Response of Weld Joints in Stainless Steel 304LN Pipe to Low Temperature Sensitization

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ABSTRACT

Heat affected zones adjacent to the welds are generally considered sensitive locations for failure of heat transport system pipelines (made of austenitic stainless steels) in nuclear power industries. Present study includes understanding the sensitization and IGC behavior of nuclear grade stainless steels (AISI 304LN) at low temperatures. Two different solution annealed (pipes) AISI 304LN and weld joints were exposed to 400 and 450°C for 125-8000 hours followed by furnace cooling. Sensitization was quantified in terms of degree of sensitization (DOS) by using double-loop electrochemical potentiokinetic reactivation (DL-EPR) method. The oxalic acid (in 10% oxalic acid solution) etching and copper-copper sulfate-sulfuric acid test as per the ASTM 262 Practice 'A' and 'E' were performed to detect and quantify the susceptibility to intergranular corrosion. Specimens from two different pipes showed variations in susceptibility to sensitization and IGC. Specimens designated, as 304LN-P1 was much less prone to sensitization as compared to 304LN-P2. While HAZ of former showed 'step' type structure the other one (304LN-P2) produced mostly 'dual' and 'step', in a few cases, during oxalic acid etching. While bending after boiling in copper-copper sulfate- sulfuric acid solution, certain specific time/ temperature combinations produced fissures or even large cracks on the weld pool of both stainless steels.

Key Words: Low temperature sensitization, Stainless steel 304LN, Degree of sensitization, EPR test, ASTM 262.

Introduction

Intergranular corrosion (IGC) of sensitized austenitic stainless steels is frequently observed in several service environments. Sensitization is chromium carbide precipitation concomitant with the depletion of chromium from adjacent to the grain boundaries when they undergo a heat treatment in temperature ranging from 550-800°C. This reduces corrosion resistance of stainless steels along the grain boundaries. Povich et.al have shown that stainless steel welds were severely sensitized in heat affected zones (HAZs) after they were exposed to <500°C [1-2]. The HAZ are known to be the IGC susceptible regions in austenitic stainless steels. This is because such regions encounter sensitizing temperature range for significantly long time. It has been shown that the number of carbide particles <500°C remained same while the size of the carbides increased substantially [1-2]. This was termed as low temperature sensitization (LTS). The phenomenon of LTS has strong relevance in several industrial processes such as: during welding, thermo-mechanically processing, slow cooling from solution annealing, and stress relieving temperature that can cause the formation of carbide nuclei in stainless steel which can grow leading to failure of the component during subsequent high temperature aqueous service. LTS is one of the life limiting degradation mechanism in nuclear power plants as the operating temperature is close to ~300°C (LTS prone). Extensive intergranular stress corrosion cracking (IGSCC) failures of pipelines in boiling water reactor (BWR) driven by low temperature sensitization combined with high purity water dissolved in oxygen have been reported [1-3]. Povich and Rao [2] extrapolated that the welded AISI 304 piping component failed by LTS enhanced IGSCC within 10 years of service in boiling water reactor. Hiroyuki et.al showed it to fail after 7 years of exposure at 300°C [3]. The AISI 304L and AISI 316L, candidate materials for storage of nuclear waste had also reported to fail from HAZ locations by LTS enhanced IGSCC. The canister surface exposed to temperature from 100-300°C generated by radioactive decay of radionuclides that caused the chromium depletion near the boundaries [4-5]. A model with a few preliminary experiments had predicted the AISI 316 sensitized within 10 days at 450°C [5].

The weld pool in addition to HAZ is also reported to produce significant sensitization. It was shown that weld pool produced higher sensitization as compared to the base substrate [6] due to high sensitization susceptibility at ferrite-austenite interphase. Weld pool contains about 3-8% delta ferrite useful to prevent hot cracking which however, may be harmful as it may transform to brittle intermetallic phases (such as sigma and G-phase) on long-term exposure to low temperature. This deteriorates mechanical properties of stainless steels [7].

This paper reports the results of low temperature sensitization studies of welded 304LN stainless steel aged at 400 and 450°C for various durations. The ageing durations at different temperature were worked out by considering the activation energy of carbide precipitation ~ 160 kJ/mol. The sensitization was quantified in terms of degree of sensitization (DOS) using double loop electrochemical polarization reactivation (DL-EPR) tests. This was supported by oxalic acid etching according to ASTM 262 practice A [8] and ASTM 262 Practice E tests.

Experimental Details

Solution annealed stainless steels 304LN from two different pipes of diameter 168 mm and 324 mm and wall thickness of 14.2 mm and 25.2 mm respectively were considered for this study. The chemical compositions of these steels are given in following Table-1.

Table-1: Chemical composition of two stainless steels

Steel	C	Si	Mn	Cr	Mo	Ni	N	Co	Cu	Nb	Fe
304LN-P1 (168 mm dia. pipe)	0.01	0.49	1.75	18.46	0.22	9.1	0.11	0.09	0.22	0.06	Bal.
304LN-P2 (324 mm dia. pipe)	0.01	0.34	1.62	18.39	0.24	8.4	0.15	0.12	0.28	0.56	Bal.
304LN-P1 Weld pool	0.138	0.31	1.62	19.35	0.173	8.15	0.08	0.107	0.3	0.03	Bal.
304LN-P2 Weld pool	0.127	0.72	1.08	19.26	0.119	9.08	0.1	0.077	0.279	0.041	Bal.

Stainless steel plates were cut into 5.5 x 2.5 x 0.4 cm and 3.8 x 1.3 x 0.6 cm (for larger and smaller pipe respectively) sizes that contained the weld pool and HAZ from the pipe of two different diameters. The specimens were subjected to ageing treatment at 400 and 450°C for 125-8000 hours followed by furnace cooling. The specimens after ageing treatment were grind and polished on coarse to fine (1200 grit) emery papers. They were cloth polished by using 0.05 micron alumina slurry followed by cleaning in acetone. Oxalic acid etching was carried out in freshly prepared 10% oxalic acid solution at a current density of 1.0 Ampere/cm^2 continued for 1.5 minutes [8]. Specimens were then rinsed with water and seen under the optical microscope to categorize them under step, dual, and ditch structure in order to classify their susceptibility to sensitization.

Another sets of coarse finished (120 grit paper) specimens free from oxides were subjected to boiling in copper-copper sulfate –16% sulfuric acid solution for about 72 hours. This test was carried out according to ASTM 262 practice E. After boiling the specimens were bent through 180° and bent location was observed under low magnification microscope for presence of fissure or cracking in HAZ or weld pool.

The degree of sensitization was determined by the double loop EPR method at ambient temperature. Samples were successively polished with coarse 220 to 1200 grit emery papers followed by cloth polishing with diamond paste (~0.05 micron) and degreasing in acetone solution. The test solution 0.5M H_2SO_4 + 0.01M KSCN was prepared from reagent grade chemicals in distilled water. Before polarizing, the specimens were cathodically cleaned at a potential of –1000 mV with respect to Saturated Calomel electrode (SCE) for 60 s. Scanning was initiated at a potential of -100 mV (with respect to the open circuit potential (OCP) and reversed at a potential of +300 mV (vs. SCE) at a scan rate of 6V/h. A saturated calomel electrode was used as a reference electrode. The degree of sensitization was evaluated by measuring the ratio of I_r/I_a, where I_r is the peak reactivation current density and I_a the peak activation current density. The DOS was measured at different locations such as HAZ and weld pool as schematically shown in Figure 1.

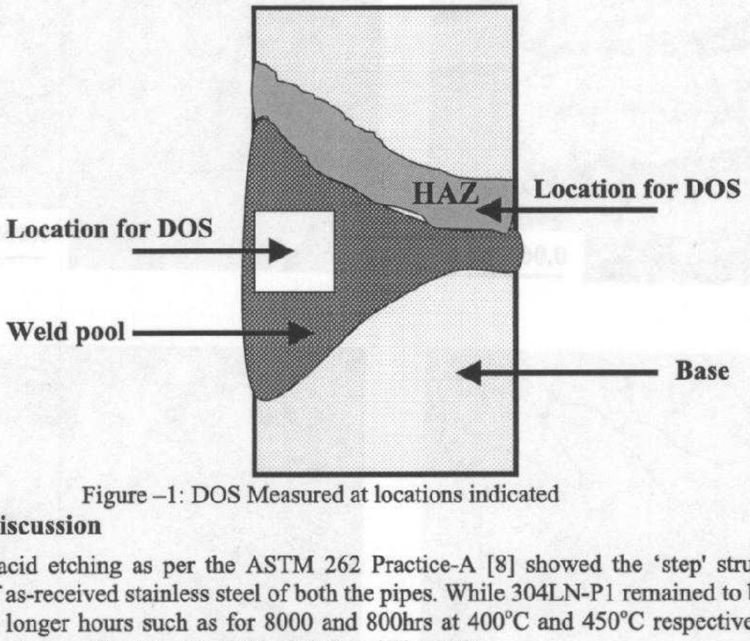


Figure –1: DOS Measured at locations indicated

Results and Discussion

Oxalic acid etching as per the ASTM 262 Practice-A [8] showed the 'step' structure in heat-affected zone of as-received stainless steel of both the pipes. While 304LN-P1 remained to be 'step' even after ageing for longer hours such as for 8000 and 800hrs at 400°C and 450°C respectively, 304LN-P2 showed dual structure as illustrated in Table-2 & 3 and Figure-2.

Table-2: Results of oxalic acid etching and DOS for ageing at 400°C

Aging time(Hrs) at 400°C	304LN-P1			304LN-P2		
	Etch structure	%DOS		Etch structure	%DOS	
		HAZ	WELD		HAZ	WELD
600 Hrs	Step	0.3104	0.489	Step	0.212	0.10
3000 Hrs	Step	1.1596	2.098	Step	0.368.	0.1623
5000 Hrs	Step	2.17	1.592	Dual	0.32	0.151
8000 Hrs	Step	1.01	0.1	Dual	0.4386	0.3265

Table-3: Results of oxalic acid etching and DOS for ageing at 450°C

Aging Time(Hrs) at 450°C	304LN-P1			304LN-P2		
	Etch structure	%DOS		Etch structure	%DOS	
		HAZ	WELD		HAZ	WELD
125 Hrs	Step	0.243	0.208	Dual	0.105	0.1655
500 Hrs	Step	1.00	4.4175	Dual	0.165	1.68
800 Hrs	Step	1.49	9.27	Dual	0.289	1.546
1300 Hrs	Step	1.504	4.641	Dual	0.504	2.98

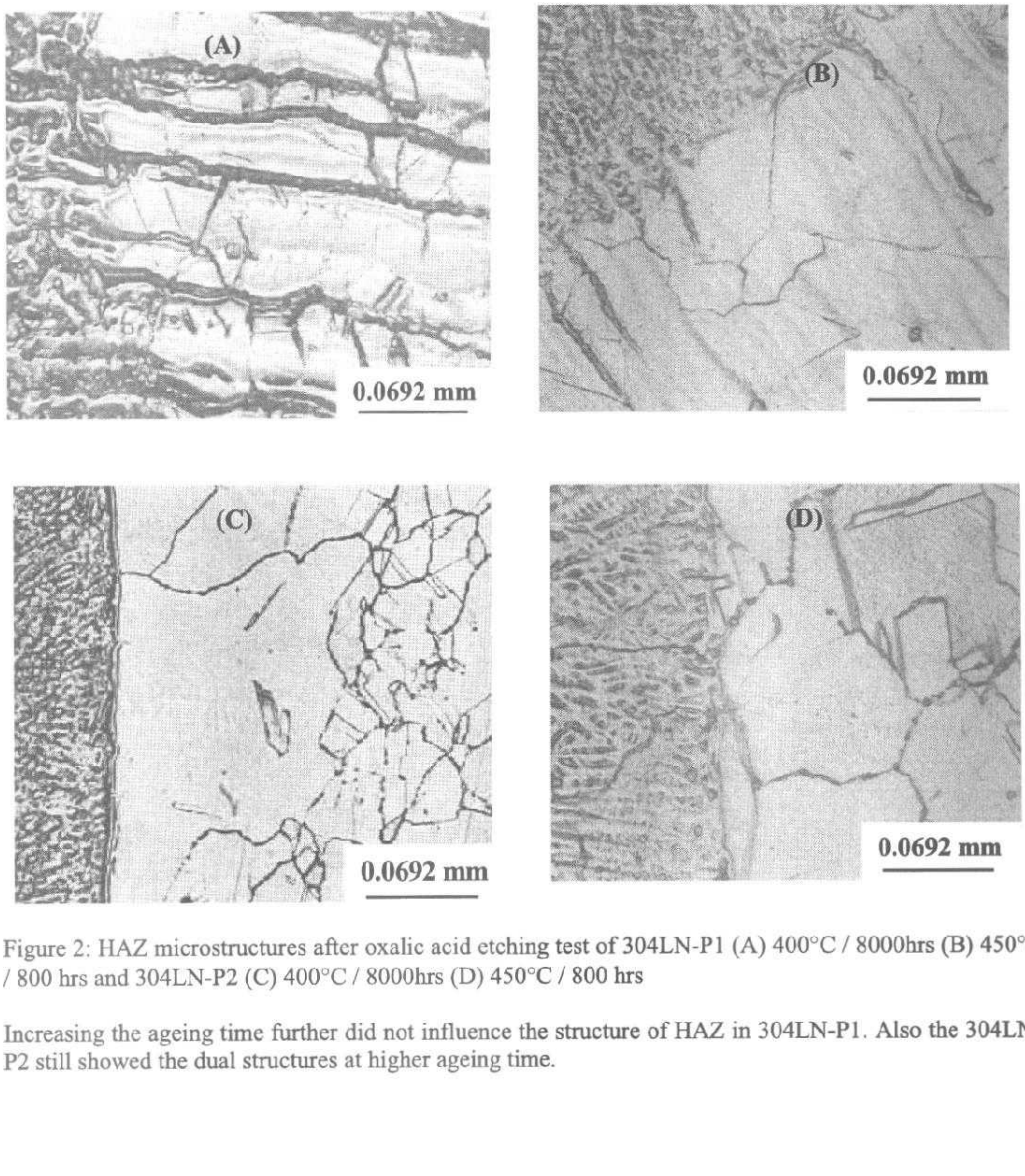


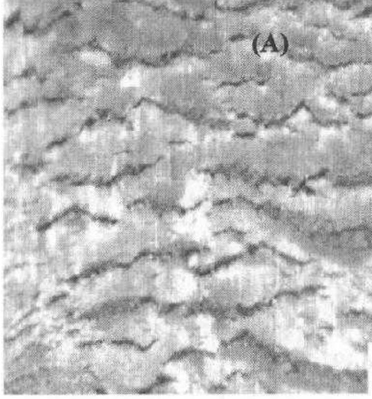
Figure 2: HAZ microstructures after oxalic acid etching test of 304LN-P1 (A) 400°C / 8000hrs (B) 450°C / 800 hrs and 304LN-P2 (C) 400°C / 8000hrs (D) 450°C / 800 hrs

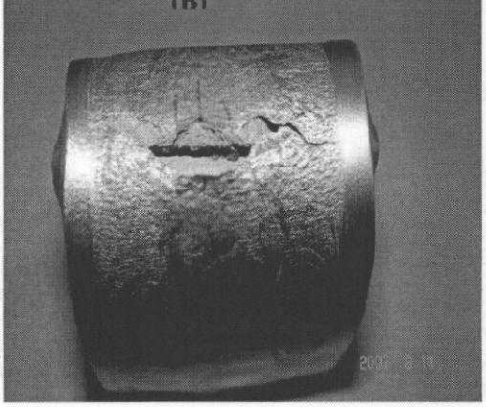
Increasing the ageing time further did not influence the structure of HAZ in 304LN-P1. Also the 304LN-P2 still showed the dual structures at higher ageing time.

The double loop EPR test showed very small DOS values of HAZ in as-received specimens from both the pipes that correspond to the step structures [9]. The DOS values obtained for 304LN-P1 after ageing at 400 and 450°C for different periods were significantly high, shown in the Table-2, though the post EPR and oxalic acid etched structures did not indicate the presence of carbide formation. However, the material revealed parallel dark lines, which probably corroded during EPR test and contributed to the higher DOS values. The dark parallel lines were analysed using SEM-EDAX and were found to be ferrite regions. Possibly the austenite-ferrite interphase is corroded at a greater rate than that of austenite or ferrite alone due to the formation of galvanic cells. Such lines were not revealed in the 304LN-P2. The DOS HAZ of 304LN-P2 was found to increase with ageing time at both the temperature i.e. 400 and 450°C (Table 3). It indicates that the material has experienced sensitization either due to the growth of the prior existed carbides, fresh nucleation or combination thereof during low temperature ageing. The obtained DOS values correspond to the 'dual' structure appeared after oxalic acid etching according to [9] as also indicated in present study.

The microstructure in the weld zone was typically dendritic as often seen the cast stainless steels where the dendrites observed to be oriented in different directions. The degree of sensitization was evaluated at the top (outer surface) of the pipe weld (fig-1). The DOS values obtained were much higher than the base and HAZ of corresponding time/ temperature conditions. It has also been shown that after subjected to the sensitisation treatment, weld metal (AISI 308L) produced higher DOS as compared to solution annealed [6]. The DOS values of weld zone from 304LN-P1 were apparently higher than the 304LN-P2 but did not show specific trend. However, DOS in 304LN-P2 was observed to increase with ageing time at 400 and 450°C.

As a result of bending after boiling in copper-copper sulfate-16% sulfuric acid (practice E), fissures were clearly revealed on the weld region of certain specific conditions. This is illustrated in Figure-3. For 304LN-P1, fissures were appeared on the specimens aged at 400°C/8000 hrs (Fig A) while for 304LN-P2 specimen treated at 400°C/8000 hrs (Fig B) and 450°C/1300 hrs (Fig C) showed the fissures. The 304LN-P2 that was aged at 400°C/8000 hrs was almost fractured during bending. The specimen at above conditions therefore may be categorized as IGC susceptible. The weld region is also known to produce brittle phases during long-term exposure. This is however yet to confirm whether such transformation was the reason of fissures or cracking.





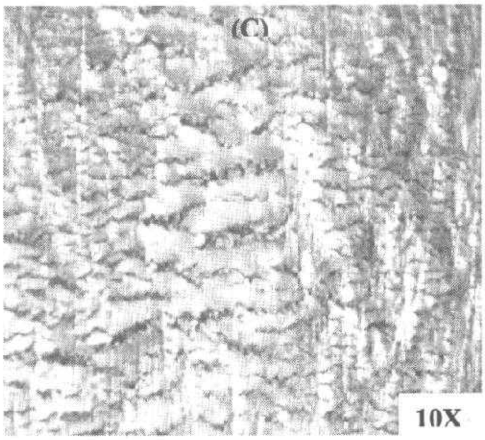


Figure 3: Fractographs of bent location after Copper-copper sulfate- sulfuric acid (Practice E) test (A) 304LN-P1 at 400°C/8000hrs (B) 304LN-P2 at 400°C/8000hrs (C) 304LN-P2 at 450°C/1300hrs

Conclusions

1. The HAZ of 304LN-P1 showed 'step' structure, at studied time/temperature combinations, during oxalic acid etching but revealed parallel dark lines, which were corroded during EPR test and enhanced the DOS values.
2. The HAZ of 304LN-P2 showed 'dual' structure during oxalic acid etching and showed increase in DOS with ageing time at 400 and 450°C during EPR test.
3. The DOS values in the weld pool were significantly higher than that observed along the HAZ or base for specimen of both pipes.
4. Fissures were found on the bent specimen of 304LN-P1 aged at 400°C/8000 hrs and of 304LN-P2 specimens treated at 450°C/1300 hrs during ASTM 262 Practice E test. The 304LN-P2 aged at 400°C/8000 was almost fractured during bending.

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