Corrosion Property Comparisons of S32003 (ATI 2003™ Lean Duplex) to other Stainless Steels

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Abstract: UNS S32003 lean duplex stainless steel was developed for the purpose of being an economic alternative for 316L and 2205 where applications would allow. This paper provides comparative corrosion properties in various media for S32003 versus its stainless and duplex stainless counterparts. The data should serve to help answer questions on the practical corrosion limits of S32003 in various product forms, including sheet, plate and welded pipe and tube.

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1 Introduction

UNS S32003 LDSS alloy is a nitrogen enhanced lean duplex stainless steel recently developed by ATI Allegheny Ludlum, an Allegheny Technologies Company [1]. This alloy was developed to be used in the environments where high strength and good corrosion properties are required. With a Pitting Resistance Equivalent number (PREN) greater that 30, S32003 LDSS was developed to fill the gap between Types 316L and alloy 2205. Its composition (Nominally 21%Cr, 1.8%Mo, 0.17%N and 3% Ni) provides this alloy with outstanding resistance to a broad range of corrosive environments. There is a significant difference compared to type 316L in terms of corrosion resistance, strength and cost. The chemical compositions and PREN of S32003 alloy is compared to other selected alloys in Table1.

S32003 LDSS has the high strength characteristic of duplex stainless steels. The higher strength of the duplex grade is reflected in higher allowable design stresses in ASME Code Case 2503-1. S32003 compares closely with the traditional 2205 duplex alloy but has a distinct advantage over type 316L. Depending on the design loading of the equipment, it may be possible to reduce significantly the thickness of the material when using duplex stainless steel, which becomes an opportunity for cost savings.

Table 1. Chemical compositions of the alloys tested

Alloy	Cr	Ni	Mo	Mn	N	PREN
Type 304L (S30403)	18.2	8.1	0.1	1.8	0.06	19.5
Type 316L (S31603)	16.2	10.1	2.2	1.6	0.06	24.4
Type 317L (S31703)	18.2	11.1	3.1	1.6	0.06	29.4
S32101	21.5	1.5	0.25	5.0	0.22	25.8
ATI 2102*	21.5	1.5	0.25	2.8	0.22	25.8
S32304	22.0	3.5	0.15	2.0	0.13	24.5
S32003	21.5	3.7	1.8	1.6	0.17	30.2
Type 2205 (S32205)	22.5	5.5	3.3	1.5	0.16	36.0

(PREN = % Cr + 3.3 %Mo + 16 %N)
* New alloy, no UNS assigned yet.

2 Experimental Procedure

Small samples (1 x 2”) were ground with 120 grit paper and then were tested in representative corrosion media. The samples were degreased in acetone and acid cleaned in a 20% nitric acid solution at 130°F for 10 minutes before the corrosion testing. Duplicate samples were tested in each medium. The corrosion rates of the samples in boiling solutions containing different acids were determined by testing the samples for five 48-hour periods. The average value of the five periods is reported. The corrosion rate of S32003 alloy is also determined in sodium hydroxide and ammonium sulfate solutions. The critical pitting and critical crevice temperature of the samples were also determined using ASTM G150 and G48 Practice B procedures. The samples were also tested to determine their susceptibility to intergranular attack using the ASTM A262 Practices B, C and E procedures. Stress corrosion cracking of S32003 LDSS was studied under various conditions. Additional experiments were conducted to determine uniform corrosion rates of the samples using the procedures of ASTM G157. The goal was to determine the critical temperature in which the corrosion rate exceeded 5 mpy (0.13mm/y).

3 Results and Discussion

3.1 Pitting Corrosion

The Critical Pitting Temperature (CPT) of S32203 LDSS was measured using the ASTM G150 procedure as being 35℃. The CPT of S3200 3 is compared to some other materials in Figure 1. S32003 alloy is about the same as Type 317L in this test and it is much more pit resistant than Type 316L. This places S32003 LDSS between 316L and 2205 in terms of resistance to pitting in aqueous chloride environments.

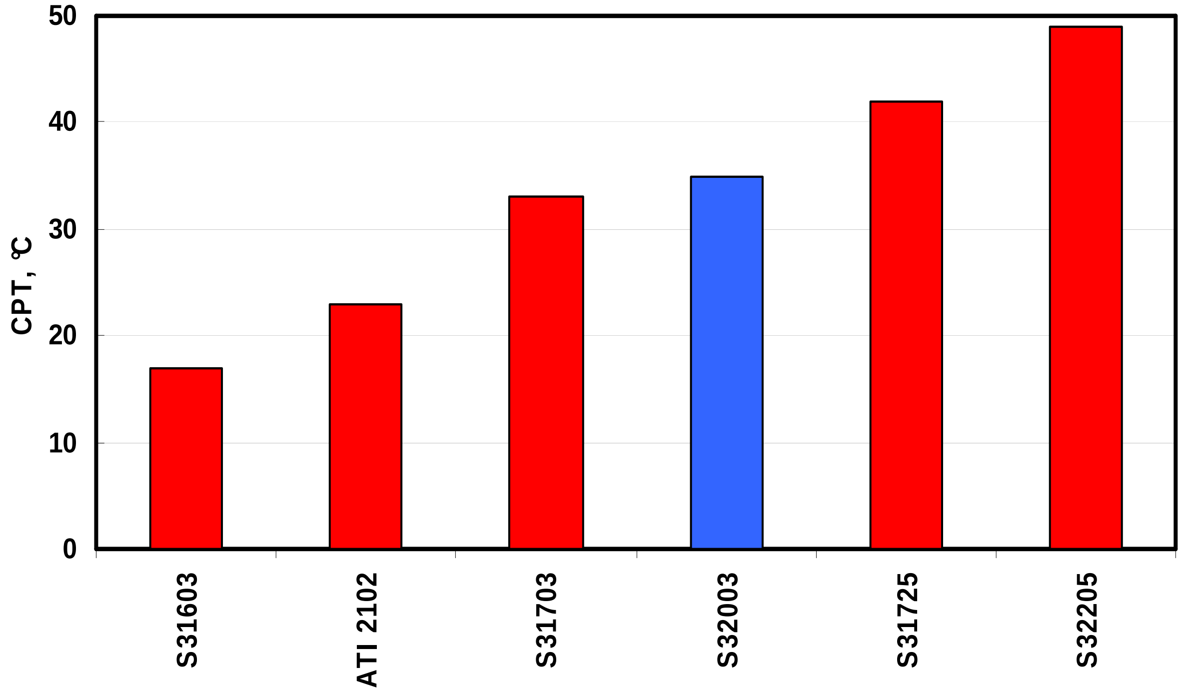

Figure 1. Critical Pitting Temperature of S32003 LDSS compared to other alloys as determined by ASTM G150.

3.2 Crevice Corrosion

The Critical Crevice Corrosion Temperature (CCCT) of S32003 LDSS is about 16℃ when measured using ASTM G48 Practice B. As shown in Figure 2, the CCCT of S32003 alloy is well above that of Type 316L and is between those of Type 317L and 2205 DSS.

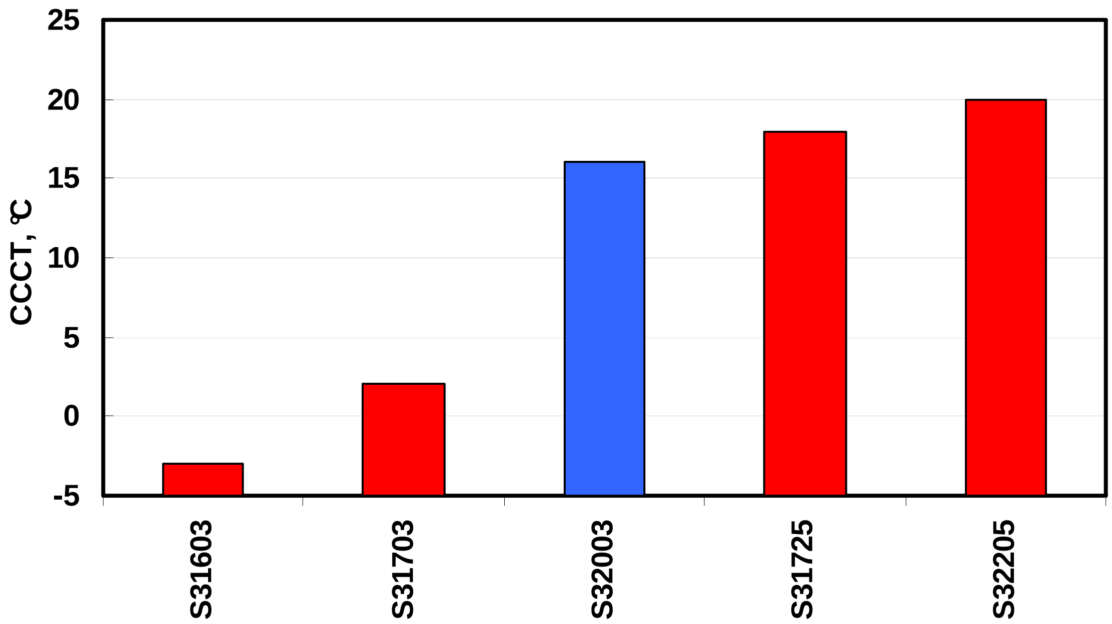

Figure 2. Critical Crevice Corrosion Temperatures measured using ASTM G48 Practice B.

3.3 Weld Testing

Samples of 6 mm thick S31603, S32101, S32304 and S32003 material were TIG welded using ER2209 filler. These samples were tested without post-weld pickling or passivation. Results of ASTM G150 CPT testing (duplicate samples) [2] are shown in

Table 3. Results of G150 CPT testing of as-welded alloys.

	Literature Values		Test Values	
Material	**Base Metal**	**Weld Metal**	**Base Metal**	**Weld Metal**
S32304	18-20°C	---	15.3°C	12.8°C
S32101	15°C	10°C	9.2°C	8.2°C
S32003	35°C	---	31-35°C	30°C
S31603	17-25°C	---	8.0°C	7.1°C

ASTM G48-E CPT tests were also performed using an acceptance criterion of 4 g/m^2 maximum mass loss. Results of those tests are shown in Table 4 as weight loss in g/m^2.

Table 4. Results of G48-E CPT testing of as-welded alloys – weight loss in g/m^2.

Base Metal	**11℃**	**15℃**	**20℃**	**25℃**
S32304	**0.3**	**0**	**0.7**	**19.0**
S32101	**6.6**			
S32003	**0.2**	**0**	**0**	**0**
S31603	**11.1**			
Weld Metal	**11℃**	**15℃**	**20℃**	**25℃**
S32304	**3.9**	**34.2**		
S32101	**81.0**			
S32003	**1.1**	**0.5**	**3.4**	**25.8**
S31603	**149.5**			

3.4 Stress Corrosion Cracking

Duplex stainless steels are not immune to Chloride Stress Corrosion Cracking (CSCC), but they are much better than the common austenitic stainless steels. Experiments were conducted to determine the SCC resistance of S32003 LDSS and some other alloys in boiling 26% NaCl. The results are summarized in Table 3. No cracking was observed on S32003 alloy or Type 2205 material after 1000 hours of testing. However, cracking was observed on Type 316 between 530 and 940 hours of testing. S32003 also was tested in 25 and 50% NaOH solutions at 80 and 110°C. No cracking was observed on S32003 alloy in NaOH solutions under the experimental conditions as shown in Table 4.

Table 3. Results of SCC testing of alloys in boiling 26% sodium chloride solution.

Alloy	**Boiling 26% NaCl**
Type 304	Failed (850 Hours)
Type 316	Failed (530 – 940 Hours)
Type 317L	Failed (1000 Hours)
S32003	Passed (1000 Hours)
Type 2205	Passed (1000 Hours)

Table 4. Results of SCC Testing of S32003 LDSS in sodium hydroxide solutions.

% NaOH	**Temp., ℃**	**Result**
25	80	No Apparent Cracking after 1008 hours
50	80	No Apparent Cracking after 1008 hours
25	110	No Apparent Cracking after 1008 hours
50	110	No Apparent Cracking after 1008 hours

Additionally, CSCC testing was performed by an independent lab. Sintef [3] tested S32003 C-rings to simulate salt concentrating on the top side of an offshore oil platform. Previous testing of 316L and 2205 alloys establish cracking thresholds of 60 and 100℃ respectively. S32003 material did not crack after 2200 hours of exposure in the temperature range of 80 to 110℃. Thus, S32003 alloy can be considered to have excellent CSCC resistance in comparison to these other alloys.

Other tests were performed in H_2S environments, simulating varying degrees of sour service. The resistance of S32003 welds to Sulfide Stress Cracking (SSC) and SCC was evaluated using the Four Point Bend (FPB) test method in accordance with EFC 17.[4] Tests were performed at room temperature and at 160℃. The following test conditions were used to simulate exposure to formation water from a North Sea oil field.

- P_{H2S} = 10 mbar, P_{CO2} = 7.4 bar, P_{tot} = 13.5 bar at 160℃
- pH 5.8
- 87,400 mg/l NaCl, 1,261 mg/l $NaHCO_3$ formation water
- 100% of Yield Strength
- 720 hours

In this environment, no cracking or pitting was observed in the as-welded S32003 material. Thus, S32003 welds were found to be resistant to SSC / SCC in simulated formation water based on actual North Sea conditions.

Further testing was recently performed at higher levels of H_2S. SSC testing at an independent lab [5,6] of unwelded and welded S32003 LDSS in accordance with EFC 17 was completed using the following conditions:

Produced Water:

- 20% Sodium Chloride
- 0.1 bar H_2S
- 1.2bar CO_2
- pH=3.5
- 100% of Yield Strength
- 90℃
- 30 days

Condensed Water:

- 1000 ppm Chloride + 500 ppm acetic acid
- 0.1 bar H_2S
- 1.2bar CO_2
- pH=3.0
- 100% of Yield Strength.
- 90℃
- 30 days

S32003 LDSS did not crack, thus demonstrating that S32003 LDSS offers the level of SSC resistance required of 2205 duplex stainless steel. This same level of resistance was also demonstrated for a cast equivalent to S32003 LDSS.

3.5 Acids and Bases – IGA Corrosion

Experiments were also conducted to determine the corrosion rate of S32003 LDSS in various boiling acid solutions (Table 5). The results for the same solutions are also compared to other alloys in Table 5. S32003 LDSS shows good corrosion resistance in all solutions except 10% $H_2SO_4$and 1% HCl. Even in those environments, its performance still compares favorably to Type 316.

Samples of S32003 LDSS were tested according to ASTM 262 Practices B, C and E. The results from the Intergranular Attack (IGA) testing are summarized and compared to various alloys in Table 6. The corrosion rate of S32003 alloy in boiling solutions of ASTM A262 is 0.53 and 0.78 mm/a for Practices B and C, respectively.

The samples passed the Practice E corrosion-bend test. The corrosion rate of S32003 LDSS in ASTM A262 solutions are at least as good as Type 316L.
Table 5. Corrosion rates of S32003 compared to other alloys in different acid media.

Boiling Solution	**Corrosion Rate, mm/a**			
	Type 316L	**Type 317L**	**S32003**	**2205**
1% Hydrochloric Acid (HCl)	1.49	1.43	1.22	0.307
10% Oxalic Acid ($H_2C_2O_4$)	1.23	1.19	0.097	0.198
20% Acetic Acid ($H_4C_2O_2$)	0.000	0.006	0.000	0.000
10% Sulfuric Acid (H_2SO_4)	16.2	7.49	6.58	5.25
10% Sulfamic Acid (H_3NO_3S)	3.16	2.11	0.211	0.559
45% Formic Acid (HCOOH)	0.59	0.290	0.376	0.124
20% Phosphoric Acid (H_3PO_4)	0.002	0.018	0.009	0.005

Table 6. Results from IGA corrosion testing per ASTM A262

Test Medium	**Corrosion Rate, mm/a**			
	S32003	**Type 2205**	**Type 316L**	**Type 317L**
ASTM A262 Practice B	0.527	0.506	0.631	0.597
ASTM A262 Practice C	0.783	0.524	0.567	1.23
ASTM A262 Practice E	Passed	Passed	Passed	Passed

The corrosion resistance of S32003 LDSS was also measured according to ASTM A923 Practice C. The results are summarized in Table 7. The samples passed at 27℃, but failed at 29.4℃. Samples fail this test if the corrosion rate is greater than 10 mg/dm^2 per day (mdd).

Table 7. Results of corrosion testing S32003 material per ASTM A923 Practice C at different temperatures for 24 hours.

Temperature, °C (°F)	**Corrosion Rate, mdd**
21.1 (70)	2.62
26.7 (80)	4.67
29.4 (85)	12.5

As shown in Table 8, the corrosion rate of S32003 LDSS is very low in boiling solutions containing 50% ammonium sulfate and 50% ammonium sulfate contaminated with 500 PPM chloride. The corrosion rate for Type 316L is about 100 times higher than S32003 in the same solutions.

Table 8. Corrosion testing of S32003 LDSS and Type 316 in 50% ammonium sulfate solutions.

Alloy	Corrosion Rate in boiling 50% Ammonium Sulfate, mm/a	Corrosion rate in boiling 50% Ammonium Sulfate with 500 PPM Chloride, mm/a
Type 316L	0.234	0.564
S32003	0.020	0.050

Table 9 gives the experimental results for samples exposed to solutions containing different amounts of NaOH at different temperatures. The corrosion rate of S32003 is comparable to that for Type 316L in NaOH solutions up to 80℃ for solutions containing up to 50% NaOH. For temperatures greater than 80°C, S32003 does not provide sufficient resistance to NaOH.

Table 9. Corrosion rates of S32003 LDSS and Type 316L stainless steel in NaOH solutions under various conditions. (The results are the average of two samples).

Alloy	% NaOH	Temp., °C	Total exposure time, hours	Corrosion Rate, mm/a
S32003	20	43	240	0.013
Type 316L	20	43	240	0.014
S32003	25	80	336	0.0045
S32003	25	110	336	0.283
Type 316L	25	80	336	0.0026
Type 316L	25	110	336	0.0047
S32003	50	80	336	0.0568
S32003	50	110	336	0.483
Type 316L	50	80	336	0.0302
Type 316L	50	110	336	0.301

3.6 CORROSION TESTING PER ASTM G157

Samples of S32003 LDSS were corrosion tested in different solutions per the testing program developed by Materials Technology Institute (MTI) [7] and standardized as ASTM G157. The solutions that are specified by ASTM G157 are given in Table 10. However, the samples were not tested in 50% NaOH solution. The goal was to determine the corrosion resistance of samples in these solutions at various temperatures to find the critical temperature, i.e. the lowest temperature at which the corrosion rate exceeded 5 mills per year (0.127 millimeters/annum).

The experimental results on corrosion testing of S32003 in HCl solutions are summarized in Table 11. The corrosion rate of S32003 in 0.2% HCL solution was very low (0.06 mpy). The corrosion rate in 1% HCl solution is much higher. The critical temperature at which the rate exceeds 0.127 mm/a is greater than 95℃. The corrosion rate of S32003 alloy becomes very high when the solution contains 5%HCl, with the critical temperature in this environment being less than 5℃. Addition of 0.3%

ferric chloride ($FeCl_3$) further increases the corrosion rate (see Table 11). The corrosion rate is about 0.132 mm/a at the critical temperature (50℃). The critical temperatures for S32003 in HCl solutions are compared to Type 304 and Type 316L in Table 12. S32003 LDSS has higher critical temperatures than Type 304 and Type316L. The results show that S32003 LDSS has better corrosion resistance in HCl containing solutions than other alloys such as Type 304 and Type 316L.

Table 10. Test solutions specified by ASTM G157.

Solution	**Formula**	**Concentration, wt.%**
Hydrochloric acid	HCl	0.2, 1.0, 5.0
Sulfuric acid	H_2SO_4	10, 60, 90
Nitric acid	HNO_3	10, 70
Phosphoric acid	H_3PO_4	85
Formic acid	HCOOH	50
Acetic acid	CH_3COOH	80
Sodium hydroxide	NaOH	50
Hydrochloric acid + Ferric chloride	HCl + FeCl3	1.0 HCl + 0.3 $FeCl_3$
Acetic acid + acetic anhydride	$CH_3COOH + (CH_3CO)_2O$	50/50
Sodium hydroxide	NaOH	50 (not tested)

Table 11. Corrosion rate of S32003 in HCl solutions at different temperatures.

Solution	**Concentration, %**	**Temperature, ℃**	**Rate, mm/a**
HCl	0.2	Boiling	0.001
HCl	1.0	65	0.002
HCl	1.0	80	0.002
HCl	1.0	90	0.002
HCl	1.0	95	0.005
HCl	1.0	Boiling	1.26
HCl + $FeCl_3$	1% HCl + 0.3% $FeCl_3$	30	0.001
HCl + $FeCl_3$	1% HCl + 0.3% $FeCl_3$	50	0.133
HCl + $FeCl_3$	1% HCl + 0.3% $FeCl_3$	55	0.191
HCl	5.0	5	1.01
HCl	5.0	20	4.47

The results on corrosion of S32003 LDSS in sulfuric acid solutions at different temperatures are given in Table 13. The corrosion rates in 10% H_2SO_4 are 0.048, 0.414 and 2.718 mm/a at 80, 85 and 90℃, respectively. The rates become much higher in 60% H_2SO_4 solution. For example, the corrosion rate is about 14. 402 mm/a at 25℃. Experiments were also conducted with concentrated (96.5%) sulfuric acid that exhibits an oxidizing character. The corrosion rate in 96.5% H_2SO_4 is about 14 mpy at 50℃. The critical temperatures at which the corrosion rate is higher than 0.127 mm/a (5 mpy) for S32003 alloy versus other alloys are summarized in Table

14. In most cases, the critical temperature of S32003 alloy is higher than that of Type 316L stainless steel.

Table 12. Critical temperature (ASTM G157) for S32003 and other alloys in HCl.

Test Solution	**Concentration, %**	**Critical Temperature, °C**		
		316L	**304**	**S32003**
HCl	0.2	>BP	>BP	>BP
HCl	1.0	30	30	95
HCl + $FeCl_3$	1% HCl + 0.3% $FeCl_3$	25	25	50
HCl	5.0	-	-	<5

Table 13. Corrosion rate of S32003 in H_2SO_4 solutions at different temperatures.

Solution	**Concentration, %**	**Temperature, °C**	**Corrosion Rate, mm/a**
	10	80	0.049
H_2SO_4	10	85	0.413
	10	90	2.72
	60	20	0.001
H_2SO_4	60	25	14.4
	60	30	45.8
	96.5	35	1.92
H_2SO_4	96.5	40	8.64
	96.5	50	14.1

Table 14. Critical temperature (ASTM G157) for S32003 and other alloys in sulfuric acid.

Test Solution	**Concentration, %**	**Critical Temperature, °C**	
		316L	**S32003**
H_2SO_4	10	50	80
H_2SO_4	60	<15	20
H_2SO_4	96.5	45	35

Examination of data shown in Table 15 reveals that the corrosion rate of S32003 alloy in 10 and 70% nitric acid is very low. The corrosion rates in boiling 10 and 70% nitric solutions are 0.0006 and 0.3203 mm/a, respectively. The corrosion rate is also low in 85% boiling phosphoric acid (0.348 mm/a). The critical temperature in which the corrosion rate is higher than 0.127 mm/a is given in Table 16 and is compared to other alloys. Again, S32003 LDSS has a higher critical temperature than Type 304 and Type 316L stainless steels.

Table 15. Corrosion rate of S32003 in nitric and phosphoric acids.

Solution	Concentration, %	Temperature, ℃	Rate, mm/a
HNO_3	10	Boiling	0.006
HNO_3	70	90	0.037
HNO_3	70	95	0.095
HNO_3	70	100	0.092
HNO_3	70	105	0.132
HNO_3	70	Boiling	0.320
H_3PO_4	85	80	0.021
H_3PO_4	85	90	0.111
H_3PO_4	85	95	0.224

Table 16. Critical temperature (ASTM G157) for S32003 and some other alloys in nitric and phosphoric acids.

Test Solution	Concentration, %	Critical Temperature, ℃		
		316L	304	S32003
HNO_3	10	>BP	>BP	>BP
HNO_3	70	100	100	105
H_3PO_4	85	95	80	90

The corrosion data for S32003 alloy in acetic and formic acids are given in Table 17. The corrosion rate is very low in boiling acetic and formic acids. As shown in Table 18, the critical temperature for S32003 alloy in acetic and formic acids is much higher than Type 304 and Type 316L stainless steels.

Table 17. Corrosion rate of S32003 and other alloys in organic acids.

Solution	Concentration, %	Temperature, ℃	Rate, mm/a
CH_3COOH	80	Boiling	0.002
CH_3COOH +$(CH_3CO)_2O$	50 + 50	Boiling	0.133
HCOOH	50	90	0.002
HCOOH	50	95	0.007

Table 18. Critical temperature (ASTM G157) for S32003 and other alloys in organic acids.

Test Solution	Concentration, %	Critical Temperature, ℃		
		316L	304	S32003
CH_3COOH	80	>BP	100	>BP
CH_3COOH +$(CH_3CO)_2O$	50 + 50	120	>BP	BP
HCOOH	50	40	<10	>100

4 CONCLUSIONS

S32003 LDSS can be used for many applications due to its good corrosion resistance and high strength. This alloy is a good alternative to traditional 316L stainless steel due to its strength and corrosion resistance advantages as well as providing the benefit of lower cost of raw materials such as nickel and molybdenum.

The corrosion rate of S32003 alloy was studied in many environments and found to be high in 10% H_2SO_4 and 1% HCl, suggesting limits for its application. Its corrosion rate is also slightly higher than desirable in 45% formic acid. The corrosion rate of S32003 was very low in all other media (oxalic, acetic, sulfamic and phosphoric acids) studied. The corrosion rate of S32003 alloy was much lower than Type 316L in ammonium sulfate containing solutions. The results show that S32003 alloy had higher corrosion resistance in most medium studied than did Type 316L. However, the corrosion rate was higher than duplex 2205 in some environments, as would be expected for the leaner composition.

S32003 also has much better chloride stress corrosion cracking resistance than Types 304 and 316. It also has very good resistance to cracking in NaOH solutions. In sulfide stress corrosion cracking resistance testing, the S32003 LDSS did not crack. S32003 demonstrated the level of SSC resistance required of 2205 duplex stainless steel.

The corrosion rate of S32003 alloy in ASTM G157 solutions was measured. The critical temperature in which the rate is higher than 0.127 mm/a (5 mpy) was determined for each solution. The corrosion rate of S32003 was lower than Type 304 and Type 316L in most of the solutions, and the corresponding critical temperature for S32003 alloy was higher. The results show that S32003 alloy has better corrosion resistance than Type316L in most environments and therefore can be used in the environments where 316L is used, within the temperature limits established for duplex stainless steels.

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