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Effect of cold work on low-temperature sensitization behaviour of austenitic stainless steels

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Abstract

The effects of cold work and low-temperature sensitization heat treatment of non-sensitized austenitic stainless steels have been investigated and related to the cracking in nuclear power reactors. Types 304, 304L and 304LN developed martensite after 15% cold working. Heat treatment of these cold worked steels at 500 °C led to sensitization of grain boundaries and the matrix and a desensitization effect was seen in 11 days due to fast diffusion rate of chromium in martensite. Types 316L and 316LN did not develop martensite upon cold rolling due to its chemical composition suppressing the martensite transformation (due to deformation) temperature, hence these were not sensitized at 500 °C. The sensitization of the martensite phase was always accompanied by a hump in the reactivation current peak in the double loop electrochemical potentiokinetic reactivation test, thus providing a test to detect such sensitization. It was shown that bending does not produce martensite and therefore, is a better method to simulate weld heat affected zone. Bending and heating at 500 °C for 11 days led to fresh precipitation due to increased retained strain and desensitization of 304LN due to faster diffusion rate of chromium along dislocations. The as received or solution annealed 304 and 304LN with 0.15% nitrogen showed increased sensitization after heat treatment at 500 °C, indicating the presence of carbides/nitrides.

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1. Introduction

Austenitic stainless steels are used in various applications in the chemical and nuclear power industries. Though resistant to uniform corrosion, austenitic stainless steels are prone to localized corrosion and stress corrosion cracking (SCC). These stainless steels are prone to sensitization – a process by which chromium carbides form at grain boundaries with adjacent depletion of chromium [1–3]. This happens at the temperature range of 550–800 °C such as during welding. Sensitization is the basic reason for intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC). Nuclear power plants especially boiling water reactors (BWRs) have experienced extensive IGSCC of stainless steel components in the recirculation pipelines and in-core components in the past three decades. The extensive cracking observed till late 1980s in the recirculation pipelines are attributed [4–7] to low-temperature sensitization (LTS). The cracking of the in-core components are attributed [8,9] to irradiation assisted stress corrosion cracking. In both the cases the reactors components operate at 280–300 °C and high purity water with dissolved oxygen is the environment that is well known [10,11] to cause IGSCC of sensitized stainless steels.

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Low-temperature sensitization occurs at a temperature below 500 °C by growth of pre-existing carbides. Earlier studies [4–7] have shown that LTS requires the presence of carbides at grain boundaries (either from welding or from slow cooling from solution annealing). Upon exposure to plant operating temperatures of ~300 °C, chromium diffuses from the grain matrix towards the chromium depleted regions around the existing (chromium-rich) carbides. This causes growth of chromium carbides at temperatures as low as 300 °C. It was clearly shown [4–6] that at 500 °C the number of carbides remained the same but the area of the carbides increased. It had been shown that LTS can occur by this process at temperatures between 300 and 500 °C. Above 500 °C the classical sensitization process proceeds by the precipitation and growth of chromium carbides at grain boundaries. While LTS is typically simulated in laboratories using heat treatments at 500 °C, it is possible to develop classical sensitization in certain heats of type 304 after a long term heating at 500 °C. All these studies on LTS were on either welded or sensitized stainless steels. However, stainless steels can have pre-existing precipitates in their as received/solution annealed conditions also. Some steels develop precipitates at low-temperatures (<500 °C) either in cold worked condition or from martensite present as a result of fabrication processes. The processes of cutting and grinding have also been shown [12] to promote LTS. However machining or cold working resulted [12] in plastic deformation and caused martensite formation within grains and the LTS heat treatment/exposure lead to precipitation of carbides inside the grains. It was suggested in one study that a threshold level of cold work is required [13] for type 304 stainless steel to become prone to LTS. In the present study, the LTS behaviour of different grades of austenitic stainless steels is studied in their as received and solution annealed condition.

To overcome the problem of LTS-related cracking in recirculation pipelines, the material related remedy [14,15] was to switch to a sensitization resistant material like type 316NG in place of 304 that was initially used. A sensitization resistant material would not have pre-existing precipitates formed during welding hence LTS would not take place during service. In type 316NG, the chemical composition, especially molybdenum and low carbon (up to 0.02 wt%) and added nitrogen (up to 0.12 wt%) help in avoiding precipitation of either carbides or nitrides during welding. Any precipitation due to high heat input also does not develop a high degree of sensitization (DOS) [16,17] due to a shallower depletion of chromium. Types NG were preferred over low carbon stainless steels as their strength levels were comparable to those of normal carbon stainless steels. The recirculation piping was replaced [14] in most of the BWRs by the late 90s with type 316NG stainless steel. This helped to avoid cracking in recirculation pipelines of BWRs. Many reactors switched over [14,18,19] to hydrogen water chemistry (HWC) to reduce the operating potentials of stainless steels to a value below −230 mV vs. standard hydrogen electrode (SHE). This method effectively controls operating potentials in the water phase, e.g. recirculation pipelines and has been shown to avoid IGSCC of even sensitized stainless steels.

The mechanism of cracking of BWR core shrouds [20–22] made of low carbon (non-sensitized) type 304L/316L stainless steel is now emerging. While cracking in core shrouds made from type 304L stainless steel with carbon as low as 0.009% has been observed after a long service life (approximately nine effective full power years), signs of irradiation induced segregation has not been observed [20,21]. These stainless steels are not expected to be sensitized during welding. Measurement of retained strain and increased dislocation density in the weld heat affect zone (HAZ) had been reported [22] with traces of martensite formation at the surface. Cold work, radiation induced segregation (RIS) or non-equilibrium segregation of vacancies are suspected to cause changes in microstructure during long term ageing [20–22]. Warm working that avoids martensite formation but increases yield strength of stainless steels has been shown to make the material more prone to IGSCC in BWR simulated environments [23,24]. It has been shown in these studies that it is the increased yield strength of the material that makes it prone to IGSCC even with its non-sensitized microstructure.

Cold deformation is invariably present in components used in plants due to fabrication techniques used in machining, bending and cold rolling. Stresses present due to cooling from high temperatures during welding and welding in constrained geometries cause deformation in materials and high stresses/strains. Cold or even warm deformation has been shown to increase the susceptibility of non-sensitized stainless steels to IGSCC in BWR simulated water chemistry [23–25], However, the role of cold working on LTS behaviour of stainless steel has not been investigated in detail.

New generations of nuclear reactors are now being designed [26] for an operation life of 100 years. This brings in additional aspects that were not considered earlier as the design life of reactors was typically 30 years. The weld pool of stainless steels has a delta ferrite level of 3–10% to avoid hot cracking during welding. During long term operation at 300 °C the concern is that the delta ferrite would transform to phases that are brittle and it would impair the impact strength of the material. While there is limited experimental and plant data on this aspect, it is brought out [27] by studies on the weld material as well as cast stainless steels that leaner ferrites have a lesser tendency to transform while richer ferrites transform easily. These results are from studies conducted at temperatures as low as 420 °C. Studies at lower temperatures take longer time (tens of years) and there is no basis to extrapolate the data obtained at 400–500 °C to behaviour at 300 °C. In absence of data on low-temperature embrittlement (LTE), the only experimental results available at temperatures above 400 °C show that molybdenum containing stainless steels, e.g. type 316 are more prone to LTE compared to types 304. This brings into focus the choice of type 304 for a long design life of reactors. Even type 304 welds have been shown to have lower impact properties after exposure at 343 °C for 50 000 h when the delta ferrite content is more than 8% [28]. The LTS behaviour of different varieties of type 304 for a long operation life has not been investigated so far.

The LTS behaviour of types 304, 304L and two heats of 304LN (with nitrogen content of 0.12 and 0.15 wt% respectively) has been studied in this work. As the problem of cracking in core shrouds of BWR is seen with non-sensitized stainless steels, the LTS behaviour of these stainless steels are studied in their as received or solution annealed conditions. The activation energy usually taken for LTS phenomenon at 300–500 °C and the issue of simulation of LTS in the weld HAZ by heat treatment at 500 °C has been questioned. The strain present in the weld HAZ is simulated by cold working and then LTS studies have been done on types 304 and 316 stainless steels including L and LN varieties. The contribution of martensite formation as a result of cold working or fabrication techniques has been highlighted and the effect of martensite on LTS brought out clearly. The role of retained strain produced by bending and without formation of martensite has also been studied.

2. Materials and experimental procedures

2.1. Materials and heat treatment

The chemical compositions of stainless steels used in this study are given in Table 1. These materials were mostly studied in the as received (mill annealed) condition with some in the solution annealed condition. Solution annealing was conducted on the as received materials at 1050 °C for 60 min followed by water quenching. The 304LN materials were in the form of welded pipes, type 304LN1 a pipe of 147 mm diameter and 14 mm thickness and the type 304LN2 a pipe of 294 mm diameter and 28 mm thickness. The two heats of type 304LN were first hot rolled to 6 mm thickness and then cold rolled to 2 mm thickness. These were then solution annealed at 1050 °C for 1 h and water quenched.

The sensitization treatment of type 304 and 304L and 304LN was 675 °C for 1 h. Type 316L and 316LN were sensitized at 750 °C for 25 h as it was shown [29] by establishing its time–temperature-sensitization diagram that it sensitizes most easily at 750 °C. All of the sensitization heat treatments were followed by water quenching.

The temperature at which a true strain of 30% produces 50% martensite in an annealed stainless steel is termed Md30 and was calculated [30,31] using the Eq. (1),

$$\mathrm{Md30} = 413–462(\mathrm{C}+\mathrm{N})–9.2(\mathrm{Si})–8.1(\mathrm{Mn})–13.7(\mathrm{Cr}) \\ –9.5(\mathrm{Ni})–18.5(\mathrm{Mo}), \quad (1)$$

with all of the elements in wt%. The Md30 temperatures calculated for the heats of stainless steels used in this study are shown in Table 1.

2.2. Cold working and LTS heat treatment

All of the stainless steels were cold worked by rolling at room temperature. Types 304, 304L, 304LN1 and 304LN2 were cold rolled to 15% reduction in thickness. Some of these stainless steels were cold rolled in the as received condition while others were cold rolled after a solution annealing treatment to understand the role of starting structure on LTS. Types 316L and 316LN in their as received condition were cold rolled to obtain 20% reduction in thickness.

Most of the reported studies on LTS of austenitic stainless steels used heat treatment at 500 °C for 1 day to simulate service life exposure at 300 °C for 10 years. This is based on activation energy of 150 KJ/mole measured [4–6] for the LTS. Based on this activation energy a longer term, 11 days heat treatment at 500 °C was used in this study to simulate service life at 300 °C for 100

Table 1
Chemical composition (in wt%) and the Md30 temperature (°C) of different stainless steels used in this study

Stainless Steel	Cr	Ni	Mo	Mn	Si	C	N	P	S	Md30 (°C)
304	18.40	9.60	0.10	1.50	0.45	0.045	0.04	0.035	0.020	12.31
304L	19.40	11.80	0.10	0.70	0.35	0.023	0.04	0.032	0.010	−4.73
304LN1	17.30	11.40	0.26	1.30	0.34	0.020	0.12	0.030	0.004	−15.46
304LN2	18.70	10.50	0.30	1.50	0.35	0.020	0.15	0.031	0.004	−42.40
316L	16.50	10.20	1.93	2.00	0.50	0.031	0.04	0.050	0.015	0.74
316LN	17.40	13.20	2.57	1.73	0.64	0.019	0.16	0.021	0.030	−100.92

years. The LTS treatments were conducted at 500 °C for either 24 h (referred to as LTS1) or 11 days (referred to as LTS2), followed by water quenching.

Bending was used to increase the retained strain in the material. 304LN1 coupons were machined from a thickness of 14 mm to a thickness of 8 mm. A 15 cm long and 15 mm wide section was bent by 90° at room temperature. This bent section was then heat treated at 500 °C for 11 days to study its LTS behaviour.

2.3. Double loop electrochemical potentiokinetic reactivation test

The double loop electrochemical potentiokinetic reactivation test (DL-EPR) was conducted to assess the degree of sensitization of stainless steels. For all types of stainless steels the test was conducted at room temperature and a solution of 0.5 M $H_2SO_4 + 0.01$ M KSCN (deaerated) was used. The electrochemical potential was varied from the open circuit potential to +300 mV (SCE) and then back to the open circuit potential at a scan rate of 100 mV/min. For 316L and 316LN, a more sensitive version [32] of the test was used in which the test solution was 1 M $H_2SO_4 + 0.1$ M KSCN (deaerated), whereas all the other conditions were kept the same. The ratio of the reactivation current to the activation current multiplied by 100 was taken as the DL-EPR value and was taken as a measure of the DOS. The reported values are an average of three tests for each sample. The samples were mounted to expose either the cross-sectional face or the longitudinal face (surface) in order to study differences in DOS, if any.

The DL-EPR test for type 304LN1 that was bent by 90° and LTS2 treated was done using the same methodology as described above. Only the bent regions were exposed for the EPR test and the rest were masked by applying lacquer.

2.4. Microstructural characterization

The microstructures of all the stainless steel samples were examined after electrochemical etching in oxalic acid according to practice A, A262, ASTM [33]. For types 304LN1 and 304LN2, the structures were developed on both surfaces the longitudinal sections and the cross-sections.

2.5. Ferrite meter measurements

The martensite produced by cold working as well as that present in the fabricated (as received) condition was measured by ferrite meter. The conversion from the ferrite number measured from the ferrite meter to % ferrite (magnetic phase) was done using the calibration curve for the ferrite meter. Since the only magnetic phase that forms in these stainless steels is martensite, the ferrite meter readings were taken as a measure of martensite produced in the material due to either fabrication procedure or cold working.

2.6. Microhardness measurements

As martensite is a hard phase, the hardness of the austenitic stainless steel increases with increasing content of martensite. Microhardness measurements were done on cross-sectional and longitudinal sectional faces of different stainless steels using a load of 300 g and a dwell time of 15 s.

3. Results

3.1. DL-EPR results

3.1.1. Types 304 stainless steels

The DL-EPR values of 304, 304L and 304LN steels in different conditions are given in Table 2. The DL-EPR values are shown in Fig. 1(a) for 304 stainless steels in the as received or solution annealed and LTS treated conditions. These DL-EPR values are not normalized to any one grain size. The grain size had increased upon solution annealing and is given in the section on results of microstructural characterization. It is evident from Fig. 1(a) that types 304 showed maximum DOS (DL-EPR ratio of 0.05) among all types of 304 SS, even in its solution annealed condition. In its as received (mill annealed) condition the DOS was much higher at a DL-EPR ratio of 0.5. Upon LTS2 treatment, the DOS in these two conditions increased to 0.87 and 0.80 respectively. From Fig. 1(a), it is clear that the DOS value of type 304LN2 with 0.15% nitrogen also increased after LTS treatment in its as received condition. A solution annealing treatment had reduced the DOS value as a result of which the LTS2 treatment did not increase DOS. For 304LN1, a similar trend was seen after solution annealing. The solution annealing was effective against increasing DOS after LTS2 treatment. In as received conditions 304L and 304LN1 did not have much effect of the LTS2 treatment.

Fig. 1(b) shows typical DL-EPR curves for 304 stainless steels in as received condition after LTS2 treatment. The high DOS is indicated clearly for types 304 and 304LN2 by high current densities during the reactivation stage. Fig. 1(b) clearly shows that type 304L developed least DOS after LTS2 treatment among 304 types of stainless steels.

The DL-EPR values for 304 stainless steels in cold worked and sensitized and LTS conditions are shown in Fig. 2(a). Typical DL-EPR curves are shown in Fig. 2(b) for the cold worked and LTS2 treated conditions for 304 type stainless steels. Again type 304 showed maximum DOS (DL-EPR ratio of 2.96) followed by type 304LN2

Table 2
DL-EPR values for types 304 stainless steels in different conditions

Material and starting condition	DL-EPR values				
	In starting condition	After LTS2	After 15% cold work + LTS1	After 15% Cold work + LTS2	Starting condition + Sensitization
304L (AR)	0.013	0.016	NT	24.37	0.022
304 (AR)	0.50	0.80	NT	25.67	2.96
304 (Ann)	0.05	0.87	NT	22.20	2.90
304LN1 (AR)	0.007	0.048	NT	3.17(CS) 5.31 (LS)	0.018
304LN1 (Ann)	0.0088	0.0083	0.535	0.321	NT
304LN2 (AR)	0.039	0.52	NT	0.28 (CS) 11.21 (LS)	0.80
304LN2 (Ann)	0.0070	ND	0.145	0.173	NT

LTS 1: at 500 °C for 1 day; LTS 2: at 500 °C for 11 days; AR: as received; Ann: solution annealed; ND: not detected; NT: not tested; CS: cross-section; LS: longitudinal section (surfaces).

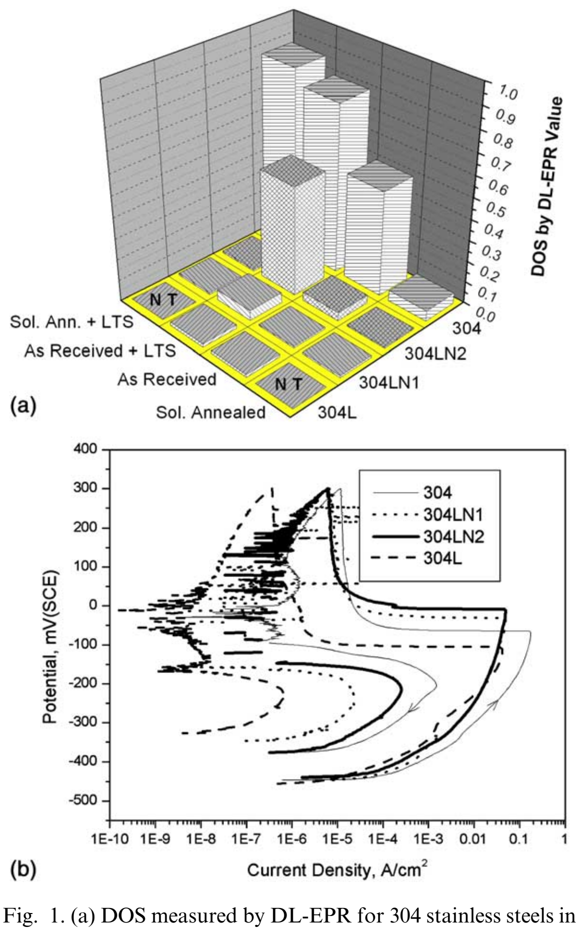

Fig. 1. (a) DOS measured by DL-EPR for 304 stainless steels in as received or solution annealed and LTS2 treated conditions. NT indicates not tested. (b) DL-EPR curves for 304 in as received condition and LTS2. The forward scan of the DL-EPR test is shown by the forward arrow and the reactivation scan is shown by the backward arrow for type 304.

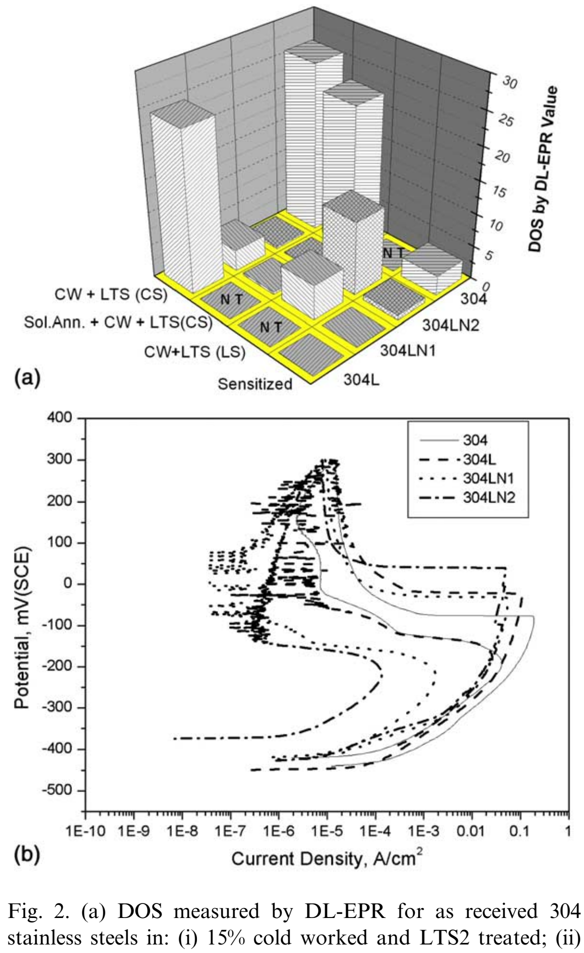

Fig. 2. (a) DOS measured by DL-EPR for as received 304 stainless steels in: (i) 15% cold worked and LTS2 treated; (ii) sensitized conditions. The DOS for solution annealed 304 after cold working and LTS, measured on cross-sectional face are also included. NT indicates not tested. CS denotes cross-section and LS denotes longitudinal section (surfaces). (b) DL-EPR curves for 304 with 15% cold working and LTS2.

(DL-EPR ratio of 0.80) after a sensitization treatment at 675° for 1 h. Types 304LN1 and 304L showed low values after the same sensitization treatment. However, as evident from Fig. 2(a) and (b), types 304L and 304 showed maximum and comparable DOS values after LTS2 treatment on their as received and cold worked structures. The 304LN2 developed the least DOS after cold rolling and LTS2 treatment. This is clearly seen in Fig. 2(b) which also shows comparable and high DOS for types 304L and 304. Types 304LN1 and 304LN2 did develop higher DOS on their surfaces (longitudinal sections) compared to that on cross-sectional regions upon the same level of cold rolling and LTS2 treatment. Type 304 developed the same level of DOS even when the starting structure was solution annealed and then cold worked and LTS2 treated. However, types 304LN1 and 304LN2 developed lesser DOS when the starting structure was solution annealed than as received structure, after cold rolling and LTS2 treatment.

3.1.2. Types 316 stainless steels

The DL-EPR test could not detect sensitization in any of the as received, solution annealed or sensitized coupons of 316L and 316LN. The modified DL-EPR test detected reactivation in the as received and LTS2 treated, 20% cold worked and LTS2 treated and the as received and sensitized coupons of 316L (Fig. 3(a)) and also in the sensitized coupon of 316LN (Fig. 3(b)). Fig. 3(a) shows that the 20% cold rolling and LTS2 treatment resulted in a higher DOS for type 316L than that for its LTS2 treated or even sensitized conditions. The as received and LTS2 treated and the 20% cold worked and LTS2 treated coupons of 316LN did not show any reactivation even in the modified DL-EPR test. The comparative reactivation behaviour from the modified EPR test for 316L and 316LN are shown in Fig. 3(a) and (b), respectively.

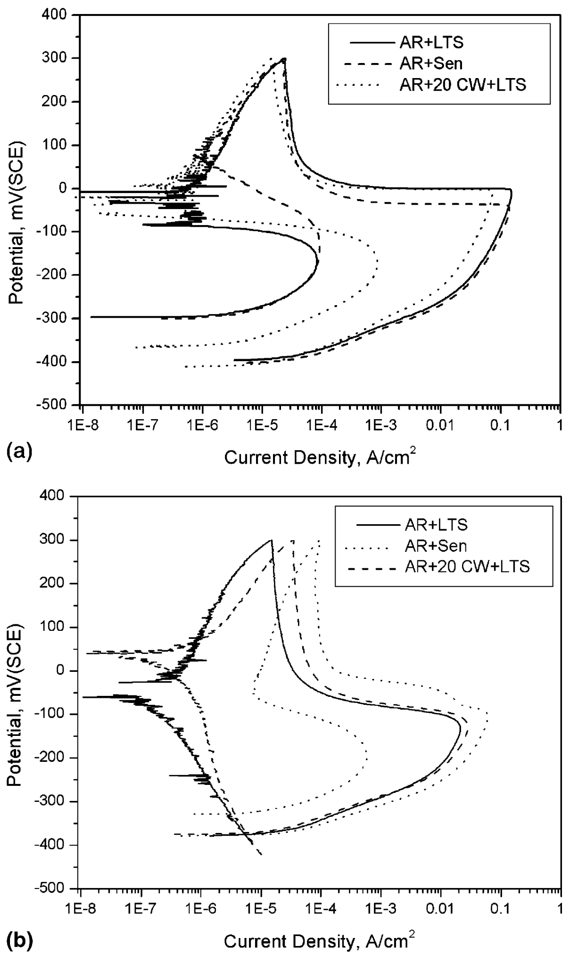

Fig. 3. (a) DL-EPR curves for 316L after the modified EPR test. The DL-EPR values are 0.055 for as received and LTS2 treated, 1.19 for the 20% cold worked and LTS2 treated and 0.066 for the sensitized 316L. (b) DL-EPR curves for 316LN after the modified EPR test. The DL-EPR value is 0.98 for the sensitized 316LN.

3.2. Martensite formation

In type 304 austenitic stainless steels the ferrite content is taken as a measure of martensite as no other magnetic phase forms in these stainless steels due to cold working. No magnetic phase forms in these stainless steels due to heat treatment either. The ferrite meter measurements done on type 304 stainless steels are given in Table 3. It is clear from this table that the low carbon or carbon + nitrogen varieties (type 304L and 304LN1), developed more martensite upon cold rolling compared to higher carbon or carbon + nitrogen varieties. The surfaces of 304LN1 developed more martensite (~3.5%) upon 15% cold rolling as compared to its cross-sectional regions (1.4–2.0%). The solution annealed materials developed much less martensite upon same degree of cold rolling.

The 90° bent sample of type 304LN1 did not show any increased magnetic phase in its cross-sectional face. However the machined surfaces did show 3–4% magnetic phase.

Since martensite is a harder phase, its formation is also indicated by hardness measurements. The measured microhardness values for types 304LN are given in Table 4. All the microhardness values are on samples after the LTS2 treatment. The microhardness values increased with cold rolling. For both 304LN1 and 304LN2, the hardness values on the surfaces were more than that on the cross-sectional regions indicating formation of harder martensitic phase at and near the surfaces.

3.3. Microstructural characterization

The grain size of stainless steels increased after solution annealing. For 304 the ASTM grain size num-

Table 3
Martensitic phase (%) in austenitic stainless steels as measured by ferritemeter on the cross-sectional surfaces

Material	As received	As received + cold worked	Solution annealed	Solution annealed + cold worked
304	<0.2	<0.2	–	–
304 (annealed)	–	–	<0.1	0.2–0.3
304L	0.7	2.5–3.4	–	–
304LN1[a]	0.4	1.4–2.0	–	–
304LN1 (annealed)	–	–	<0.1	∼0.2
304LN2	0.3–0.4	0.3-0.4	–	–
304LN2 (annealed)	–	–	<0.1	<0.1
316L	<0.1	<0.1	–	–
316LN	<0.1	<0.1	–	–

[a] On surfaces of cold rolled sample: ∼3.5.

Table 4
Microhardness values for 304LN, expressed in HV

Material	As received+ LTS2	15% CW + LTS2 (cross-section)	15% CW + LTS2 (longitudinal section)
304LN1	190–195 (8–9.5)	260–288 (24–28.2)	288–305 (28.2–30.3)
304LN2	190–192 (8–9.1)	230–245 (18.2–21.8)	297–318 (29.3–32.0)

The values in bracket are equivalent values in HRC. After solution annealing: 304LN1 190–200 (8.5–11.5), 304LN2 200 (11.5).

ber increased from 5 in the mill annealed condition to 3 in the solution annealed condition. For 304LN1, the grain size number increased from 6 to 4 upon solution annealing. For 304LN2 the grain size number changed from 4.5 to 4 upon solution annealing.

Typical microstructures developed after the DL-EPR tests are given in Figs. 4–7 for 304, 304L, 304LN1 and 304LN2 respectively. The as received or solution annealed stainless steels after the LTS2 treatment did not show any intragranular attack in the DL-EPR test as shown in Figs. 4(a), 5(a), 6(a) and 7(a) for types 304, 304L, 304LN1 and 304LN2 respectively. While the developed sensitization after LTS2 treatment is indicated by attacked regions at grain boundaries for type 304 in Fig. 4(a), discreet attacked regions at grain boundaries are clearly seen in Figs. 6(a) and 7(a) for types 304LN1 and 304LN2. Fig. 4(b) and (c) show high degree of attack after the DL-EPR tests on the cold rolled and LTS2 treated samples. In both the as received and solution annealed conditions, the attack is inside the grains as well as at the grain boundaries (Fig. 4(b) and (c)). The same feature is seen for type 304L in Fig. 5(b). For types 304LN, the attacked regions on the surfaces (longitudinal surfaces) of cold worked and LTS2 treated samples are clearly observed to be intra and also to some extent intergranular in Fig. 6(b) for type 304LN1 and Fig. 7(c) for type 304LN2. The extent of attack in the DL-EPR test is clearly more for 304LN1 than for type 304LN2 in their cold rolled and LTS2 treated conditions as shown in Figs. 6(c) and (d) and 7(b)and (d).

Typical microstructures of cold rolled and LTS2 treated samples, developed after the oxalic acid etching, are shown in Fig. 8. The microstructures show that the surfaces of types 304LN developed high DOS as is indicated by heavy intragranular and intergranular attack (Fig. 8(a) and (c) for type 304LN1 and 304LN2 respectively). The degree of attack in the oxalic acid test was much higher for type 304LN2 than for type 304LN1 as is clear from these two figures. The developed sensitization was limited to surfaces for these stainless steels. While for type 304LN1, the sensitization developed after cold rolling and LTS2 treatment was high upto a distance of at least 500 μm, it was upto a lesser distance of around 200 μm for type 304LN2. This is shown in Fig. 8(b) and (d) respectively. However, the 15% cold rolling had increased the level of precipitation in type 304LN1 as is clear from Fig. 8(e) that shows attacked precipitates (and its chromium depleted regions) that are primarily at grain boundaries. In these regions, away from surfaces, the degree of cold working is not enough to cause formation of martensite as indicated by absence of any intragranular attack.

3.4. Bending and LTS

The 90° bent sample of 304LN1 after LTS2 showed the DL-EPR ratio of 0.77 in the cross-sectional face at

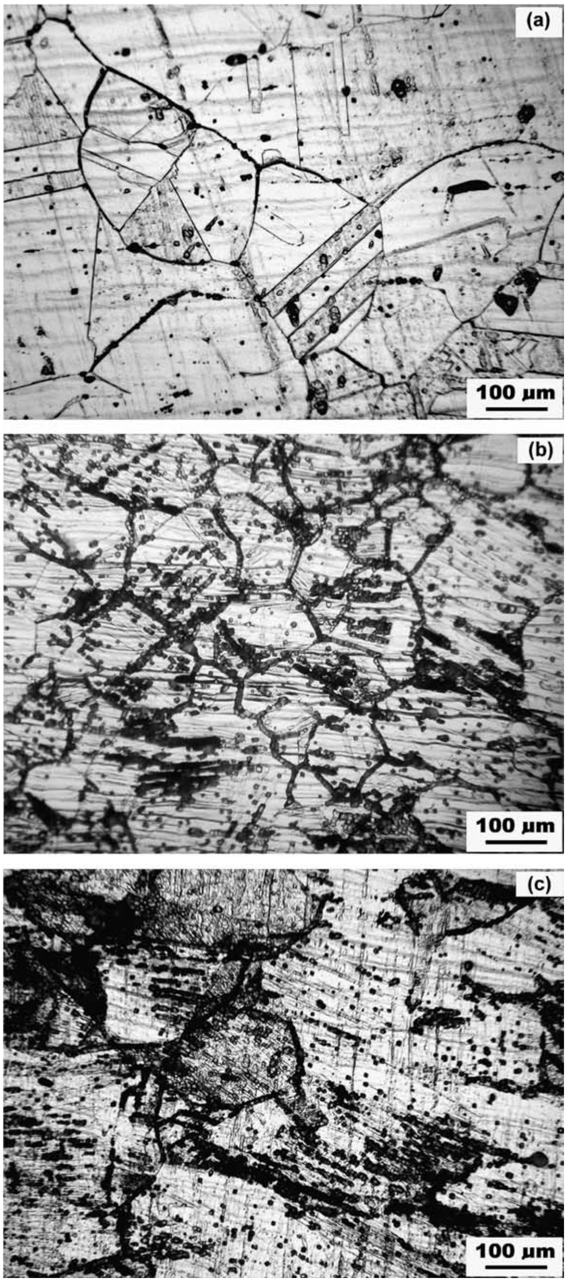

Fig. 4. Microstructures after the DL-EPR testing of 304. (a) Solution annealed and LTS2. (b) As received, 15% cold rolled and LTS2. (c) Solution annealed, 15% cold rolled and LTS2.

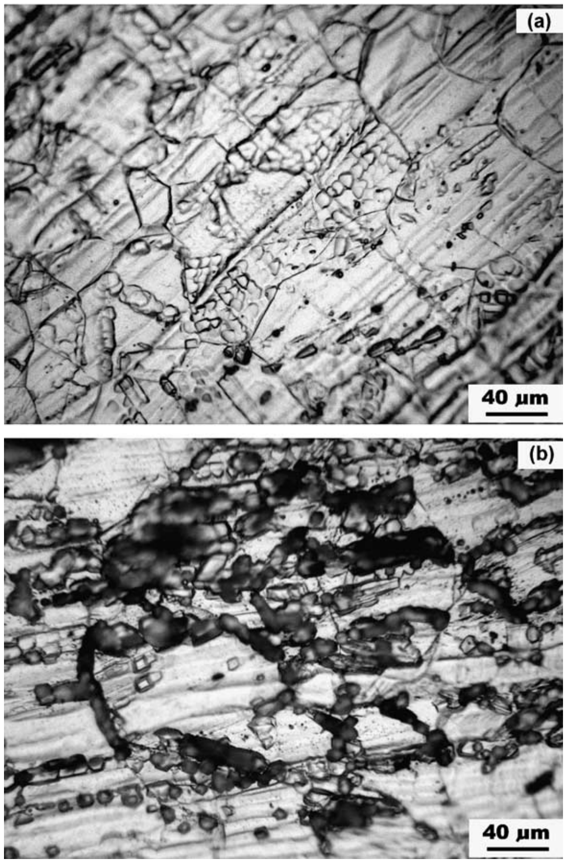

Fig. 5. Microstructures after the DL-EPR testing of 304L. (a) As received and LTS2 heat treated. (b) As received, 15% cold rolled and LTS2 condition.

the maximum bent region. The degree of sensitization was higher compared to even the sensitized (after 675 °C for 1 h) sample that had shown a DL-EPR value of 0.018 Table 2). The microstructure of the sample after the EPR test is shown in Fig. 9(a). There were attacked regions (around precipitates) at grain boundaries and as is also evident from Fig. 9(a), at twin boundaries. This shows presence of chromium depleted regions at these locations. A small fraction of grain boundaries are covered with the attacked precipitates after the oxalic acid etching of the EPR tested sample, at the same region as shown in Fig. 9(b). A bent and LTS2 treated sample that was freshly polished shows many such attacked regions after oxalic acid etching as seen in Fig. 9(c). Even some twin boundaries are attacked indicating precipitation after bending and LTS2 treatment.

3.5. Detection of martensite induced sensitization

The DL-EPR curve for 304 that was solution annealed and then rolled to have 15% cold work and LTS2 treatment showed a hump (at E_{ms}) as shown in Fig. 10. These humps are similar to those shown by other cold rolled and LTS2 treated materials as shown in Fig. 2(b). Fig. 10 compares the DL-EPR curves for type 304 that was cold rolled and LTS1 treated. The same figure also shows the DL-EPR curve for the type 304 that was sensitized at 675 °C for 1 h.

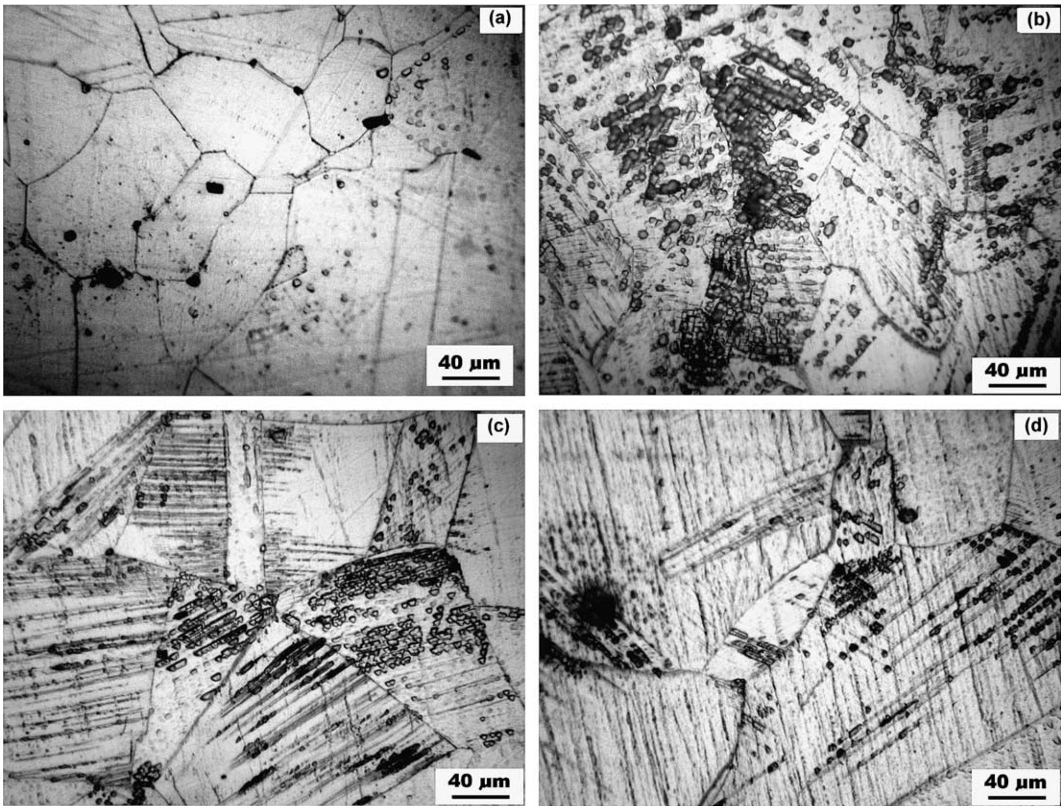

Fig. 6. Microstructures after the DL-EPR testing of 304LN1. (a) As received and LTS2. (b) As received, 15% cold rolled and LTS2, surfaces. (c) Solution annealed, 15% cold rolled and LTS1. (d) Solution annealed, 15% cold rolled and LTS2.

4. Discussion

The effect of cold work on sensitization had been reported in earlier studies [34–37]. It is commonly accepted that the susceptibility to sensitization of austenitic stainless steels increases with increasing cold work till a maximum susceptibility is obtained at 15–20% cold work. Above ~20% cold work, the degree of sensitization (after a sensitization heat treatment between 550–800 °C) decreases as carbides start nucleating within the grain matrix and intragranular carbide precipitation dominates. Cold work levels up to 15–20% increase retained energy in the material and as a result the energy required to nucleate a carbide at grain boundary decreases. After ~20% cold working, even the sites inside the grain matrix have high energy and carbides can nucleate there easily. It had been shown that upon cold working the sensitization was observed at a lower temperature of 500 °C for 304 stainless steel [36].

The role of cold working on LTS has not been completely understood. It had been reported [37,38] that cold work increases the number of dislocations/dislocation pipes along which the diffusion rate of chromium is very high (as compared to that in the austenitic matrix). This increases the susceptibility to LTS [38]. Martensite formation [31,39] in austenitic stainless steels can be of two types. Stress assisted martensite develops when stress levels provide for reduction in driving force for nucleation of martensite. This martensite is in a plate form. The second type of martensite is α' martensite that is strain induced martensite and is in the form of laths. It is formed by plastic deformation of the parent austenite where the proper defect structure is created and acts as an embryo for the transformation product. The martensite formed is ferromagnetic and detected by magnetic measurements. It had also been shown [39–42] that 304 transforms to martensite upon cold rolling and martensite gets easily sensitized after short term exposures to temperatures from 350–500 °C. However the extent of retained strain (cold work without formation of martensite) and its result on LTS have not been identified. The cracking of BWR recirculation pipelines have taken place at weld HAZ and attributed to LTS increasing the DOS. It had been shown [20–22] by measurements on the weld HAZ in recirculation pipelines and other components (e.g. core shroud) that: (1) about 10–20% strain exists in the HAZ and (2) number of dislocations in the heat affected zones are more than

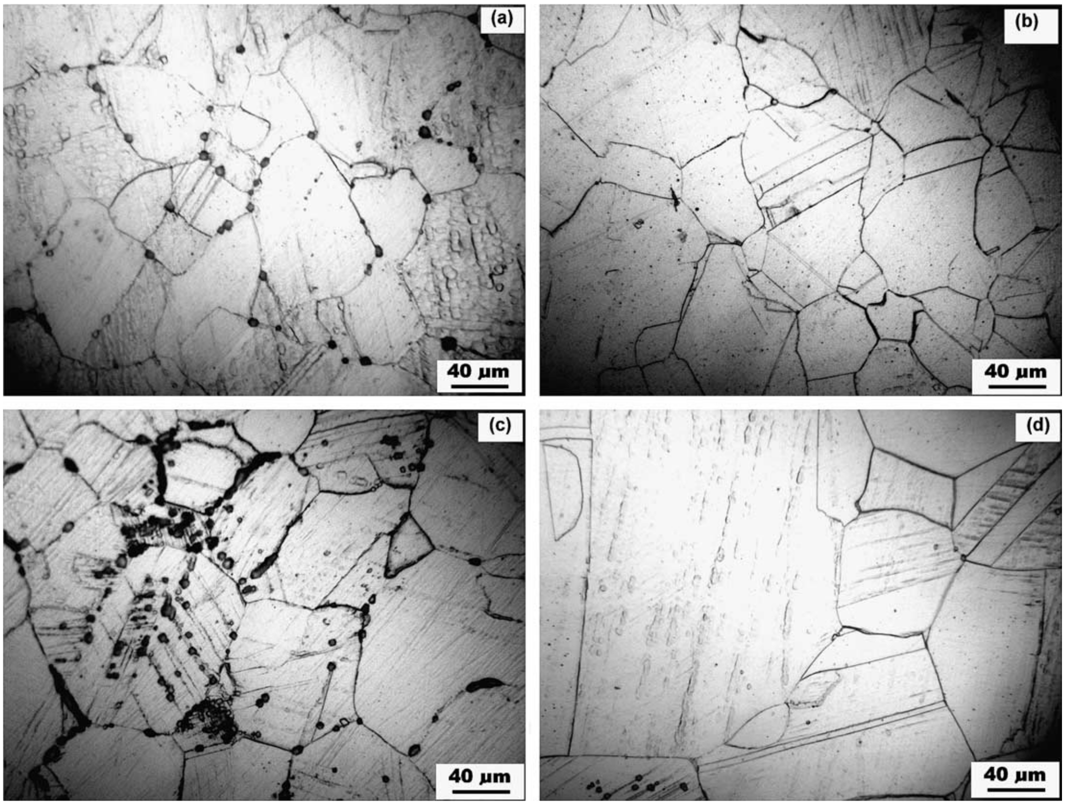

Fig. 7. Microstructures after the DL-EPR testing of 304LN2. (a) As received and LTS2. (b) As received, 15% cold rolled and LTS2, cross-sectional region. (c) As received, 15% cold rolled and LTS2 (surface). (d) Solution annealed, 15% cold rolled and LTS2.

in the base material away from the HAZ. These are attributed to weld cooling stresses in constrained geometry welds. Any stainless steel that is resistant to carbide precipitation in the heat affected zone should be resistant to LTS. However, it had been shown in a study [13] that 304 stainless steel required a threshold cold work level of 8–10% for inducing LTS without pre-existing carbide. Therefore in this study, cold work of 15% was used to simulate the heat affected zone of BWR recirculation pipelines and core shroud. To have cold work without formation of martensite, samples were bent.

4.1. Effect of cold work

The 15% cold rolling of 304 and 304L resulted in a substantially high degree of sensitization after the LTS treatment. These DL-EPR values are much higher than that for the sensitized (at 675 °C for 1 h) stainless steels as shown in Table 2 and Fig. 2(a). The microstructures after the EPR test (Figs. 4(b) and (c) and 5(b)) showed heavy attack inside the grains. The banded (lath) structure is typical of martensite. The presence of martensite in cold worked samples was confirmed by ferrite measurement (Table 3). In 304L about 3% martensite was present after 15% reduction in thickness by cold rolling. Martensite has been shown by other investigators to precipitate chromium rich carbides at temperatures at or much lower than the temperatures for austenitic grain boundaries, hence much more prone to LTS [40–42]. Martensite is a body centered tetragonal phase that is strained due to presence of carbon atoms and upon slight activation by heating at temperatures 350–500 °C the chromium carbides precipitate out from the laths of martensite. Since the laths are distributed inside the grains of austenitic stainless steels, the resultant sensitization is mainly intragranular as shown in Figs. 4(b) and (c) and 5(b).

It is seen from the microstructure (Fig. 4(b) and (c)) of 304 after cold working and LTS2 that there are attacked (chromium depletion) regions at grain boundaries visible after the EPR test. The as received or the solution-annealed 304 and 304L did not show heavy attack (Table 2 and Fig. 1(a) and (b)) at grain boundaries (Figs. 4(a) and 5(a)) even after the LTS2. This indicated that sensitization developed even at 500 °C for types 304 stainless steels due to cold working. It had been reported [36] that the sensitization temperature

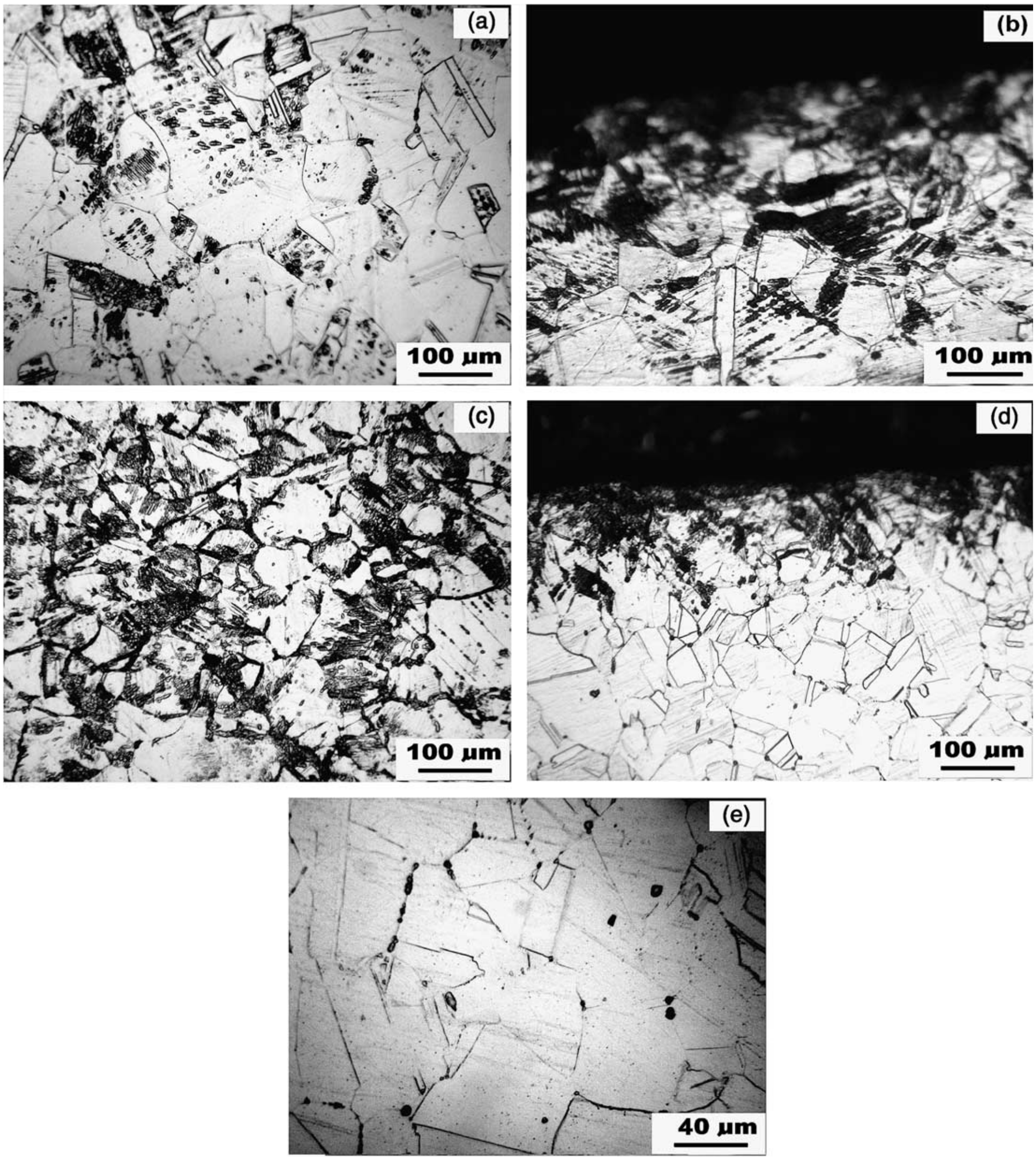

Fig. 8. Microstructures after oxalic acid etching for 304LN in the as received and 15% cold rolled conditions after LTS2: (a) 304LN1 (surface); (b) 304LN1 (cross-section); (c) 304LN2 (surface); (d) 304LN2 (cross-section); (e) 304LN1 stainless steel (cross-section, away from surfaces).

range widens to lower temperatures for cold worked stainless steels and sensitization in a 15% cold worked 304 is shown after a heat treatment at 500 °C for 100 h. In addition to development of sensitization in the cold worked condition, the martensite resulted in precipitation of chromium carbides in the laths present within the grains. Thus 304 showed indications of sensitization due to both reasons, martensite and lowering of sensitization temperature range due to cold working. The martensite had been shown [40–42] to result in precipitation of chromium rich carbides at temperatures much lower (350–500 °C) than sensitization temperature and at time durations much shorter than those for sensitization. It is clear from these results that there is precipitation at grain boundaries also after the LTS treatment of cold worked samples, even in 304L in its as received/annealed condition. An earlier study [42] had calculated the activation energy for sensitization due to martensite phase in austenitic stainless steel from experimental data from 350–500 °C and found it to be 53 kcal/mol, a value close

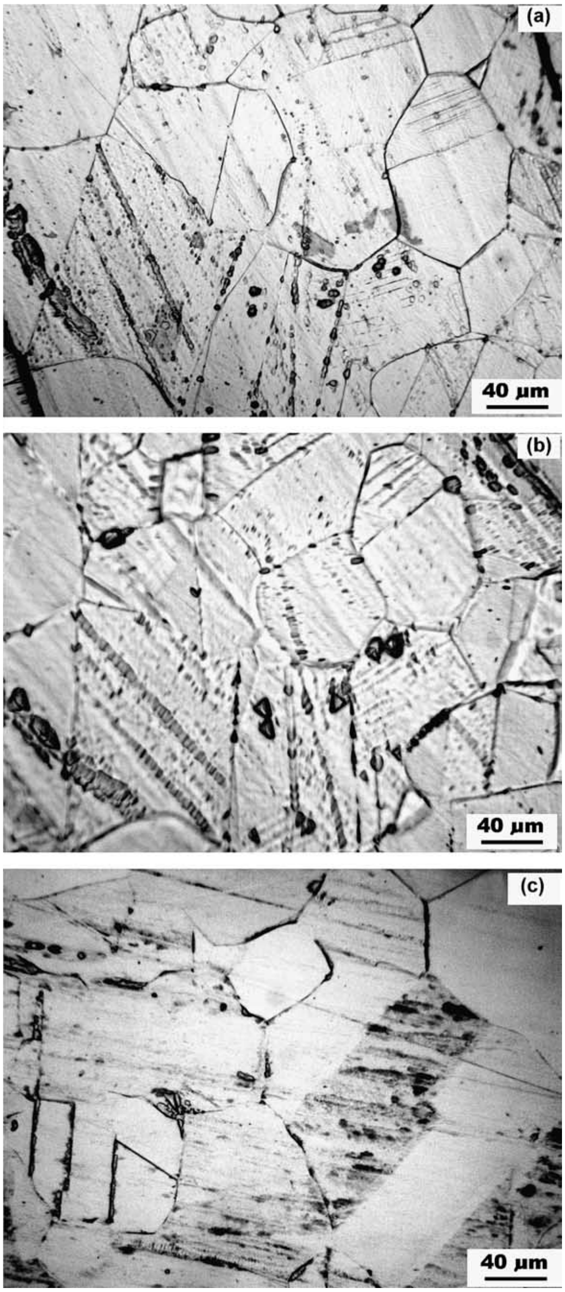

Fig. 9. Microstructure of 304LN1 after bending by 90° and LTS2 after: (a) DL-EPR test; (b) oxalic acid etching at the same area; (c) freshly polished and oxalic acid etched sample.

to activation energy for diffusion of chromium in martensitic matrix. Extrapolation of that experimental data was shown to predict that martensite would sensitize at operating temperature of 300 °C of nuclear reactors in less than 10 years.

304LN1 and 304LN2 also showed higher DOS values after 15% cold working and LTS2 (Table 2 and Fig.

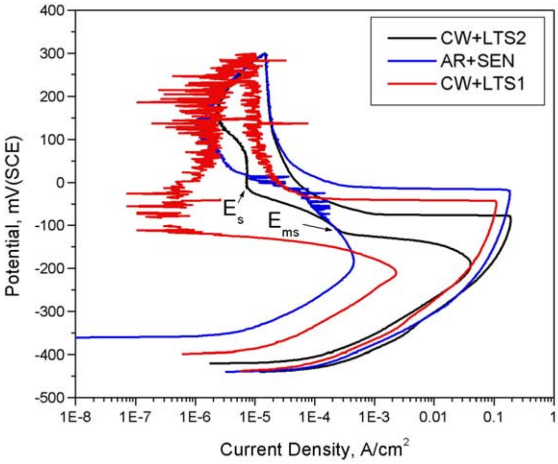

Fig. 10. A DL-EPR curves for cold worked and LTS2 treated, cold worked and LTS1 treated and as received and sensitized (675 °C for 1 h) type 304 stainless steel. The hump at E_{ms} refers to reactivation start for martensite induced sensitization and the potential E_s refers to reactivation start from classical sensitization at grain boundaries.

2(b)). 304LN1 has lesser austenite stabilizers (0.12% nitrogen) therefore cold working resulted in formation of about 1.5–2.0% martensite. However on the surfaces of the material a higher amount of martensite was observed on all the cold worked stainless steels. 304LN1 and 304LN2 showed ~3.5% martensite on the surfaces. As a result the DOS measured on the longitudinal surfaces was much higher compared to that measured on the cross-sectional surfaces. Fig. 8(a)–(d) clearly show the depth of martensite formation on the surfaces (about 2–3 grains have much more martensite formation). This difference is clearer for 304LN2 that has more austenite stabilizer (0.15% nitrogen). This material did not show enhanced magnetic phase readings on the cross-sectional face but did show almost the same high ferrite meter reading (~3.5%) on the longitudinal surfaces as that obtained for the lower nitrogen, 304LN1. After LTS2 of the cold worked samples, this resulted in a high DL-EPR value on the longitudinal surfaces while on the cross-sectional surface the DL-EPR value was not abnormally high for type 304LN2 (Table 2 and Fig. 2(b)).

A comparison of the LTS behaviour of 304LN2 shows that the DOS value is higher after LTS treatment of the as received material (DL-EPR ratio of 0.52) than that for the cold worked and LTS treated material (DL-EPR ratio of 0.28) indicating healing of chromium-depleted regions or 'desensitization' due to cold working (Table 2 and Figs. 1 and 2). This is also clear from Figs. 7(b) and 8(d) for the cold worked and LTS sample. The oxalic acid etching attacks both the carbides/nitrides and the chromium depletion regions whereas the EPR test attacks only the chromium depletion regions. It shows that there the carbides/nitrides grew after the LTS for the cold worked sample (Fig. 8(d)) but the chromium depletion regions are not present (Fig. 7(b)). This is attributed to faster diffusion rates of chromium in the cold worked sample. Desensitization effects had been shown after formation of martensite due to cold working in austenitic stainless steels and LTS for a short time [41,42]. Even in a matrix without presence of martensite, cold working increases diffusion rate of chromium as the dislocation density and dislocation pipes provide a faster path for diffusion. This is seen here to have resulted in desensitization after a heat treatment at 500 °C for 11 days. Ferrite meter readings confirmed absence of martensite (Table 3) in cold worked and LTS treated condition of 304LN2. This is also reflected in lower hardness values for 304LN2 than for 304LN1 in its cold rolled and LTS2 treated condition (Table 4).

The surfaces of both the heats of 304LN (with 0.12% and 0.15% nitrogen) did show indications of formation of martensite upon cold working. This was confirmed from the ferrite meter measurements (Table 3) and the EPR results (Table 2 and Fig. 2(a)). After the cold working and LTS, the DOS values were very high (Table 2 and Fig. 2(a)). It is clear from the photomicrographs after the EPR tests on cold worked and LTS samples (Figs. 6(b) and 7(c)) that the grain boundaries of the 304LN2 had sensitization developed while sensitization developed in the martensitic phase is mainly inside the grains in 304LN1. To confirm if carbides/nitrides were present in this material even after cold working and LTS, the microstructure of this sample after oxalic acid etching (Fig. 8(a)) is compared. This shows precipitates at grain boundaries in addition to martensite induced sensitization inside grain boundaries. It had been reported that martensite nucleates at grain boundaries [39] in addition to regions inside the grains in austenitic stainless steels. The sensitization observed at grain boundaries in cold worked and LTS treated stainless steels of even low carbon variety could be due to this martensite formation at grain boundaries. Figs. 6(b) and 8(a) show that desensitization effect does take place even for 304LN1 after cold working and LTS2. The lower DOS values for 304LN1 (5.31) compared to that for type 304LN2 (11.21) also confirm this observation.

4.1.1. Effect of starting condition and cold work

The solution annealing of the 304LN followed by cold working and LTS showed interesting behaviour. The 304LN1 with lower nitrogen at 0.12% showed a higher DOS after LTS1 (0.535) than after the longer LTS2 (0.32). The microstructures after the EPR test after these two treatments (Fig. 6(c) and (d) respectively) also show this difference indicating desensitization taking place by the 11 days heat treatment at 500 °C. 304LN2 with higher nitrogen at 0.15% also developed lesser DOS (0.17) after the LTS2. The structure after the EPR test (Fig. 7(d)) shows absence of chromium depleted regions whereas Fig. 8(d) and (e) show presence of carbides/nitrides at grain boundaries after oxalic acid etching in the as received condition. This again confirms that desensitization takes place due to LTS heat treatment at 500 °C for 11 days for the cold worked stainless steels, including those not containing martensite.

Another interesting observation is after solution annealing of 304LN (Table 2, Figs. 1(a) and 2(a)). Lower DL-EPR values after LTS treatment indicated that the stainless steels in the as received condition itself were in cold worked condition. These are evident from lower DOS values measured in the EPR test for solution annealed, cold worked and LTS treated samples of 304LN stainless steels (Table 2, Figs. 1, 2, 6(c) and (d) and 7(d)). This is also confirmed from ferrite meter measurement (Table 3) that the as received 304LN had about 0.4% martensite that reduced upon solution annealing. After 15% cold working this increased to 1.4–2.0% martensite in 304LN1 but did not increase much for 304LN2 that contained a higher amount of austenite stabilizer (0.15% nitrogen). However the surfaces of both the stainless steels had ~3.5% martensite. This difference could be due to higher cold deformation (strain) experienced by the surfaces during rolling.

However the effect of cold working on formation of martensite (and its subsequent effect on LTS) is much higher for the stainless steels in as received condition than in solution annealed condition. The starting materials that had some fabrication done (e.g. pipe formation for 304LN1 and 304LN2) had more residual strain present even in the as received condition. This is reflected in small amount of martensite phase indicated by magnetic measurements (Table 3) and also higher hardness values (Table 4). Upon cold working the amount of martensite formed is much higher for such materials having prior residual strain (or prior martensite in this case). Once a solution annealing removes martensite (and residual strain) from the as received (mill annealed and fabricated) condition, the subsequent cold working produces a smaller amount of martensite. It resulted in LTS lower than that produced on as received, cold worked and LTS treated 304LN2 (Table 2 and Fig. 2(a)). Removal of martensite by annealing is confirmed by lower hardness (and comparable to hardness of austenite) values of 190–200 HV for the as received material (Table 4). It is to be noted that the diffusion rate of chromium in martensite is much higher [42] than that in austenite. Due to this reason desensitization effect takes place at a shorter time at 500 °C in martensite.

4.1.2. Cold rolling vs. bending

304LN1 did not develop martensite even after a severe 90° bending. No magnetic phase was detected even after this bending. The machined surfaces however had developed martensite and were not included in the area that was tested by EPR. The region of maximum strain in bending showed no martensite in the grains but signs of cold work e.g. slip bands within grains (Fig. 9(a)–(c)). There was clear precipitation of carbides at grain boundaries and the degree of sensitization was higher at 0.77 compared to even the sensitized (after 675 °C for 1 h) sample. Thus bending is the one of the method to study the effect of retained strain in the material without producing martensite. This enhanced degree of sensitization at a low-temperature of 500 °C is due to the effect of cold work in increasing the dislocation density in the material. There is clearly fresh precipitation of carbides at grain boundaries and a small fraction of grain boundaries are covered with the attacked chromium rich precipitates after the oxalic acid etching (Fig. 9(b) and (c)). A comparison of microstructures after the EPR test (Fig. 9(a)) and after the oxalic acid etching (Fig. 9(b)) at the same region on the EPR tested sample shows that the heat treatment at 500 °C for 11 days had resulted in desensitization as the carbides are attacked in oxalic acid etching (Fig. 9(b)) while chromium depletion regions are not observed after the EPR test (Fig. 9(a)). Freshly polished and oxalic acid etched surfaces of the bent sample showed more such attacked precipitates at boundaries (Fig. 9(c)).

4.1.3. Simulation of weld heat affected zone and LTS

The above results show that the common practice of simulating low-temperature sensitization by a heat treatment at 500 °C does not always result in growth of existing carbides but results in fresh precipitation of carbides as well. The sensitization temperature range is lowered to 500 °C, e.g. for stainless steels with retained strains. Also the heat treatment at 500 °C for 11 days is shown in this study to result in desensitization due to faster diffusion of chromium in cold worked samples not containing martensite. This is important as all failures related to LTS have been observed at the weld HAZ in reactors. The weld HAZ also has been shown to have retained strains (increased hardness and higher dislocation density) but no formation of martensite. Only a thin layer on the surfaces has been shown to have the presence of martensite for type 304L and that is expected to have come from either surface preparation or machining of the surfaces or plastic stress/strain caused by welding shrinkage stresses in the HAZ regions. Therefore simulation of weld HAZ can be done by bending the samples of 304 (low carbon, high carbon and the LN varieties). It has been reported [23–25] that 'warm working' also increases dislocation density and hardness of the material but avoids formation of martensite. The LTS studies of warm worked materials have not been reported. The heat treatment of cold worked materials to accelerate the LTS at 500 °C should not be used. A heat treatment at lower temperatures, close to 400 °C would better simulate the processes occurring in the reactors during operating temperatures of ~300 °C. Hanninen and coworkers had shown [6] that the activation energies are different in temperature ranges of 300–400 °C (100 kJ/mole) and 400–500 °C (220–235 kJ/mole). They also showed that the mechanism of LTS changes below 400 °C and migration of grain boundaries coupled with slow diffusion of chromium caused wider chromium depletion regions. Another study also indicated a difference in IGSCC behaviour for austenitic stainless steel heat treated at temperatures below 450 °C [43]. Determination of this exact temperature at which no fresh precipitation of carbides occurs in a cold worked (but not containing martensite) stainless steel requires long term exposure at temperatures varying from 350 to 500 °C, of stainless steel bent or warm worked to obtain different degrees of retained strain. This long term exposure study is beyond the scope of this work.

4.1.4. Detection of martensite induced sensitization

The Fig. 10 shows a typical DL-EPR curve for 15% cold rolled 304 after LTS1 and LTS2 treatments and compares it with that for as received and sensitized (at 675 °C for 1 h) material. From the reactivation curve for the sensitized material, it is clear that the reactivation current starts early, at potentials as active as +40 mV (SCE). This is the case when the attack during the EPR test is on chromium depletion regions around grain boundary precipitates only. These depletion regions are expected to have deep chromium-depletion profiles that are susceptible to attack at much less severe conditions (less active potentials in the EPR test). The cold worked and LTS1 treated sample on the other hand has sensitization mainly induced by martensite. The intragranular precipitates in the martensitic laths are expected to have a shallower chromium-depletion profile as diffusion kinetics of chromium in martensite is very fast. These shallow chromium depleted regions in martensite require more aggressive conditions during the EPR test to get attacked. This happens at more active potentials (~−100 mV (SCE)). The cold worked and LTS2 treated type 304 material shows a combination of these two features as shown in Fig. 10. First the reactivation starts at chromium depletion regions at grain boundaries that had formed due to fresh precipitation at grain boundaries. This happens at potential denoted by E_s. At a more active potential, denoted by E_{ms}, the reactivation also starts from the chromium depletion regions produced due to heat treatment of martensite. The reactivation peak at potentials more active than E_{ms} is a combination of current contribution coming from attack on chromium depletion regions at grain boundaries and those formed due to martensite.

Therefore, the hump in the DL-EPR curve itself gives an indication about the contribution from martensite for the sensitization in a stainless steel. All the stainless steels of type 304 that contained martensite showed this hump in the reactivation peak of the EPR test as seen in Fig. 2(b). Bending by 90° that did not produce martensite but increased retained strain in the material did not show a hump in the reactivation peak. Thus the EPR test provides a method to detect the contribution of martensite to the sensitization of 304 stainless steels. The microstructures developed after the EPR test showing typical intragranular attack (as shown in Figs. 4(b) and (c), 5(b), 6 (b) and (d) and 7(c)) also clearly indicate the martensite induced sensitization.

4.2. Effect of starting structure

It is seen from Table 2, Fig. 1(a), 4(a) and 5(a) that 304 in the as received (mill annealed) condition has a higher value of DOS after LTS2 than that for 304L. This is due to the mill annealed 304 having carbides (as indicated by DL-EPR value of 0.80 in as received and LTS2 condition). Upon solution annealing at 1050 °C (and fast quenching) the 304 showed a lower DOS value of 0.05. However this annealed stainless steel also showed a high DL-EPR ratio of 0.87 after LTS2. Fig. 4(a) confirms that 304 has pre-existing carbides at grain boundaries that grow during low-temperature sensitization and increase the DOS. It should be noted here that it is not only the level of carbon but a combination of carbon, nickel and chromium [44,45] represented by a parameter $Cr^{effective}$ [44] that determines the tendency for precipitation of carbides. The low carbon type 304L, even in mill annealed condition had carbon, nickel and chromium levels so balanced as to avoid carbide precipitation. This is confirmed from a low value of DOS (0.016) and absence of chromium depleted zones after the EPR test (Fig. 5(a)) for the LTS2 treated 304L. The increase in DOS due to LTS for as received 304 is shown in a reported study [43] also.

304LN (with 0.12 and 0.15 wt% nitrogen) in as received condition showed low values of DOS. The DL-EPR values for 304LN2 (with 0.015 wt% nitrogen) was 0.039 which decreased to 0.007 after a solution annealing heat treatment whereas 304LN1 (with 0.12 wt% nitrogen) showed a DL-EPR value of 0.007 in its mill annealed (as received) condition itself. The DOS measured by DL-EPR after the LTS increased to a value of 0.52 for the as received 304LN2 material. The chromium depletion regions that grew around pre existing carbides in the as received condition of this material are seen clearly in Fig. 7(a). The 304LN1 material with lower nitrogen (0.12%) did not show such carbides even after the LTS treatment (Fig. 6(a)). This indicates that with higher levels of nitrogen there is a tendency for stainless steels to have pre-existing chromium carbides/nitrides even in the mill annealed condition.

4.3. Effect of composition

316LN (with a high nitrogen level of 0.16%) did not show any sign of pre-existing carbides/nitrides in the mill annealed condition as it is much more resistant to precipitation of carbides/nitrides. This is mainly due to the presence of higher molybdenum content and the interaction between molybdenum, nitrogen and carbon [29] in type 316LN. It would require longer exposure (or higher temperatures) for chromium depletion to be developed as a result of growth of carbides/nitrides. However 316L (with a carbon level of 0.03%) showed an increase in DOS after LTS2 of its as received sample whereas 316LN did not (Fig. 3(a) and (b)). Therefore in their as received (mill annealed) condition, 316LN is more resistant to LTS than 316L. However the DOS of type 316 stainless steels was evaluated by a more sensitive EPR test that uses more aggressive solution [32] and capable of detecting low DOS of even irradiation induced sensitization. Therefore these DOS values should not be compared with that evaluated by the standard DL-EPR test for 304.

4.3.1. Molybdenum addition and cold work

316LN did not show any reactivation during the DL-EPR test even in its cold worked and LTS condition. In fact detection of sensitization in the sensitized condition (after 750 °C for 25 h) for both 316L and 316LN was not possible when tested by the DL-EPR test as used for 304. A modified (and more aggressive) EPR test was employed to detect even very low DOS in molybdenum containing grades. This test was able to detect small DOS in the sensitized samples of 316L and 316LN stainless steels (Fig. 3(a) and (b)). However the DOS developed in the molybdenum containing stainless steels was very small even after a severe sensitization heat treatment at 750 °C for 25 h and an aggressive test solution used in this testing. 316L with 0.03% carbon did show increase in DOS after the LTS at 500 °C for the as received material. The 20% cold rolled and LTS treated sample showed a higher value of DOS (Fig. 3(a)). However 316LN did not show any reactivation (DOS) even after the LTS to its as received sample and to its 20% cold rolled samples (Fig. 3(b)). This indicates absence of pre-existing carbides/nitrides in the as received condition of 316LN though it contains 0.16% nitrogen. These stainless steels did not show any sign of formation of martensite, as measured by ferrite meter and also examination of microstructure, even after a 20% cold work by rolling at room temperature. The stability of these molybdenum bearing and higher nickel content grades against martensite formation is also indicated by lower Md30 temperatures (Table 1). Therefore, even after 20% cold working and LTS at 500 °C for 11 days these steels did not develop sensitization.

4.4. Implication for IGSCC

It had been shown [46,47] in earlier studies that sensitized stainless steels with DOS values above Pa = 2 C/cm^2 from the single loop (or above DL-EPR value = 1.0 from the double loop) EPR test were prone to IGSCC in high pressure, high purity water at 280–300 °C. It is to be noted that these tests were done to simulate cracking in high operating potential regions (e.g. those with high dissolved oxygen content as encountered in recirculation pipelines). LTS treated stainless steels were also susceptible [43] to IGSCC in simulated BWR environment. In the present study it is shown that the stainless steels in their as received (mill annealed) or solution annealed conditions became sensitized after LTS at 500 °C. However the DOS developed was always lower (Table 2 and Fig. 1(a)) than the threshold value of sensitization mentioned above for susceptibility to IGSCC. Therefore, the austenitic stainless steels in their as received condition are not expected to be susceptible to IGSCC in high operating potentials of recirculation pipelines, even after long exposures at the reactor temperature. However, cold work increased the DOS for these stainless steels above the threshold value required for IGSCC because of martensite formation, especially on the surfaces. Even 304L developed martensite after 15% cold working with a LTS heat treatment producing a very high DOS of 24.37. The sensitization developed after cold working and LTS heat treatment was intragranular (in martensite, inside the grains) as well as intergranular (at grain boundaries) as shown in Figs. 4(b) and (c), 5(b), 6(c) and (d) and 7(c). Therefore initiation of intergranular cracks is expected in BWR simulated environment for these cold worked and LTS treated conditions. It is important to note that 316L or 316LN did not develop sensitization after 20% cold working and 11 days treatment at 500 °C. 316LN did not show any trace of sensitization even after testing by an aggressive EPR test that otherwise detects low levels of DOS. Therefore these effects on microstructures are expected on Core Shrouds made of 304 stainless steels and not those made with 316 stainless steels.

A major question is if simulation of weld HAZ can be done by cold rolling and LTS treatment at 500 °C. It had been shown that cold rolling increases dislocation density as is the case in weld HAZ. However cold rolling also leads to phase transition to deformation induced martensite. It had been reported [20,21] that in core shrouds made of 304L, martensite has been detected on the surfaces. Therefore the surfaces of the weld HAZ containing martensite can be simulated by cold rolling. However core shrouds made of type 316L did not have formation of martensite but had strong signs of cold working (slip bands inside grains), possibly from fabrication stages. The surface of the stainless steel sections used in piping and core shrouds can be simulated by bending, a deformation process which does not lead to martensite formation as shown in this study or by warm working as reported [23–25]. In case of a bent and LTS treated stainless steel, the DOS value did not increase beyond the threshold value for IGSCC. The initiation on the surfaces due to martensite and LTS exposure in BWR simulated environment provides a possible explanation for cracking seen in non-sensitized 304L in BWR core shrouds of very low carbon content. 316 stainless steels are much more resistant to formation of martensite therefore are much more resistant to initiation of IGSCC after cold working and LTS in their non-sensitized condition. The simulated weld HAZ of type 316 stainless steel was also shown to be resistant to IGSCC even after LTS [48]. However, recent observations of IGSCC in core shroud materials (both 304L and 316L) that showed heavy slip lines within grains indicating cold work but without any trace of sensitization, have been attributed [20–24] to increased yield strength of the material hence increased susceptibility to IGSCC.

5. Conclusions

The following can be concluded from the study for stainless steels in their as received or solution annealed condition:

- A 15% reduction in thickness by cold rolling showed martensite formation in all the grades of 304 type stainless steels. Type 304L and 304 showed the maximum martensite formation as their austenitic matrix is not stable upon deformation at room temperature.
- Nitrogen addition to type 304 reduced the tendency for martensite formation. However, with addition of 0.15% nitrogen also, martensite formation was detected on the surfaces.
- The martensite produced heavy sensitization at 500 °C in all the grades of 304 stainless steels. In the martensite matrix, the sensitization kinetics was fast due to supersaturation of carbon and the desensitization kinetics was also rapid due to fast diffusion rate of chromium.
- The martensite found on the surfaces of weld heat affected zones in core shrouds of nuclear reactors can be simulated by cold working for 304 type stainless steels. The cold worked steels of even low carbon variety produced martensite that got heavily sensitized at 500 °C. Such a sensitization makes even low carbon stainless steels of type 304 susceptible to IGSCC in BWR simulated environment.
- Molybdenum containing type 316 grades did not show any sign of deformation induced martensite even after 20% cold rolling, as compositional differences lower the martensite start (due to deformation) temperature much below the room temperature.

- Simulation of weld HAZ after a long term exposure at plant operating temperature is shown to be done by bending and heat treatment at a temperature lower than 500 °C. Bending produces conditions that increase retained strain in 304 without formation of martensite. Heating of bent (or cold worked) 304 type steels at 500 °C lead to fresh precipitation of carbides/nitrides due to higher retained energy at grain boundaries and also a desensitization effect due to fast diffusion rate of chromium along dislocations introduced due to cold working.
- Studies on annealed or as received materials do not simulate the weld HAZ region as the HAZ has high retained strains and increased dislocation density that affect the LTS process.
- Cold working without formation of martensite (bending) is also sufficient to cause the start of desensitization effect as the diffusion rates of chromium along dislocations in austenitic matrix are faster.
- The reactivation due to chromium depletion inside martensite phase is identified by a hump in the reactivation curve during the EPR test. The reactivation due to grain boundary chromium depletion starts first, at $\sim +40$ mV (SCE). The reactivation from martensite induced sensitization starts contributing from ~ -100 mV (SCE). The microstructure after the EPR test clearly identifies typical intragranular attack indicating martensite induced sensitization.
- Types 304 stainless steels are more prone to LTS than the molybdenum containing type 316 stainless steels because the chemical composition of type 316LN (especially molybdenum, low carbon and higher nitrogen contents) increases the resistance to precipitation of carbides/nitrides. The mill annealed type 316 steels did not have pre-existing carbides/nitrides and did not produce martensite upon cold working.
- Type 304 stainless steel in both the as received and the solution annealed conditions and type 304LN with 0.15% nitrogen developed LTS when heated at 500 °C for 11 days. This is attributed to the presence of pre-existing carbides/nitrides in high carbon and/or nitrogen steels but the developed DOS was not sufficient to make it susceptible to IGSCC in BWR simulated environment.

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