaviour of the weld different from that of the parent metal. If the composition of the weld metal differs from that of the parent metal, galvanic corrosion occurs. Severe attack on the weld metal will occur if the weld metal is anodic with respect to the parent metal. This is due to the small area of the anode compared with the area of the cathode. If the weld metal is cathodic with respect to the parent metal, the corrosion problem is less serious because the attack is distributed over the large anodic area. There have been reports of corrosion rates of up to 10 mm/y at steel welds (Uusitalo 1961). This severe corrosion was attributed to the differences in electrochemical potential between the weld metal and the parent metal. Weld metal tends to display a more strongly electronegative behaviour than the parent metal. The factors that are primarily responsible for the potential differences are composition, metallurgical processes and heat treatment.

Preferential weld metal corrosion has been observed in marine structures. In these structures, ASTM A36 steel was joined to API 2H steel by shielded metal arc welding (SMAW). Cathodic protection is given to the steel structures. However, pits are seen only on the weld metal. We have carried out general corrosion, pitting corrosion, galvanic corrosion, cathodic protection and field exposure studies at Tuticorin seawater to know the reasons for the preferential weld corrosion and also to prevent pitting corrosion on the welds (Balakrishnan *et al* 1991; Sozhan 1991).

2.1 *Materials and welding*

The chemical composition of the ASTM A36 steel, API 2H steel and E7018 weld metal is given in table 1. A36 steel was joined to API 2H steel by shielded metal arc welding using E 7018 supertherme welding electrode ranging in diameter from 3·15 mm to 4 mm. The welding parameters are given in table 2. The stress relief heat treatment for the weld metal specimens was carried out in the furnace at 600°C for 1 h after which the specimens were cooled in the furnace.

Table 1. Chemical composition of the weld metal and parent metals.

Steel	C	Mn	S	P	Si	Cu	Ni	Cr	Al
A 36	0·15	1·17	0·018	0·013	0·11	0·042	nil	0·014	0·078
API 2H	0·23	1·17	0·010	0·011	0·18	0·110	0·23	0·016	0·043
Weld metal	0·07	1·03	0·021	0·010	0·33	0·046	0·068	0·030	0·035

Table 2. Welding parameters.

Pass no.	Electrode size		Amp.	Volts (mm/min)	Travel speed
1	3·15	110–115	24–25	70–80	
2	3·15	125–130	24–25	45–50	
3	4·0	155–165	24–25	45–55	
4	4·0	155–165	24–25	60–80	
5	4·0	155–165	24–25	60–80	
6	4·0	155–165	24–25	60–80	
7	4·0	155–165	24–25	60–75	
		Back gauge and ground			
8	4·0	170–185	24–25	50–70	
9	4·0	170–185	24–25	50–70	

2.2 *General corrosion*

2.2a Polarization studies: The general corrosion behaviour of the weldments in 3·5% NaCl solution and synthetic seawater was determined through polarization studies and the results are given in tables 3 and 4 respectively. It can be seen from the tables that the corrosion rate of the weld metal is higher than both the parent metals. Postweld heat treatment improves the corrosion resistance. It can be seen from table 4 that the corrosion rates in synthetic seawater for API 2H steel and A36 steel are 8·4 $\mu A/cm^2$ and 9 $\mu A/cm^2$, respectively while for the weld metal, the corrosion rate is 15 $\mu A/cm^2$. Thus, the weld corrodes two times higher than the parent metals. After post-weld heat treatment, the corrosion rate of the weld is 7 $\mu A/cm^2$ which is equivalent to the corrosion rate of the parent metals.

2.2b Electrochemical impedance measurements: Impedance measurements were carried out on the weld metal, parent metals and PWHT metal in synthetic seawater at the corrosion potential in the frequency range of 10 kHz to 10 mHz using the Model M 378 impedance measurement system, EG and G PAR, USA. Figure 1 shows the impedance diagrams for the weld metal, PWHT metal and the parent metals. The charge transfer resistance values, estimated from the impedance diagrams are given in table 5. The charger transfer resistance is inversely proportional to the corrosion rate. The weld metal has low R_t value than the parent metals, indicating higher corrosion rates than the parent metals. Postweld heat treatment significantly improves the corrosion resistance.

2.3 *Pitting corrosion*

The resistance of the weldments to pitting corrosion was evaluated in 0·04 N NaOH + 600 ppm chloride and synthetic seawater + 10^{-5} M Na_2S through potentiostatic

Table 3. Polarization data in 3·5% NaCl solution.

Metal	Corrosion current ($\mu A/cm^2$)
API 2H steel	8·0
A36 steel	11·0
Weld metal	20·0
PWHT	6·0

Table 4. Polarization data in synthetic seawater.

Metal	Corrosion current ($\mu A/cm^2$)
API 2H steel	8·4
A36 steel	9·0
Weld metal	15·0
PWHT	7·0
Welding rod	18·0

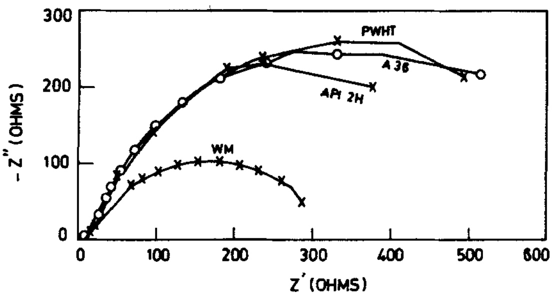

Figure 1. Impedance diagram in synthetic seawater at the corrosion potential.

Table 5. The charge transfer resistance values estimated from the impedance measurements.

Metal	Charge transfer resistance value (Rt. cm^2)
API 2H steel	487
A36 steel	667
Weld metal	300
PWHT metal	645

polarization studies. The pitting potentials estimated from polarization curves in these solutions are given in tables 6 and 7. The weld metal has lower pitting corrosion resistance than the parent metals. PWHT improves the pitting corrosion resistance of weld metal.

2.4 *Galvanic corrosion*

The galvanic corrosion currents were measured for (i) weld metal vs A36 steel, (ii) weld metal vs API 2H steel, (iii) PWHT vs A36 steel, (iv) PWHT vs API 2H steel, (v) weld with Cu and Ni vs A36 steel and (vi) weld with Cu and Ni vs API 2H steel couples in 3·5% NaCl solution and synthetic seawater (Sozhan 1991). The galvanic currents measured for the above couples after 48 h of exposure are given in table 8. It can be seen from the table that the unalloyed weld is always anodic with respect to both the parent metals. At the end of 48 h, the galvanic current density was the highest for the weld—API 2H couple (11·8 $\mu A/cm^2$) and lowest for the weld—A36 couple (4·8 $\mu A/cm^2$) in synthetic seawater. Thus, the galvanic current density for the weld—API 2H couple is 3 times higher than the weld—A36 couple. The higher galvanic currents measured in weld—API 2H couple is due to the difference in the composition of the weld metal and API 2H steel. The weld metal contains higher silicon content (0·33%) than API 2H steel (0·18%). The metals with Si content > 0·25% behave as most unnoble metals (Parkinson *et al* 1989). Moreover, API 2H steel contains more Cu and Ni than the weld metal which make it more nobler than the weld metal. Hence, the weld—API 2H couple has higher galvanic current density than the weld—A36 couple.

The galvanic currents measured for the weld coupled to A36 steel and API 2H steel are for an area ratio of 1 : 1. But, in the existing structures, the actual area ratio between the weld metal and parent metals is very much higher than 1 : 1, and hence higher galvanic currents may be expected between the weld and the parent metal couples.

Weld metal corrosion in ships was attributed to the galvanic corrosion between the weld metal and parent metal (Uusitalo 1966). Premature failure of A53 steel pipe by weld corrosion in the process stream was observed (Liening 1986). This was due to the galvanic corrosion between E 6010 weld metal and A53 steel pipe, and weld was anodic with respect to the steel pipe.

Table 6. Pitting corrosion data in 0·04 N NaOH + 600 ppm chloride.

Metal	Pitting potential (mV vs SCE)
API 2H steel	+245
A36 steel	+110
Weld metal	+95

Table 7. Pitting corrosion data in synthetic sea water + 10^{-5} M Na_2S.

Metal	Pitting potential (mV vs SCE)
API 2H steel	−814
A36 steel	−773
Weld metal	−848
PWHT	−805

Table 8. Galvanic current measurements after 48 h of exposure in 3·5% NaCl and synthetic seawater.

Galvanic couple	Galvanic currents (μA/cm^2)		Remarks
	3·5% NaCl	Synthetic seawater	
Weld vs A36 steel	−4·2	−4·8	Weld is anodic
Weld vs API2H steel	−10·9	−11·8	Weld is anodic
PHWT vs A36 steel	+2·9	+0·8	Weld is cathodic
PHWT vs API2H steel	−1·6	−2·3	Weld is anodic
Welding electrode with Cu and Ni vs A36 steel	+4·0	+3·6	Weld is cathodic
Welding electrode vs API 2H steel with Cu and Ni	−1·0	−1·4	Weld is anodic

PWHT improves the galvanic corrosion resistance of the weld vs A36 and weld vs API 2H steel couples. The weld corrosion can be eliminated by using a suitably balanced electrode material.

Matching composition electrodes are preferred for the highest corrosion resistance. If unalloyed weld electrodes are used, the weld itself is corroded preferentially (Uusitalo 1966). Alloying elements are added to the coated electrode as a means of modifying or controlling the chemistry of the weld metal. Weld electrodes with increased copper or nickel were more resistant to localized corrosion (Garner *et al* 1989). 1·1% Cu and 0·72% Ni were added to the E 7018 welding electrode and the galvanic corrosion resistance were made. In welding electrode with Cu and Ni vs A36 couple, weld is cathodic. In general, it would be preferable for the weld metal to be somewhat cathodic because of its relatively small area as compared with parent metal.

2.5 *Field exposure studies*

Weldments of size $6' \times 4'$ with the weld at the centre were exposed to a depth of 3 m inside the sea at Offshore Platform and Marine Electrochemistry Centre (Unit of CECRI, Karaikudi). Figure 2 shows the surface appearance of the welded sample after 1 month of exposure. Corrosion occurs first on the weld zone. Barnacles are not attached to the weld samples during this test period. After 3 months of exposure, attachment of barnacles are observed on the welded samples. The average number of barnacles attached on the weld zone and the parent metals are given in table 9. Since the weld metal is rough, a large number of barnacles are attached to the weld zone as compared to the parent metals. After 6 months of exposure, the specimens showed preferential weld zone corrosion (figure 3).

2.6 *Cathodic protection*

The most common method of preventing corrosion of welds on offshore platforms is cathodic protection. Pitting corrosion > 5 mm in depth was found in welds on some north sea platforms when cathodic protection was inadequate (Smart 1980). On offshore steel platforms, node welds are joints of high stress because stress concentration occurs due to the complex geometry at these locations. Therefore, adequate cathodic protection needs to be given to the node welds; insufficient protection leads to pitting corrosion. However, over protection should not be given to the weldments because it affects the mechanical properties of the weld metal. Hydrogen enters into the metal during overprotection leading to hydrogen embrittlement (Hoar 1969; Saeuz *et al* 1986). Electrochemical impedance technique was used to optimize the cathodic protection potential for the shielded metal arc welded steel and post-weld heat treated (PWHT) steel in 3·5% NaCl solution (Sozhan *et al* 1993). Impedance measurements were carried out at the corrosion potential and also at different constant cathodic potentials (−730, −780, −800, −850, −900, −950 and −1000 mV vs SCE) for the weld metal and PHWT metal in 3·5% NaCl solution. A protection potential of −950 mV vs SCE is necessary to protect the welds whereas −900 mV vs SCE is sufficient to protect the post-weld heat treated metal. Immersion studies were also carried out in 3·5% NaCl solution

Figure 2. Corrosion products on the weld zone after one month of exposure at Tuticorin seawater.

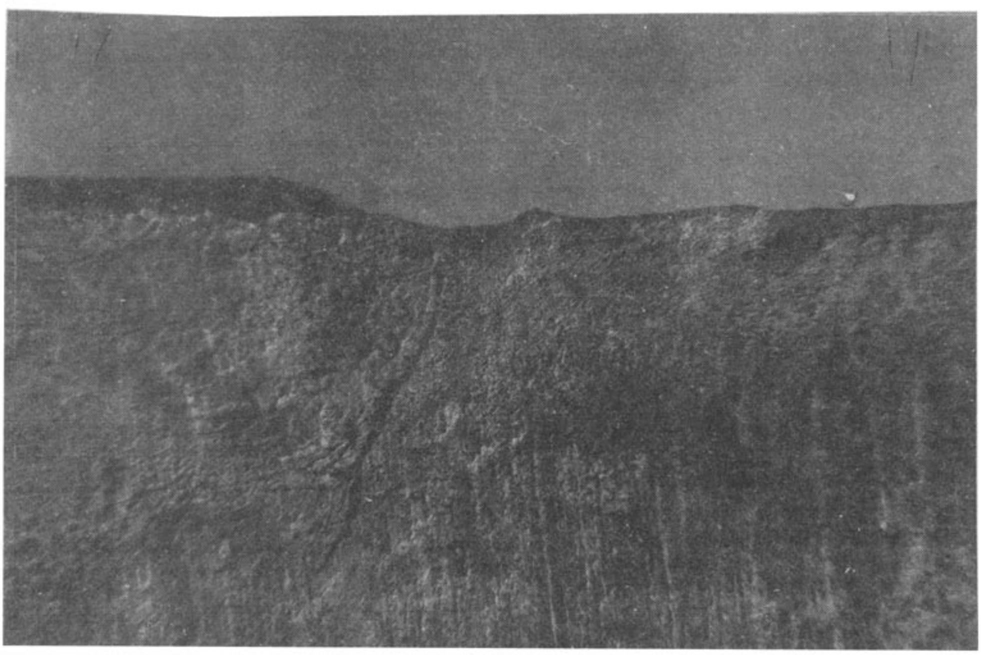

Figure 3. Weld zone corrosion after six months of exposure at Tuticorin seawater.

on SMA and PWHT welds for 120 h at various constant cathodic potentials to compare the results of impedance measurements. Weight loss data show that the corrosion rate for weld metal is minimal at −950 mV vs SCE, whereas for the PWHT it is minimal at −900 mV vs SCE. The results of the weight loss data correlate well with results from the impedance technique.

Pitting corrosion has been observed on the platform joints in North sea maintained at −850 mV vs Ag/AgCl (Du Yu *et al* 1989). Node welds are partly shielded by many intersecting structural members with areas of higher than average surface density. Hence, these node welds are inherently the most difficult to protect (Smart 1980). The pit observed on the node weld of the North sea platform protected by cathodic protection is attributed to the insufficient cathodic protection at these node welds. Now the platform is adequately protected. Analysis of the pipeline failures reported to the US Department of Transportation for the period from 1970 to 1973 showed that 76% of the external corrosion failures were attributed to the pitting corrosion. Potentials more negative than −950 mV vs $Cu/CuSO_4$ are required to prevent pits (Toncre 1989). Polarized potentials of −1000 mV vs $Cu/CuSO_4$ (−950 mV vs Ag/AgCl) are necessary to protect the structures when complete corrosion prevention is desired (Gummow 1986). Investigations at CECRI on the welded sample reveal that protection potential of −950 mV vs SCE (−970 mV vs Ag/AgCl) is required to protect the welds.

3. Corrosion of 7020 aluminium alloy weldments

Aluminium alloy is used for aerospace applications. Welding is done to fabricate tanks. The general and stress corrosion behaviour of AFNOR 7020 aluminium alloy sheet in T6 temper welded using (i) AG 4·5 Mn filler metal, (ii) AG 4Z2 filler

Table 9. Average number of barnacles attached to the weld metal and the parent metals.

Metal	Average number of barnacles/dm^2
API 2H steel	155
A36 steel	123
Weld metal	210

Table 10. Corrosion rates of the 7020 parent metal and welds after 30 days of immersion in liquid N_2O_4.

Parent metal/weld with filler metal	Corrosion rate (mmpy)
Parent metal	0·004
AG 4·5 Mn	0·006
AG 4Z2	0·004
AG 5	0·040

metal and (iii) AG 5 filler metal were determined in liquid N_2O_4 to select the best filler metal for fabrication of tanks to handle N_2O_4 (Balakrishnan *et al* 1994).

3.1 *General corrosion*

The general corrosion resistance of these weldments was evaluated through immersion studies for 30 days and electrochemical impedance measurements. The corrosion rates after 30 days of immersion in liquid N_2O_4 are given in table 10. The results show that 7020 welded with AG4Z2 has higher general corrosion resistance compared to other filler metals. The corrosion rate of this AG4Z2 weld is similar to the parent metal. The corrosion rate of other filler metal AG 4·5 Mn is about two times higher than the parent metal, and another AG 5 filler metal corrodes ten times more than the parent metal.

The electrochemical impedance measurements were carried out on the parent metal as well as on the welded sheets in N_2O_4 liquid using the frequency response analyzer (Model 1174, Solotron, UK) and the electrochemical interface (Model 1174, Solotron) over a frequency range of 1 Hz to 10 kHz. The impedance diagrams are given in figure 4. The alloy welded with AG5 filler wire behaves differently from that of other samples. The depressed semi circle of AG 5 filler wire indicates the presence of a charge transfer reaction mostly corresponding to the dissolution of the alloy. In the case of parent metal and other two filler metals, resistive and diffusion control behaviour occur due to the presence of passive film.

3.2 *Stress corrosion*

The stress corrosion behaviour of the parent metal and the welded sheets was evaluated in liquid N_2O_4 by short term and long term SCC tests.

3.2*a* *Short term SCC tests*: Constant load tests were used. The stress was applied by means of spring loaded test set-up. Stress applied was 18·1 kg/mm². The stressed

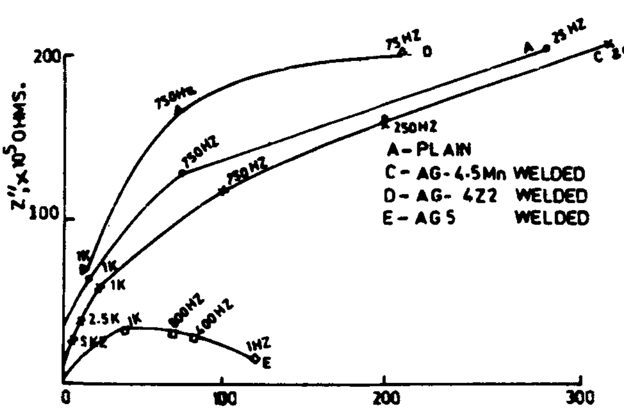

Figure 4. Impedance diagram for the parent metal and welded alloys in liquid N_2O_4.

samples were exposed to liquid N_2O_4 for 6 h. The parent metal and the welded specimens were examined using optical microscope after 6 h of exposure. Microcracks were observed near the weld line–plate joint with AG4·5Mn and AG5 filler metals. No cracks were observed in AG4Z2 filler metal and parent metal. The results of the short term SCC tests show that the welded sheet with AG4Z2 filler metal is resistant to SCC in liquid N_2O_4 at the stress level of 18·1 kg/mm^2.

3.2*b* *Long term SCC test*: Bent beam technique (four-point loading) was used to apply stress. 8·2 kg/mm^2 stress was applied to the parent metal and the welded specimens and then they were exposed to liquid N_2O_4 for 100 days. The specimens were examined using optical microscope after 100 days of exposure. No stress corrosion cracks were seen on the welded specimens with three filler metals, and the parent metal during this period of testing. The general and stress corrosion studies in liquid N_2O_4 reveal that alloy welded with AG4Z2 filler metal has corrosion resistance than the other AG4·5 Mn and AG5 filler metals.

4. Effect of heat treatment on corrosion of stainless maraging steel

4.1 *Stainless maraging steel*

The corrosion behaviour of the stainless maraging steel depends upon the composition and heat treatment. The general corrosion resistance is maximum when this steel is in solution heat treated condition. Aging, depending on the temperature, decreases the corrosion resistance of stainless maraging steel considerably. The steel aged at lower temperature has better corrosion resistance than the steel aged at higher temperature.

The stress corrosion cracking resistance varies with aging. In general, those environments which produce SCC in other high strength steels are also found to produce cracking in stainless maraging steels. Overaging improves the stress corrosion resistance (McDarmaid 1982). Coatings or cathodic protection can be given to protect the stainless maraging steel in marine environments (Papier 1988). The general pitting and stress corrosion behaviour of stainless maraging steel were evaluated in chloride environments at CECRI (Balakrishnan *et al* 1994).

4.2 *Material and heat treatment*

The stainless maraging steel used in this study was 0·72 mm cold rolled sheet. The chemical composition of this steel is given in table 11. The material was received in the solution heat treated condition (solution treated at 980°C for 30 min and air cooled). The solution treated steel was aged at 450°C for 4 h (underaged), 450°C for 5 h (peakaged) and for 7 h (overaged). The mechanical properties are given in table 12.

4.3 *General corrosion*

The general corrosion behaviour of stainless maraging steels in underaged and overaged conditions were determined in 3·5% NaCl solution through polarization and impedance measurements. The results of the studies are given in table 13. It can be seen from the table that overaged sample has higher general corrosion resistance than the underaged sample.

4.4 *Pitting corrosion*

The pitting corrosion resistance of underaged, peakaged and overaged stainless maraging steel was evaluated in 0·04 N NaOH containing 1000 ppm chloride using potentiodynamic polarization studies. The pitting corrosion data are given in table 14. The overaged sample has higher pitting corrosion resistance than the underaged and peakaged samples. Electropolishing in $H_3PO_4 + H_2SO_4 + CrO_3$ solution improves the corrosion resistance.

4.5 *Stress corrosion*

Stress corrosion tests were carried out on underaged and overaged specimens in 5% NaCl solution. The stress applied was 80% of proof stress. The results of SCC studies are given in table 15. It can be seen from the table that overaging

Table 11. Chemical composition of stainless maraging steel.

	Cr	Co	Ni	Mo	Ti	Al	Si	C	Fe
Element%	12	12	4	4	0·5	0·3	0·1	0·02	Bal.

Table 12. Mechanical properties.

Heat treatment	0·2% Yield strength (kg/mm^2)	Ultimate tensile strength (kg/mm^2)	Elongation (%)	Hardness (VPN)
450°C/4 h	138·4	145·7	8·4	485–495
450°C/7 h	132·6	141·5	9·2	480–500

Table 13. Effect of heat treatment on the general corrosion behaviour in 3·5% NaCl solution.

Type of heat treatment	Heat treatment condition	Corrosion current by polarization technique ($\mu A/cm^2$)	R_{ct}, (K ohm cm^2) by impedance technique
Solution annealed	–	0·15	> 30
Underaged	450°C, 4 h	3	3·1
Peakaged	450°C, 5 h	3·3	2·2
Overaged	450°C, 7 h	2	4·3

Table 14. Pitting corrosion behaviour of stainless maraging steel in 0·04 N NaOH + 1000 ppm chloride·.

Type of heat treatment	Heat treatment condition	Pitting potential (mV vs SCE)	Protection potential (mV vs SCE)
Mechanical polishing			
Underaged	450°C, 4 h	+ 50	− 75
Overaged	450°C, 7 h	+ 250	0
Electropolishing			
Underaged	450°C, 4 h	+ 650	+ 650
Peakaged	450°C, 5 h	+ 660	+ 660
Overaged	450°C, 7 h	+ 750	+ 750

Table 15. Constant load SCC test data.

Aging	Time to failure (h)
Underaged (450°C/4 h)	10–13
Overaged (450°C/7 h)	324

Stress: 80% of proof stress; medium: 5% NaCl solution.

significantly improves the stress corrosion resistance. The overaged sample has thirty times higher stress corrosion resistance than the underaged sample.

5. Effect of shot peening on stress corrosion

Prestressing steels are vulnerable to stress corrosion cracking (SCC) since they are held under permanent tension while in service. Many premature failures of prestressed concrete bridges, tanks and ground anchors are due to SCC of prestressing steel wires (Cornet 1964; Szialand 1969; Little John 1986). In recent years, serious corrosion failures of prestressed concrete structures have occurred. For example, the southern outer roof of the Berlin Assembly Hall suddenly collapsed. The failure is attributed to hydrogen-induced stress corrosion cracking of prestressed steel (Isecke 1983).

The feasibility of introducing surface compressive stresses using shot peening to improve stress corrosion resistance of prestressing steel has not been examined so far. CECRI has studied the effect of controlled shot peening on the stress corrosion behaviour of prestressing steel in 20% ammonium thiocyanate solution (Rengaswamy *et al* 1991). According to FIP, this solution is the most convenient and reliable one for the study of hydrogen-induced SCC of prestressing steel (FIP Report 1980).

Figure 5 shows the percentage proof stress vs time–to–failure in 20% ammonium thiocyanate solution. The threshold stress is increased from 20% to 30% for shot peened specimens. Under 80% proof stress, time–to–failure is 197 min for shot peened specimens, whereas it is only 18 min for unpeened specimens. Thus, there is a ten-fold increase in time–to–failure due to shot peening. Shot peening introduces

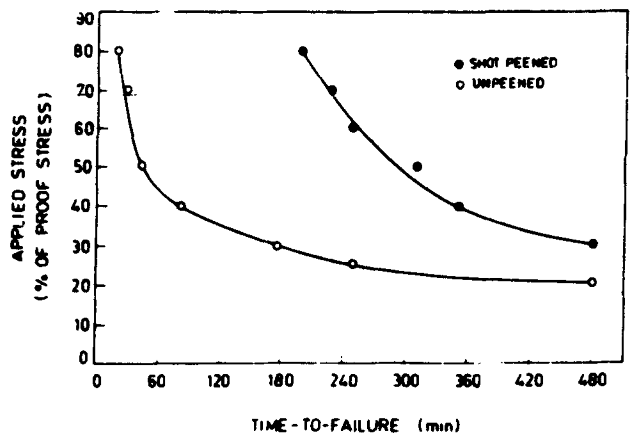

Figure 5. Applied stress vs time-to-failure data in 20% ammonium thiocyanate solution; 500 mV cathodic.

surface compressive stresses, and removes notches and other surface defects responsible for stress considerations by producing small shallow dents on the surface (Metals Handbook 1982). The surface compressive stress induced by shot peening helps to lower the level of applied tensile stress at the surface because of the superimposition of internal stresses and external applied load (Hara 1989). Shot peening mainly helps to delay the initiation of the stress corrosion cracking process.

6. Conclusions

Welding affects the metallurgical properties of the weldment. This results in increased corrosion rate of the weld metal. Higher cathodic protection potential is required to prevent corrosion of weld metal. Post weld heat treatment significantly improves the corrosion resistance of weld metal. Weld electrode containing copper and nickel are more resistant to weld zone corrosion.

The general and stress corrosion studies on AFNOR 7020 aluminium alloy in T6 temper welded with AG4·5 Mn, AG4Z2 and AG5 filler metals in liquid N_2O_4 reveal that AG4Z2 filler metal has higher corrosion resistance than other filler metals.

Overaging of stainless maraging steel improves the general, pitting and stress corrosion resistance in chloride solutions. Electropolishing in $H_3PO_4 + H_2SO_4 + CrO_3$ solution improves the corrosion resistance of stainless maraging steel.

Controlled shot peening of prestressing steel significantly increases its stress corrosion resistance. The threshold stress is increased from 20 to 30%.

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