

# Mechanism of Improved Corrosion Resistance of Type 304L Stainless Steel, Nitric Acid Grade, in Nitric Acid Environments

V. Kain, S.S. Shinde, and H.S. Gadiyar

Materials for critical components in nuclear fuel reprocessing plants are required to have low corrosion rates and long designed life because access for repairs is not possible. Stainless steel type 304L, nitric acid grade (NAG), is the new material suitable for such applications. It has guaranteed low corrosion rates and is not susceptible to intergranular corrosion (IGC) in nitric acid environments. The corrosion behavior of type 304L stainless steel, NAG, and type 304L stainless steel, commercial purity (CP), in nitric acid environments is investigated in detail. Studied are: microstructural mapping in the three directions (longitudinal, long transverse, and short transverse), effect of sensitization heat treatment, resolution annealing and sensitization heat treatment for the as-received and cold-worked samples of the two varieties on the resultant microstructures. The anodic polarization characteristics along the three directions for both varieties in 1N HNO<sub>3</sub> are compared. The susceptibility of both varieties to end grain corrosion in 9N HNO<sub>3</sub> + 1 g Cr<sup>+6</sup>/liter boiling solution is assessed, and microstructural examination of the exposed sample is carried out to compare the degree of end grain corrosion. Their susceptibility to IGC due to segregation of impurity elements to grain boundaries is also compared. It is shown that controlled microstructure (fine grain size, retained cold work, and discrete precipitation at grain boundaries) along with controlled chemical composition is responsible for improved corrosion resistance of the NAG variety. The NAG variety has much less susceptibility to corrosion along the long- and short-transverse directions and, therefore, less susceptibility to end grain corrosion. The means and consequences of controlling chemical composition are also discussed.

## Keywords

stainless steel 304L, intergranular corrosion, end grain corrosion, anodic polarization, sensitization, solution annealing

## 1. Introduction

HIGH general corrosion of stainless steels (SS) in strong oxidizing nitric acid environments occurs in the transpassive region of a polarization curve. As a consequence, any species that tends to increase the oxidizing power of the medium also increases its corrosion rate. The oxidation of Cr<sub>2</sub>O<sub>3</sub>, the surface oxide, to form chromic acid in solution tends to make the solution more oxidizing and corrosive (Ref 1-3). The chromium depleted regions in stainless steels, as are present in heat affected zones (HAZ) of weldments, due to precipitation of Cr<sub>23</sub>C<sub>6</sub> at grain boundaries, are readily attacked in these solutions, rendering the material prone to intergranular corrosion (IGC) (Ref 4-6). Further, different materials are suitable for different temperature-concentration domains of nitric acid (Ref 3, 7). Therefore, the materials to be used in nitric acid environments have to be carefully chosen so as to have minimum corrosion. The nuclear fuel reprocessing plants and nuclear waste facilities handle nitric acid service fluids of varying concentrations and temperatures up to 110 °C. The main material of construction for these facilities is type 304L stainless steel. The Nb stabilized austenitic grade 347 stainless steel also had been used in these facilities for a long time. However, this grade is afflicted

with problems related to welding (knife line attack), and the forged components are prone to end grain corrosion (Ref 8, 9). Type 304L stainless steel is now the universally used material of construction for the fuel reprocessing industry. Other materials of construction in the reprocessing industry (Ref 8, 10-12) include type 310L stainless steel, for concentrated (up to 78%) boiling HNO<sub>3</sub>, e.g. in upper parts of a dissolver where condensation from vapors takes place. Zircalloys also are suitable because they form a protective oxide coating in nitric acid service. Titanium and Fe-Si alloys are used for high-temperature, high-concentration applications only. Pumps and valves, which are generally bolted and not welded, are made from cast stainless steels, CF-8/CF-8M and not necessarily CF-3/CF-3M. Laboratory studies indicate very good corrosion resistance of Ti-5% Ta, Uranus-16\* (typical chemical composition: 0.012% C, 0.09% Si, 0.69% Mn, 18% Cr, and 12% Ni), and Uranus-65\* (typical chemical composition: 0.012% C, 0.19% Si, 0.56% Mn, 25% Cr, and 19% Ni), in boiling nitric acid and simulated nuclear fuel reprocessing streams (Ref 13).

The operating experience has shown that type 304L stainless steel (commercial purity grade) also shows many failures in these applications, indicating its susceptibility to IGC. Since susceptibility to IGC is assessed by boiling 65% HNO<sub>3</sub> (practice C of A262, ASTM) (Ref 14) and the reprocessing industry does not have service conditions (Ref 9) as severe as in the practice C test, then a material passing the practice C test would not undergo IGC in actual service. It is reported that 10% of the heats of plates/sheets of type 304L stainless steel tested as per practice C failed in the test (Ref 15) in the mid 1970s. Since then, the acceptance criterion in practice C has been further

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tightened by users; i.e., 0.61 mm/year, or 24 mils per year (mpy) for type 304L stainless steel after the sensitization heat treatment, and 0.305 mm/year (12 mpy) for the solution annealed material in five periods of practice C (Ref 15, 16). Practice C itself has been made more vigorous (Ref 14) by making it necessary to expose at least 30% of total surface area as the end faces. The requirements of the reprocessing/waste storage industry are still more stringent for materials to be used at locations where access for repairs is not possible or is very difficult. Further, the general corrosion rates should be as low as possible to help reduce the design thickness of certain components that are to be used for the long designed life of the plant and cannot be repaired during service (Ref 8). These requirements have necessitated the modification of type 304L stainless steel so as to guarantee low-corrosion rates in the practice C test for annealed as well as sensitized material. Such a material, designated type 304L, nitric acid grade (NAG), or 18/10L is available in the market and used for components where access for repairs is not possible. Type 304L is also prone to end grain corrosion (due to the presence of active inclusions) (Ref 17) and IGC due to segregation of impurity elements (Si, P, and S) to grain boundaries (Ref 18, 19) in highly oxidizing  $\text{HNO}_3 + \text{Cr}^{+6}$  solutions.

Type SS 304L, NAG, grade is guaranteed to show less than 0.41 mm/year (16 mpy) recession in five periods of practice C tests for the sensitized material and less than 0.205 mm/year (8

mpy) for the solution annealed material. This is reported to have been achieved by close chemical composition control (Ref 10, 16). The chemical composition of NAG and commercial purity (CP) variety is compared in Table 1. Typical compositions with lower levels— $<0.015\%$  C,  $<0.2\%$  Si, and  $<10$  ppb B—also have been reported for NAG variety (Ref 10, 16). The reasons for lower corrosion rates for NAG variety as compared to CP variety are probed in this investigation. Microstructural investigations, corrosion susceptibility in all three directions for both varieties, susceptibility to end grain corrosion, and IGC susceptibility due to segregation of impurity elements to grain boundaries are investigated to establish the reasons for superior corrosion resistance for the NAG variety in nitric acid service.

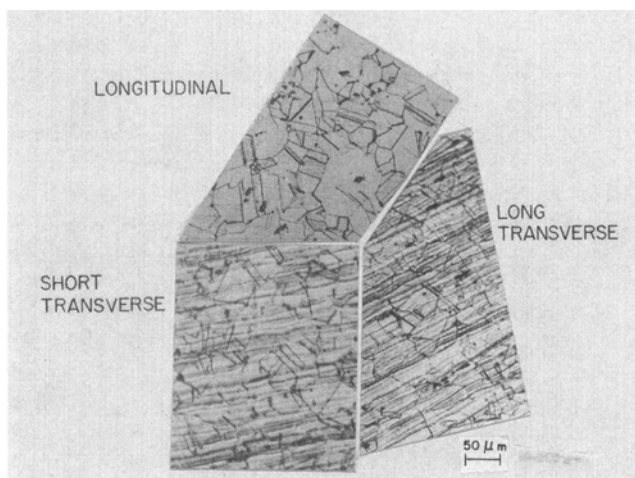
## 2. Experiment and Results

### 2.1 Heat Treatments and Microstructures

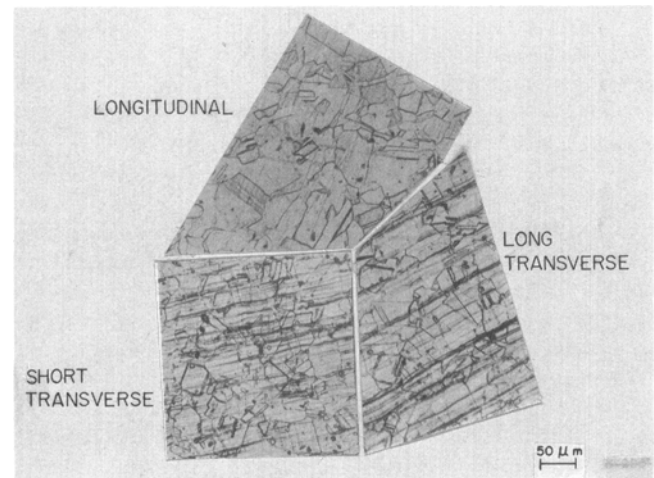
A 10 mm thick NAG plate (0.026% C, 9.2% Ni, 19.4% Cr,  $<2.0\%$  Mn,  $<0.8\%$  Si,  $<0.015\%$  S, and  $<0.018\%$  P) and a 3 mm thick CP plate sample (0.030% C, 10.8% Ni, 18.5% Cr,  $<2.0\%$  Mn, 1.0% Si,  $<0.03\%$  S, and  $<0.045\%$  P) were used in the present study. Boron contents were not analyzed because they become important when carbon levels are  $<0.015\%$  (Ref 16). Samples of the as-received material were mounted in cold setting compound so as to expose, in separate samples the longitudinal, long-transverse, and short-transverse directions, and the microstructures were developed by oxalic acid etching as per practice A of A262, ASTM. The microstructural mapping in the three directions is shown in Fig. 1(a and b) for the CP and NAG varieties, respectively. Samples of both varieties were subjected to sensitization heat treatment (Ref 15) of 677 °C for 1 h followed by water quenching (WQ), and the microstructures of their transverse sections, developed as per practice A, are shown in Fig. 2(a and b) for CP and NAG variety, respectively. The grain size was measured by the linear intercept method as per E112 (ASTM) (Ref 20) and found to be 6.5 to 7.0 for the CP

**Table 1 Chemical composition of type 304L (NAG) and type 304L (CP) stainless steels**

Element	Composition, wt%	
	SS 304L (NAG)	SS 304L (CP)
C	$\leq 0.025$	$\leq 0.03$
Si	$\leq 0.8$	$\leq 1.0$
Mn	$\leq 2.0$	$\leq 2.0$
P	$\leq 0.018$	$\leq 0.045$
S	$\leq 0.015$	$\leq 0.03$
Cr	18 to 20	18 to 20
Ni	9 to 11	8 to 12

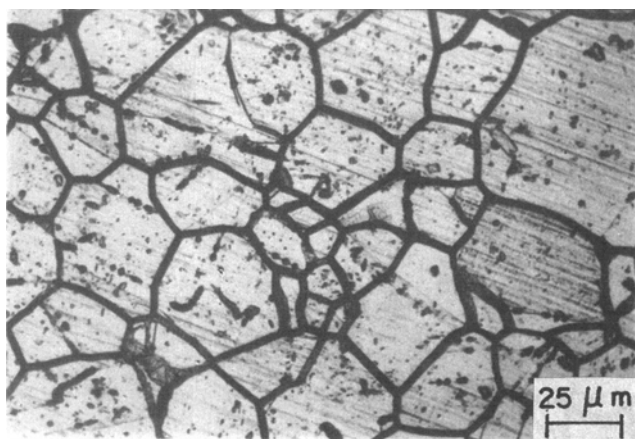


(a)



(b)

**Fig. 1** Microstructural mapping in the as-received condition. (a) Type 304L (CP). (b) Type 304L (NAG)



(a)



(b)

**Fig. 2** Microstructure along transverse direction after 677 °C one hour and WQ heat treatment. (a) Type 304L (CP). (b) Type 304L (NAG)



**Fig. 3** TEM photomicrograph showing high dislocation density for Type 304L (NAG) at the locations of streaks

variety and 8.0 for the NAG variety. The presence of prominent flow lines was observed in the transverse directions for the NAG variety, and transmission electron microscopy (TEM) examinations of the samples of NAG variety showed a high concentration of dislocations at certain regions (flow lines), which were flanked by regions having much lower dislocation density. The high dislocation density regions (Fig. 3) compared well with the dislocation density of the cold-worked sample. In order to anneal out these regions of retained cold work, resolution annealing (i.e., annealing of the as-received material, which was in control annealed condition) was carried out at 1100 °C for 30 min. The resolution annealed samples were then

sensitized at 677 °C for one hour, and the resultant microstructure showed no trace of cold work for both varieties. These microstructures are shown in Fig. 4. The grain size increased to 4.0 for CP and 6.5 for NAG variety.

## 2.2 IGC Tests

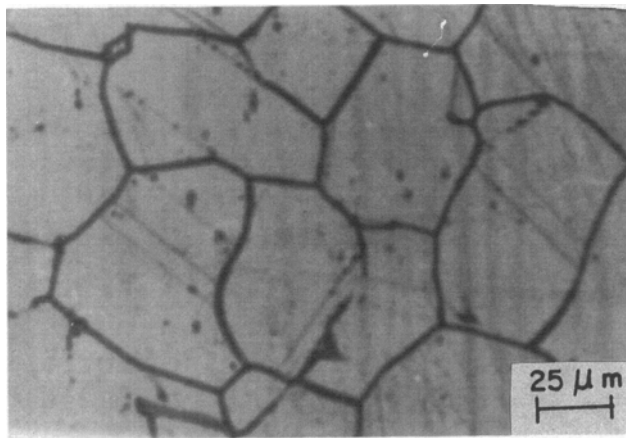
The practice C test was used to assess the susceptibility of the material to IGC. This was carried out for 5 successive periods in boiling 65% HNO<sub>3</sub>, and the average corrosion rate in the five periods was taken as the parameter to compare IGC susceptibility. The test was carried out on the following samples: as-received CP and NAG varieties, sensitized (677 °C, 1 h, WQ), and resolution annealed and sensitized CP and NAG varieties. Both varieties were rolled to give cold work of 75%, annealed at 1100 °C for 30 min, and sensitized at 677 °C for 1 h. WQ and practice C was carried out on these samples also. The results of these are tabulated in Table 2.

## 2.3 Anodic Polarization Tests

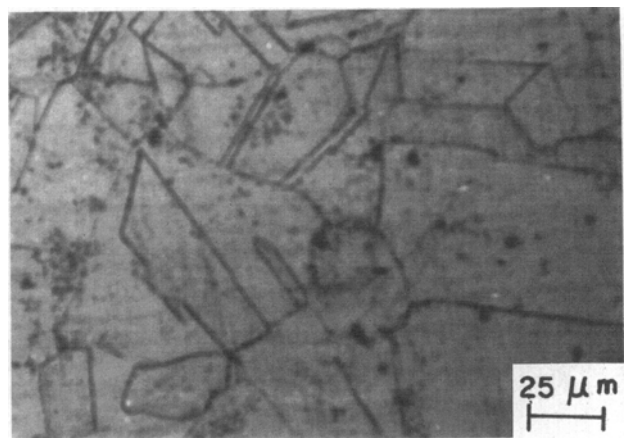
The samples of both varieties were mounted in cold setting compound to expose their longitudinal, long-transverse, and short-transverse sections, and electrical connection was provided from the opposite faces. These samples were used in the anodic polarization experiments in 1N HNO<sub>3</sub> (deaerated by passing nitrogen gas before and during the test) at room temperature. A scan rate of 20 mV/min was used. The anodic polarization curves are shown in Fig. 5(a, b, and c) for the longitudinal, long-transverse, and short-transverse directions of both varieties, respectively.

## 2.4 End Grain Corrosion Test

To assess the susceptibility to end grain corrosion, as-received samples of CP and NAG varieties were cut so as to expose end faces, which are ~30% of total exposed surface area. The surfaces were finished with 120 grit emery papers. These samples were exposed in boiling solutions of 9N HNO<sub>3</sub> + 1 g Cr<sup>+6</sup>/ liter for 4 periods of 24 h each (Ref 9). After each period, weight loss was measured and a fresh solution was used for the



(a)



(b)

**Fig. 4** Microstructure after resolution annealing (1100 °C for 30 min, WQ) and sensitization (677 °C for 1 h and WQ) heat treatment. (a) Type 304L (CP). (b) Type 304L (NAG)

**Table 2** Average corrosion rates in five periods of practice C, A262, ASTM

Heat treatment	Corrosion rate, mpy (mm/year)	
	CP	NAG
As received (AR)	12.0 (0.305)	6.0 (0.152)
AR and sensitized (677 °C, 1 h, WQ)	36.0 (0.914)	7.5 (0.191)
AR, resolution annealed(a), and sensitized	44.0 (1.117)	8.7 (0.221)
AR, cold rolled (75%), solution annealed, and sensitized	40.0 (1.016)	8.8 (0.223)

Note: 1 mpy = 0.0254 mm/year. (a) Resolution annealing is solution annealing of the as-received (annealed) material at 1100 °C for 30 min, WQ.

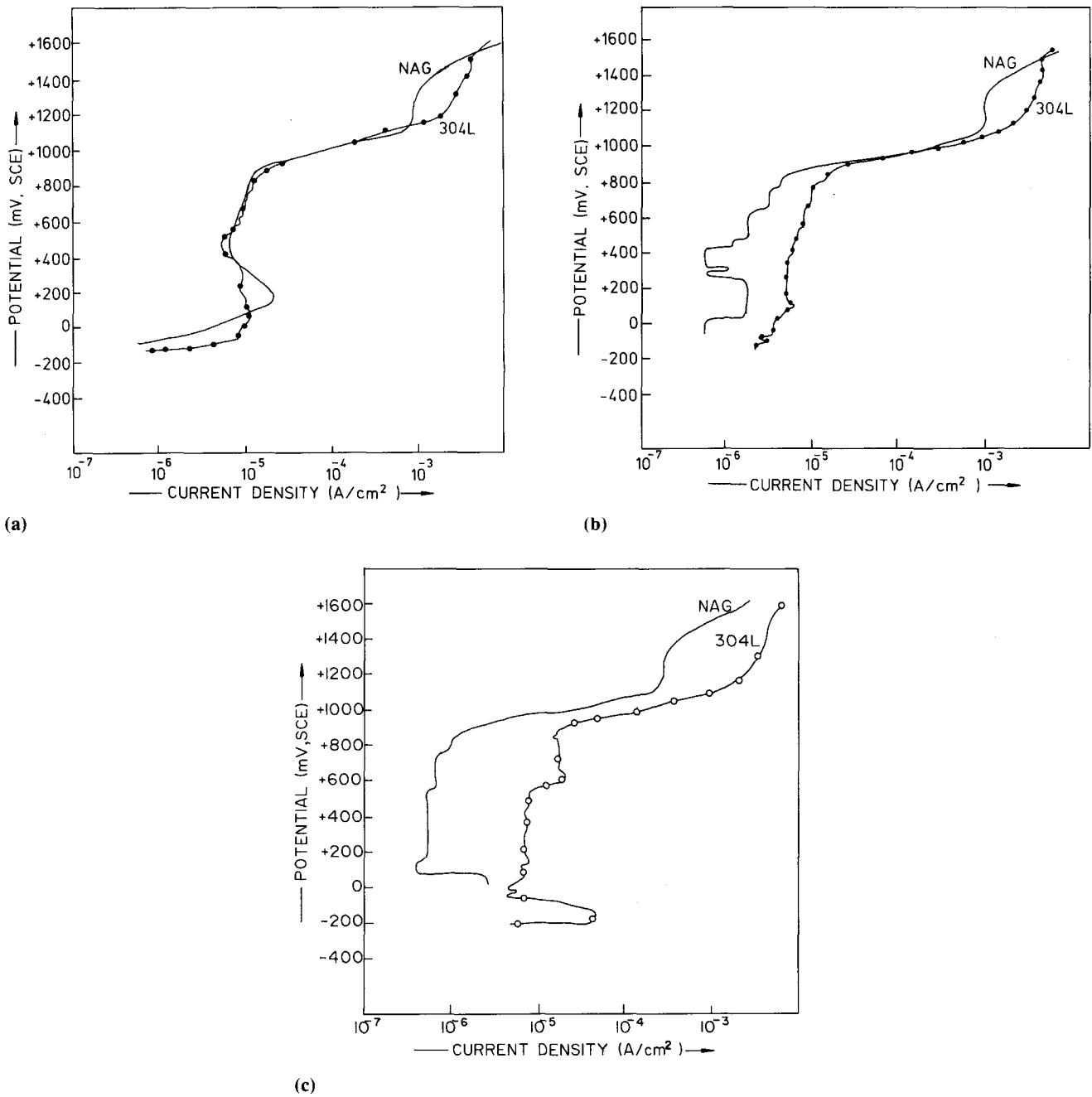
next period. The corrosion rates increased from 14.48 mm/year (570 mpy) in the first period to 19.56 mm/year (770 mpy) in the fourth period for NAG variety and from 9.15 mm/year (360 mpy) to 25.91 mm/year (1020 mpy) for CP variety. The exposed samples were sectioned, and microstructure was developed along long-transverse direction by oxalic acid etching. This revealed that the extent of end grain attack is much lower in NAG sample compared to CP sample and is shown in Fig. 6.

### 2.5 Segregation of Impurity Elements and IGC

The susceptibility to IGC due to segregation of impurity elements to grain boundaries was assessed by exposing as-received samples of both varieties in a boiling solution of 5N HNO<sub>3</sub> + 0.46N Cr<sup>+6</sup> for periods of 3 h each (Ref 18). The size and finish of samples was the same as used in the end grain corrosion test. After each period, weight loss was measured and fresh solution used for the next period. The test was carried out for 33 periods, the last period being of 4 h duration. The corrosion rates were increasing with each period for both varieties, and the corrosion rate in the final period was similar [50.8 mm/year (2000 mpy)].

### 3. Discussion

These studies indicate that apart from controlled chemical composition, the NAG variety has a controlled microstructure also. As shown in Fig. 2, the sensitized NAG has discrete precipitation (and resultant chromium depletion zones) at grain boundaries. The cold work streaks are very prominent in the structure as compared to the CP variety sample, which has almost continuous precipitation at grain boundaries. These streaks in the microstructure are established to be regions retaining high cold work (high dislocation density as observed in TEM studies, Fig. 3). The retained cold work helps in nucleation of precipitates at various locations (at grain boundaries), therefore, in discrete (discontinuous) precipitation. Further, the NAG sample has a finer grain size. These cold work streaks disappear upon resolution annealing of as-received material (Fig. 4), and NAG variety shows limited grain growth even after resolution annealing. These observations indicate that controlled solution annealing/thermomechanical treatment is given to NAG variety to keep fine grain size (i.e., increase the available grain boundary area) and retain a certain amount of cold work in the material. The result is to avoid any chance of a so called ditch structure (any single grain totally encircled by chromium depletion zones), which makes the material susceptible to IGC (Ref 5, 6, 17), upon sensitization. In such cases, slightly higher carbon contents also can be tolerated, e.g., 0.026% (for the NAG variety used in this study and correspondingly lower Ni content of 9.2%). The retained cold work is not uniformly distributed in the material, and the amount of cold work retained is also low as evidenced from discrete precipitation at grain boundaries and no precipitation within the grains for NAG variety (Fig. 2). The CP variety does not necessarily retain the cold work, which is evident from the higher grain growth during resolution annealing. This suggests that during production of NAG variety, argon oxygen decarburization (AOD)/electroslag remelting (ESR)/controlled thermomechanical treatments and combinations of cold work and solution annealing are required to produce the intended microstructure (Ref 9, 10,

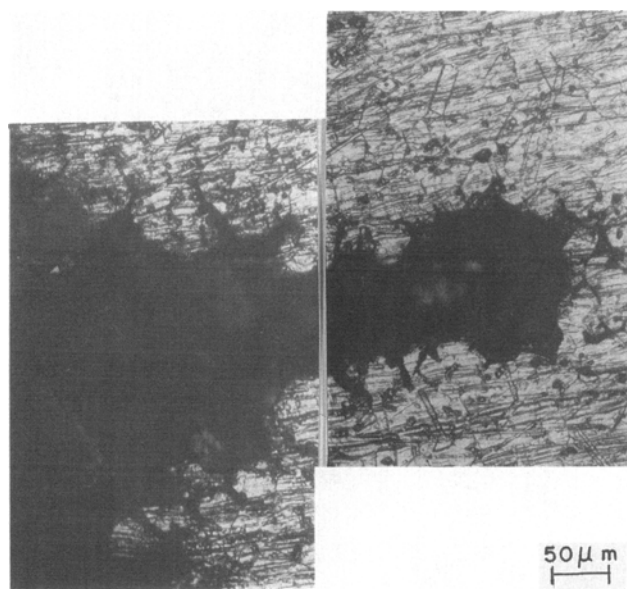


**Fig. 5** Anodic polarization curves in 1N HNO<sub>3</sub> (deaerated) at room temperature for type 304L (CP) and type 304L (NAG). (a) Longitudinal direction. (b) Long-transverse direction. (c) Short-transverse direction (Transpassive region >950 mv)

16). Grinding to remove the surface layers having heavy cold work is also required.

The controlled chemical composition controls the general corrosion rate of the material in nitric acid environments, and the controlled microstructure determines the corrosion characteristics in different cross-sections of the material. The anodic polarization curves (Fig. 5) show that NAG variety has much superior passivation characteristics in the long-transverse and short-transverse direction compared to CP variety. There is a

difference of one order of magnitude in the passivation current density for the two varieties, suggesting that NAG variety is less prone to corrosion from transverse directions; its uniform corrosion rates should be lower because of this reason also. The passivation characteristics are similar in the longitudinal direction in 1N HNO<sub>3</sub>. These results are supported by the end grain corrosion tests in boiling 9N HNO<sub>3</sub> + 1 g Cr<sup>+6</sup>/liter solution. The NAG variety shows 25% lower corrosion rate than the CP variety. It is also clear from Fig. 6 that NAG variety has much



(a)



(b)

**Fig. 6** Depth of end grain corrosion along the long-transverse direction after fourth period of the end grain corrosion test. (a) Type 304L (CP). (b) Type 304L (NAG)

lower susceptibility to end grain corrosion in oxidizing nitric acid environments. There is much less increase in corrosion rates from the first to the fourth period for the NAG variety compared to the CP variety (section 2.4). This may be attributed to lower general corrosion/IGC rates for NAG variety, which result in lesser concentration of  $\text{Cr}^{+6}$  in the solution. Note that the final solution annealing treatment (after the cold work stage or the resolution annealing heat treatment) has strong influence on the results of end grain corrosion test (Ref 9). Lower time and temperature of heat treatments promote the end grain corrosion.

Note that the NAG and CP samples used in the study have shown similar susceptibility to IGC due to segregation of impu-

rity elements (Si, P, and S) to grain boundaries in oxidizing environments ( $5\text{N HNO}_3 + 0.46\text{N Cr}^{+6}$  boiling solution) because the silicon content of the NAG sample used in the present study is high (0.8%). Other NAG heats with controlled S, P, and Si levels (<0.1%) should show improved resistance to IGC in strongly oxidizing  $\text{HNO}_3 + \text{Cr}^{+6}$  solutions (Ref 16, 18, 19).

## 4. Conclusions

The nitric acid grade of type 304L stainless steel exhibits very low corrosion rates, less than 0.205 mm/year (8 mpy) in solution annealed and less than 0.405 mm/year (16 mpy) in sensitized condition in the 65% boiling nitric acid test (practice C, A262, ASTM). The reasons for better corrosion behavior compared to commercial purity SS 304L in nitric acid environments are: (1) no possibility of "ditch" structures upon sensitization, (2) close control over C, Ni, Si, P, S, and B contents, (3) controlled microstructure (retained cold work, fine grain size, and discrete precipitation of  $\text{Cr}_{23}\text{C}_6$  at grain boundaries), (4) much less susceptibility to end grain corrosion, and (5) uniform low corrosion rates.

The production of NAG chemical composition requires argon oxygen decarburization/electroslag remelting route, and controlled thermomechanical treatments/combination of cold work and specific solution annealing treatments, are necessary to obtain the requisite microstructure. NAG variety is most suitable for those components of nuclear fuel reprocessing where access for repairs is not possible.

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