Effect of Low Temperature Sensitization on Corrosion Behaviour of 304 L SS Canister – An Application for Nuclear High Level Waste Packages in Geological Repositories

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Abstract:

The manuscript presents the effect of low temperature sensitization (LTS) on the corrosion behaviour of AISI type 304L SS in ground water. In the study, 304L SS containing 0.02 % and 0.03 % carbon were subjected to LTS treatments, representing 300° C for 10 years and 100 years of nuclear vitrified waste containment. Degree of sensitization was quantified by Double loop electrochemical potentiokinetic reactivation (DL-EPR) technique. Microstructural evaluation was carried out by optical, and electron backscattered diffraction (EBSD). The DOS of carbide nucleated 304L SS (0.02% C) was found to be low and only marginal increase occurred with LTS treatment. 304L SS (0.03% C) showed comparatively high DOS, which substantially increased with LTS treatment. EBSD revealed the presence of carbides along high angle random boundaries. Corrosion studies in simulated ground water indicated poor LTS and corrosion resistance of 304L SS (0.03 % C).

Keywords: Low temperature sensitization, 3O4L SS, corrosion resistance, ground water, EBSD

1. Introduction

In India, a three step strategy for management of nuclear high level waste (HLW) has been adopted, which involves a) vitrification of waste oxides in borosilicate glass matrix, b) interim storage of the conditioned waste under continuous cooling and surveillance, c) disposal in deep geological repositories [1,2,3]. The vitrified waste is stored in AISI type 304L SS canisters. Despite having good mechanical properties and corrosion resistance, 304L SS is susceptible to sensitization, when exposed to temperatures of 500-800°C. Sensitization of austenitic stainless steels also occurs below 500°C, due to the growth of pre-existing carbides and is termed as low temperature sensitization (LTS) [4, 5]. During vitrification, the molten glass containing HLW oxides is poured into 304L SS canisters at 1050° C [1, 2, 6]. The canister material cools through the sensitization temperature, which can lead to nucleation of chromium carbides. Due to the continuously produced radioactive decay heat, the canister is exposed to 100-300° C, during long containment periods, which allows the carbides to grow leading to LTS. This is a concern in geological repositories as the sensitized

microstructure is susceptible to IGC/IGSCC forms of corrosion, once groundwater comes in contact with the material. As the sensitization kinetics of LTS is slow at temperatures of 300° C, laboratory scale experiments are carried out at higher temperatures. In the present study, 304L SS containing 0.02 % C and 0.03 % C were subjected

to LTS heat treatment at 500 °C for 1 day and 11 days to represent temperatures of 300° C for 10 years and 100 years of nuclear waste storage. Sensitization was quantified by DL-EPR test and corrosion resistance of the two materials were compared in simulated ground water by potentiodynamic anodic polarization. Optical, EBSD, were used for microstructural evaluation.

2 Experimental

The chemical compositions and dimensions of 304L SS used in the present investigation are given in Table 1. The specimens were solution annealed at 1050° C / 1 h, subsequently, carbide nucleation heat treatment was carried out at 675° C / 1h followed by water quenching. The carbide nucleated specimens were subjected to LTS heat treatment at 500° C for 1day and 11 days.

optical microscopy. EBSD studies were carried out for carbide nucleated, LTS – 1 day and LTS – 11days treated specimens of 304L SS (0.03% C). The details of EBSD is reported in our earlier studies [8]. For DL-EPR studies, the specimens were immersed in 0.5M H_2SO_4 and 0.01M KSCN at 30° C, and the open circuit potential (OCP) was measured for 1 h, under oxygen free argon gas purging. Subsequently, the electrochemical potential was varied from OCP to 300 mV (SCE) and reversed to OCP at a scan rate of 1.67 mV/s. The % DOS was evaluated as

$$\%DOS = \left\{ \frac{i_r}{i_a} \right| x100$$

where i_r is the peak reactivation current, and i_a is the peak activation current. For corrosion testing, the polished specimens were immersed in

Table 1 Composition and dimension 304L SS specimens used for the study

Materials (10 mm x 10 mm x 10 mm)	Elements (wt %)								
	C	Cr	Ni	Fe	Mo	Mn	Si	P	S
AISI 304L SS (0.02% C)	0.02	17.92	8.71	70.14	0.33	1.65	0.480	0.038	0.022
AISI 304L SS (0.03% C)	0.03	18.11	8.87	69.76	0.33	1.64	0.484	0.041	0.024

The aging time required at 500° C to simulate the service life of 10 to 100 years at 300° C were calculated using the Arrhenius equation, considering the activation energy to be 150 kJ/mol [6,8,15].

$$\left. t_2 \right|_{t_1} = e^{\left[\frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]}$$

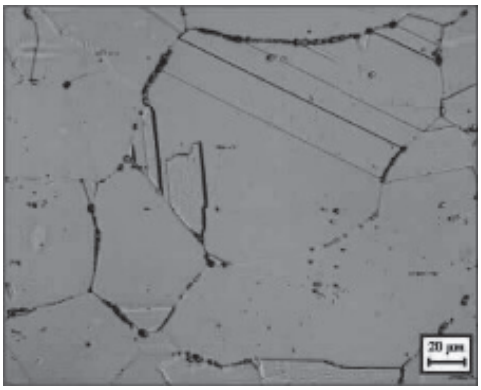
where, Q is the activation energy (150 kJ/mol), R is the universal gas constant (J/mol K) = 8.314 J/mol K, T_1 is the aging temperature (laboratory scale), T_2 is the temperature at which the life is being estimated (300° C), t_1 is the expected life, t_2 is the time required to expose at T_1. The heat treated specimens were mounted in araldite resin and further mechanically ground using SiC emery paper, polished till 1µm diamond finish and used for optical, DL- EPR and polarization studies. Polished specimens were electrolytically etched according to the ASTM standard A 262 practice A [7], and evaluated for microstructure using simulated ground water (Ca^{+2} : 195.64 ppm, Mg^{+2}:181.67 ppm, K^+: 29.39, Na^+: 1322 ppm, $SO4^{-2}$: 830 ppm, Cl^- : 2335ppm) for 30 min at OCP under Ar purging. Subsequently, potentiodynamic anodic polarization was carried out using Autolab PGSTAT 302N (Electrochemie, Netherlands), from a potential of 250 mV (Ag/AgCl) below OCP, at a scan rate of 10 mV/min. The anodic polarization was stopped at potentials, after current increased monotonically beyond transpassive potential. From the polarization curves, the breakdown potentials were determined.

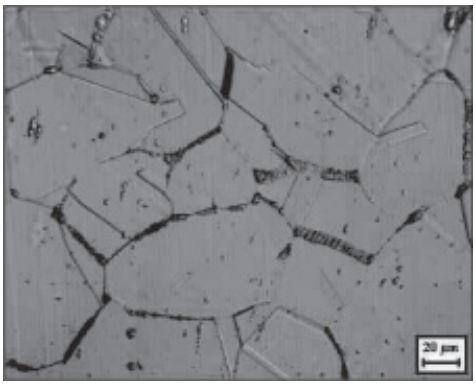
3. Results and Discussion

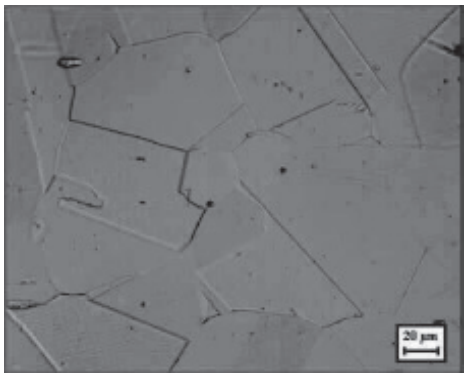
3.1 Optical microstructure and EBSD

Figure 1 & 2 represents the optical micrographs of 304L SS (0.02% C) and 304L SS (0.03% C) respectively. The solution annealed 304L SS (0.02% C) showed step structure and that for the carbide nucleated, LTS – 1 day and LTS – 11days heat treated specimens showed dual

microstructure. The solution annealed 304L SS (0.03% C) showed dual microstructure and carbide nucleated, LTS – 1 day and LTS – 11 days treated 304L SS (0.03% C) revealed ditch microstructure. Figure 3 (a, b and c) represent crystal orientation or IPF map of 304L SS (0.03 % C) for carbide nucleated (a), LTS-1day (b) and LTS -11days (c) treated specimens. From the orientation maps, it is observed that the austenitic grains are poly crystalline in nature. Figure 3 (d, e, f) represents the superimposed map of the CSL boundaries (Ó3 :red, Ó9 : blue, Ó27a : green, over the image (IQ) quality map.







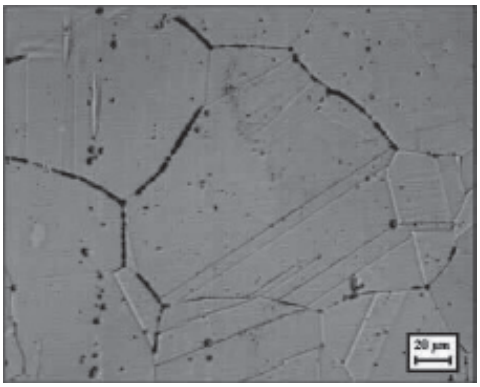


Figure 1 Optical micrographs of 304L SS (0.02% C) a) solution annealed, b) carbide nucleated, c) LTS – 1 day and d) LTS – 11 days.

The carbide phase map was also superimposed on IQ map. The analysis of the super imposed CSL and phase in IQ map reveal the presence of carbides only along high angle random boundaries and absence of the same along Ó3 CSL boundary, signifying that Ó3 CSL boundaries are resistant to carbide formation. With increase in time duration of heat treatment, no appreciable change was observed in the distribution of carbides in austenite matrix.

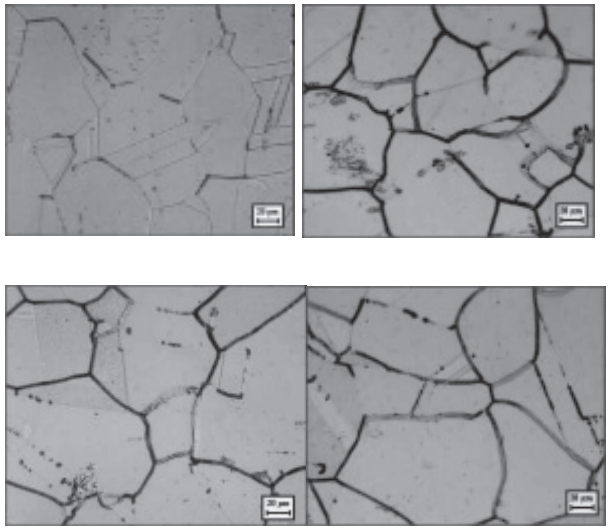


Figure 2 Optical micrographs of 304L SS (0.03% C), a) solution annealed, b) carbide nucleated, c) LTS – 1 days and d) LTS – 11 days.

3.2 Double loop electrochemical potentiokinetic reactivation (DL-EPR) test : Typical DL-EPR plot for the solution annealed, carbide nucleated, LTS-1day and LTS- 11 days samples of 304L SS (0.03% C) is shown in Fig.4 and a comparison

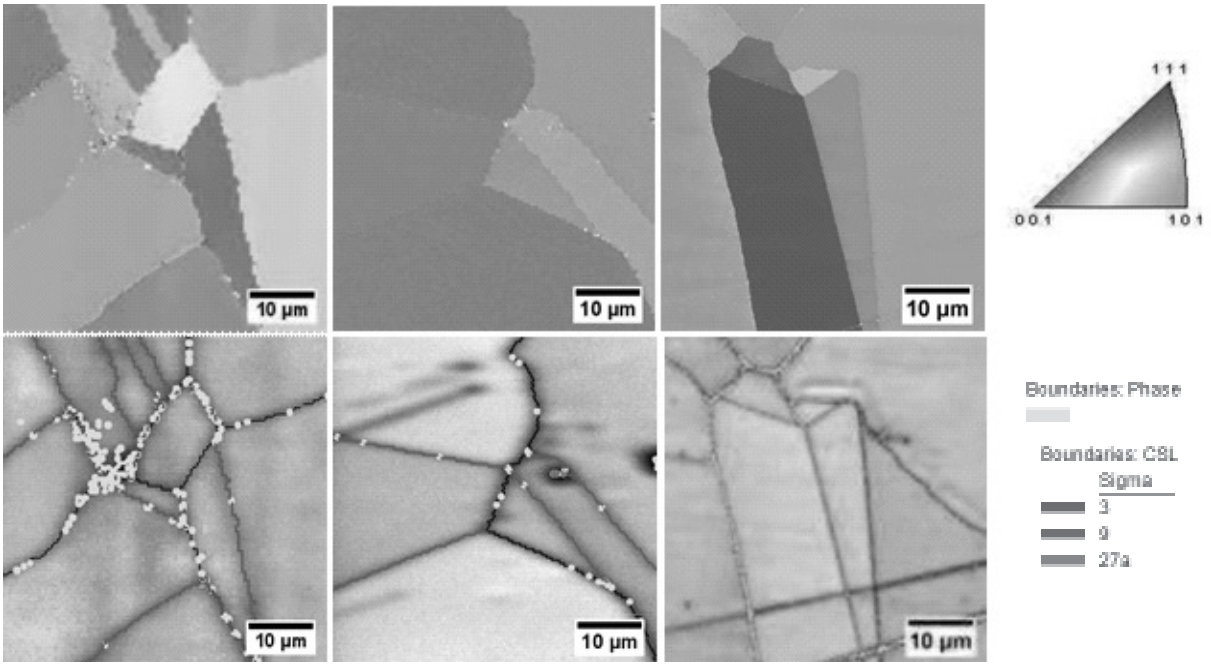


Figure 3 The crystal orientation map of 304L SS, a) carbide nucleated, b) LTS – 1 day, c) LTS – 11 days. Their respective CSL boundaries and carbide phase superimposed in image quality map is shown in d), e), f) respectively. Crystal orientation map color legend is shown in (g). h) represents phase and CSL boundaries

of % DOS of 304L SS (0.02 %C) and 304L SS (0.03% C) are tabulated in Table 2. The results indicate an increase in DOS with LTS treatments in 304L SS (0.02%C) and 304L SS (0.03%C), but the increase is marginal in 0.02% C and substantial in 0.03% C. The increase in DOS with LTS could be attributed to growth of carbides from grain boundary diffusion as the kinetics of diffusion of chromium is sluggish at 500° C. Kein et al [4] have opined that at temperatures of 300° C, chromium diffuses from the grain matrix towards the chromium depleted regions around the pre-existing (chromium-rich) carbides. This causes growth of chromium carbides at temperatures as low as 300 ° C. In addition, the % DOS is substantially higher in 304L SS (0.03% C) than 304L SS (0.02% C).The results indicated that the low carbon 304L SS (0.02% C) is resistant to LTS. Increasing the carbon content above 0.02 % has resulted in decrease in resistance to LTS.

3.3 Potentiodynamic anodic polarization in simulated ground water : Typical potentiodynamic anodic polarization curves of 304L SS (0.03 % C) in simulated ground water and a comparison of breakdown potentials

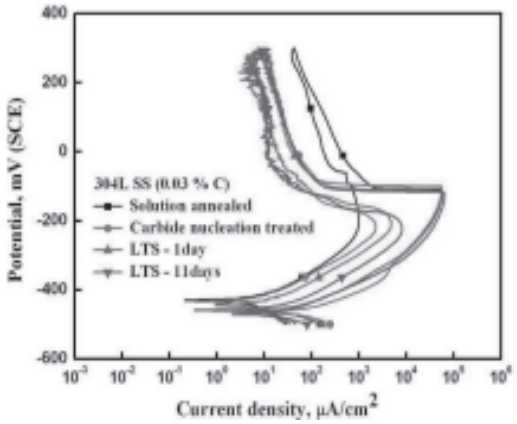


Figure 4 DL-EPR plot of 304L SS (0.03 % C)

Table 2 Comparison of degree of sensitization (% DOS) of 304 L SS (0.02% C) and 304L SS (0.03%)

Specimen	% DOS			
304 L SS	SA	Carbide nucleated	LTS-1 day	LTS-days
0.02 %C	0.1	0.6	1	1.6
0.03 %C	1.8	4	7.2	12.6

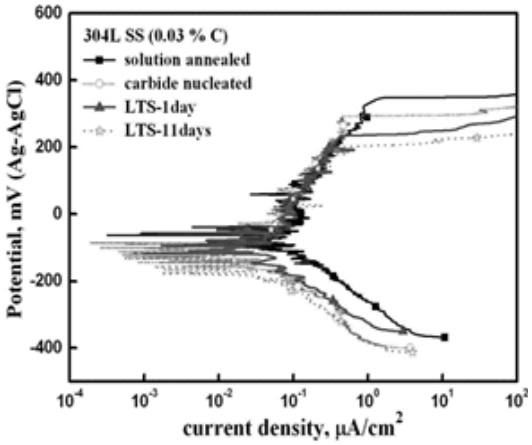
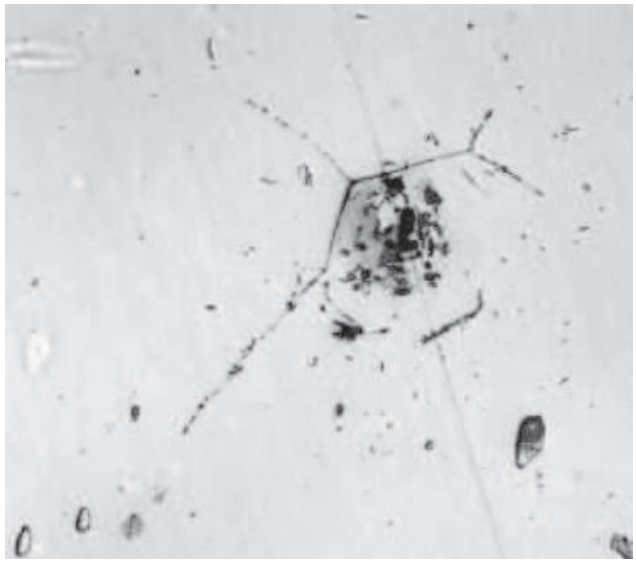


Table 3 Breakdown potentials derived from polarization curves

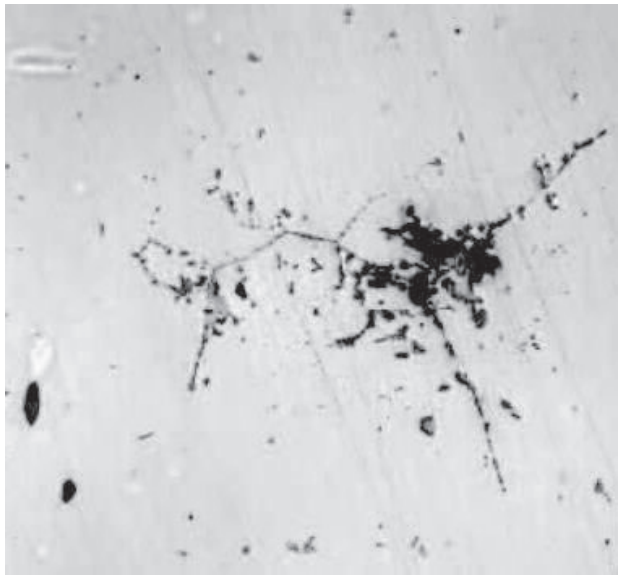
Specimen	Breakdown potentials, mV (Ag/AgCl)			
304 L SS	SA	Carbide nucleated	LTS-1day	LTS-11days
0.02 %C	528	393	392	328
0.03 %C	347	293	234	201

derived from the curves of 304L SS (0.02% C) and (0.03%C) are given in Fig. 5 and Table 3 respectively.

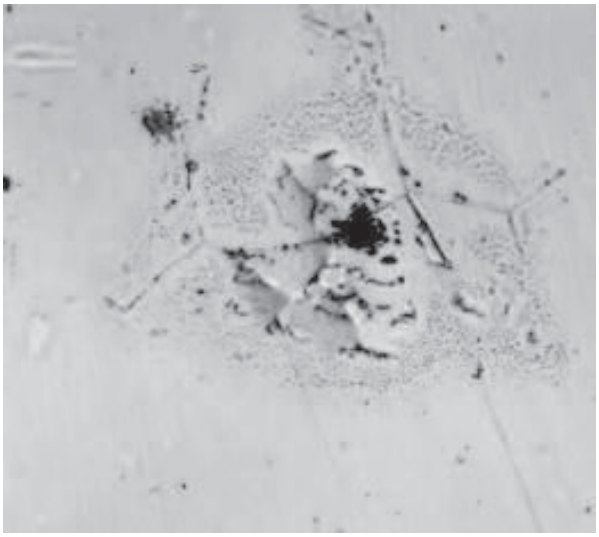
The breakdown potentials was found to decrease with carbide nucleation and further with LTS treatments for 304L SS containing 0.02% C and 0.03% C, but the decrease is marginal in the former and substantial in the latter. A decrease in breakdown potential implies a decrease in corrosion resistance. The decrease in breakdown potential could be attributed to the increase in the degree of sensitization on carbide nucleation and LTS treatments for 1 and 11 days. The decrease in breakdown potential and hence a decrease in the corrosion resistance was found to be profound for 304L SS (0.03 % C), when compared to 304L SS (0.02 % C). A good correlation was found between polarization and DL-EPR results. The corrosion resistance decreased with increase in DOS. Neverthless, 304L SS (0.02 % C) exhibited a superior corrosion resistance in simulated ground water when compared to 304L SS (0.03% C).Typical representation of IGC attack in 304L SS (0.03 %C) after corrosion testing in simulated ground water, is represented in Fig. 6. 304L SS (0.02 % C) was resistant to IGC



A



B



C

Figure 6 Optical micrograph of 304L SS (0.03 % C) showing IGC attack in a) carbide nucleated b) LTS-1 day c) LTS -11 days

4 Conclusion

It is inferred that carbon content of 304L SS plays a major role in the low temperature senstization resistance and corrosion resistance in simulated ground water. For long term containment of nuclear high level vitrified waste in 304L SS canisters, a carbon content of 0.02 % C would be resistant to LTS as well as to IGC attack in ground water.

Reference

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