JOURNAL OF MATERIALS SCIENCE **36** (2001) 3415–3422

Microstructure, corrosion and mechanical properties of 304 stainless steel containing copper, silicon and nitrogen

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The effects of 0.086–0.336% nitrogen additions on the microstructure, corrosion and mechanical properties of type 304 austenitic stainless steel (SS) containing 2% copper and 2–3% silicon were studied. This study was carried out using scanning electron microscope (SEM), potentiodynamic, weight loss, hardness number and ball-punch bulge measurements. Mutual effects between Si and N were observed in the matrix of SS. Nitrogen offset the ferrite-forming tendencies of Si and was more efficient than Ni as austenitizer, but Si decreased the solubility of N in solid solution. N additions improved the pitting resistance of SS in acidic and neutral chloride solutions. This was more evident in more aggressive solutions than in solutions with low chloride concentrations. Segregation of second N-rich phases, like Cr_2N, in SS containing 2% Cu, 3% Si and 0.237% N was occurred. This steel exhibited less pitting corrosion resistance than the plain 304 SS in most chloride solutions under study. Addition of 2% Si to 304 SS containing Cu has negative effect on the mechanical behavior. But presence of N improved the mechanical strength of steel irrespective of the drop solubility of N affected by Si.

1. Introduction

A single-phase austenitic structure is preferred in 18% Cr–8% Ni stainless steel because of its superior mechanical properties and corrosion resistance. Previously published works have assessed the performance of 18% Cr–8% Ni SS with Si (ferrite stabilizer) additions, which may be added to increase corrosion resistance, at levels low enough to maintain an austenitic structure. Wilde studied the effect of Si additions at high levels (up to 5%) and of the resultant δ-ferrite on intergranular corrosion of 18% Cr-8% Ni SS [1]. In the development of a low Cr-steel alloy, 5% Si, 1% Cu and small amounts of Mo were used to replace Cr and provide the necessary corrosion resistance [2]. Effects of alloying elements on stress corrosion cracking (SCC) and crevice corrosion resistance were studied previously in the development of an 18% Cr-8% Ni austenitic SS for domestic hot water service, such as in electric hot water tanks and kerosene-burning water heaters. This study indicated 2% Cu–3% Si steels had excellent SCC resistance [3].

Nitrogen as alloying element is a strong austenite stabilizer and a potent solid solution strengthener. Nitrogen alloying of SS to increase strength results in an increase in the pitting corrosion resistance of the steel. The amount of nitrogen present in SS typically is higher than in low-alloy steels because of the presence of chromium, which increases the solubility of this element [4]. It is possible that beneficial effects may be obtained by alloying nitrogen, either for its own sake or to offset the ferrite-forming tendencies of other alloying elements in SS. The objective of the present work was to study the effects of N additions ($0.086 \sim 0.336\%$) on microstructure, corrosion and mechanical properties of 304 austenitic SS containing 2%Cu and $2 \sim 3\%$ Si.

2. Experimental procedures

2.1. Materials

Composition of SS used are given in Table I. These steels were melted in a 30-Kg induction furnace in vacuum and then hot- and cold-rolled to sheets of 1-mm thickness, annealed at 1050°C for 3 min, and water quenched.

2.2. Preparation and electrochemical measurements

The working electrode consisted of a specimen with an square area of 1 cm^2 fabricated from the steel sheet. An insulated lead was secured to the back of each steel

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TABLE I Chemical composition (wt%) of staniless steels

SS	C	Si	Mn	Ni	Cr	Cu	Mo	N	P	S
304	0.068	0.57	1.08	8.64	18.16	0.08	0.04	0.027	0.028	0.008
F_8	0.05	1.98	1.05	10.95	18.58	1.85	0.01	0.015	0.028	0.005
F_6	0.053	2.06	0.99	8.01	18.45	1.95	0.01	0.086	0.019	0.006
F_{11}	0.053	1.93	1.04	8.4	18.71	1.95	0.01	0.217	0.023	0.006
F_{14}	0.052	1.82	1.00	8.44	18.85	1.97	0.01	0.336	0.025	0.005
F_{23}	0.026	3.07	1.04	10.91	18.9	1.91	0.01	0.237	0.024	0.006

Fe balanced.

plate with solder at low temperature. The specimens were mounted in epoxy resin in such a way that only the square surfaces were in contact with the solution. Before electrochemical measurements, the specimens were polished mechanically using wet emery papers of successively finer grades. The specimen was then washed thoroughly with redistilled water and acetone, and left in air for 30 min to obtain a reproducible air formed oxide film [5, 6].

The electrolyte was made from analytical-grade reagents and redistilled water and was deaerated using high-purity N for one hour before each experiment. The experiments were conducted in a tempered glass cell which has been described elsewhere [7]. A saturated calomel electrode (SCE) was used as the reference electrode. Electrochemical measurements were performed using a PARC EG&G potentiostat/galvanostat model 273 with model 352/252 corrosion software. The scan rate was 1 mV s^{-1} for polarization tests. This measurements were carried out at 35°C and the temperature was thermostatically controlled. SS sheet used for weight loss experiments has an area of 15 cm^2. The weight loss was determined in duplicate and the mean values are recorded. The examination of the steel surface with a SEM (JSM-5400LV) was performed after etching in the required solution.

2.3. Mechanical testing

In order to quantify the effect of nitrogen content in 304 austenitic stainless steel alloys under study on its mechanical properties, hardness and bulge tests were carried out. The hardness test was performed on specimens of a rectangular cross section 3 cm × 2 cm and 1 mm thickness using Rockwell type hardness tester. The Rockwell hardness number was determined using ball diameter of 1.25 mm and applied load of 360 N. The surface of each specimen was divided into a mesh of cell with 5 mm × 5 mm size. Hardness was determined by making 24 indentations on the surface of specimen approximately at the center of each mesh cell, and the mean value was taken. The tolerance of the obtained value was ±1.2. The ball-punch bluge test of a miniature disc specimen was applied to determine the yield stress [8]. Fig. 1 shows the setup used for the present tests. The specimens used in this test are discs of diameter 1.5 cm and thickness 1 mm. The disc was clamped between the upper and lower dies and subjected to a central load applied via a ball of 4.75 mm diameter. The lower die having bore diameter 7 mm and die inner corner radius 0.5 mm. A Finite Element analysis for the bulge test using the model shown in Fig. 2 was used to determine the bulge force-displacement curves for the specimens. The axisymmetric model used to represent a radial segment through the ball, disc and dies. The relationship between the yield stress of the specimen and the maximum bulge force has been investigated for an elastic-plastic material over the yield stress range 100 $MN/m^2 < \sigma_y <$ 600 MN/m^2. Fig. 3 shows the relationship between the maximum bulge force and the yield stress. For any specimen of the same dimensions the yield stress can be directly determined from the above mentioned figure using the measured value of maximum bulge force.

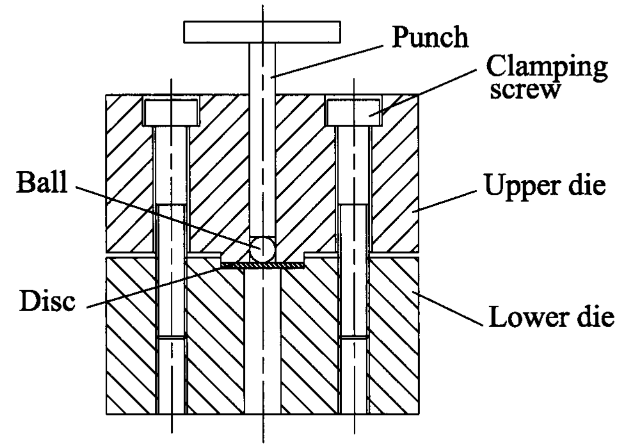

Figure 1 Miniature-disc bulge test setup.

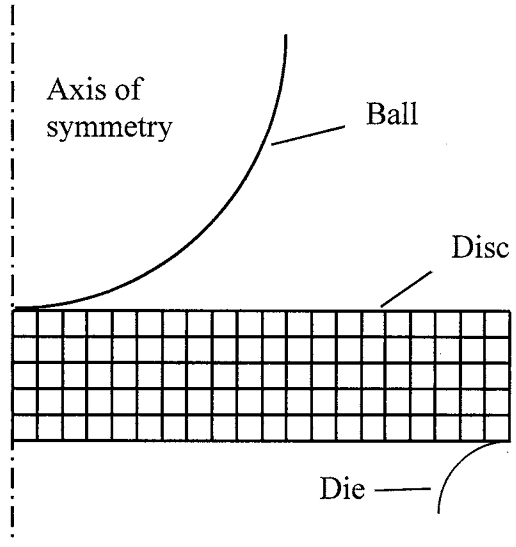

Figure 2 The finite element model.

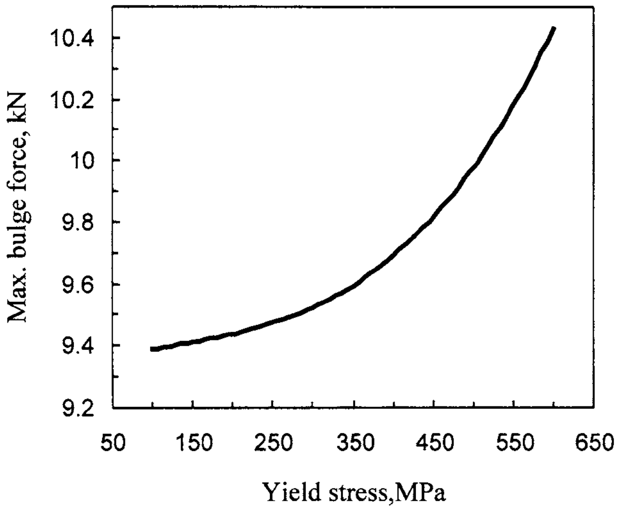

Figure 3 The relationship between the maximum bulge force and yield stress.

3. Results

The stainless steels under study were etched in a mixture of cupric chloride, hydrochloric acid and methanol to investigate the ferrite phase formed in the matrix. SEM photograph of the plain 304 SS (Fig. 4a) showed some ferrite islands. Presence of 2%Si in F_8 SS enhanced the ferrite formation although the higher Ni (austenitic stabilizer) content up to ~11% in this steel as shown in Fig. 4b. δ-ferrite islands diminished with addition of nitrogen (austenitic former and stabilizer) in F_6, F_{11} and F_{14}. In these steels Ni content was kept at level of 8%. F_{14} SS has a fully austenitic structure as shown in Fig. 4c. Higher δ-ferrite islands were observed in F_{23} SS which contains 3% Si, 0.217% N and Ni up to ~11% (Fig. 4d).

To investigate grains and grain-boundaries of the stainless steels SEM investigation was carried out after etching in nitric acid-acetic acid-hydrochloric acid-glycerin mixture. This etching solution was found to act as a rapid intergranular attack on steels containing intergranular precipitated phases [5]. The surface of F_8 showed slight grooves at grain boundaries and pits (Fig. 5a) while F_6 SS had a clean grain boundaries and the surface was free from pitting (Fig. 5b). Some pits and grooves at the grain boundaries appeared in case of F_{11} SS (Fig. 5c) and more intergranular attack and pitting occurred for F_{14} SS (Fig. 5d). Severe attack and pitting with appearance of second phases was observed on the surface of F_{23} SS as shown in Fig. 5e.

Results obtained for the corrosion and passivation behavior of type 304 SS and its alloys in deaerated 0.1 M H_2SO_4 containing 0.1 M and 0.2 M NaCl at 35°C are given in Table II. All steels exhibited active-passive transition behavior in sulfuric acid solutions. Stainless steel alloys had a corrosion potential (E_{corr}) more noble than that of 304 SS by about $50 \sim 80$ mV. This is may related to presence of copper (2%) in the alloys [5, 6]. The primary passive potential (E_{pp}) of SS alloys were more noble by $15 \sim 25$ mV than that of 304 SS. This noble shift of E_{corr} and E_{pp} in case of F_8 and F_{23} SSs were more pronounced among the alloys. The critical current density (I_{crit}) of 304 SS was suppressed by alloying additions, especially in case of F_8 and F_{23} SS alloys. Also, the passivation behaviour of 304 SS was improved by alloying additions as noticed from passive current (I_{p}) measurement. F_6, F_{11} and F_{14} SSs exhibited more pitting corrosion resistance than 304 SS in H_2SO_4 containing 0.2 M NaCl. In this solution the pitting potential (E_{pit}) of both F_{11} and F_{14} SSs was 130 mV more positive than that of 304 SS. However in lower chloride solution (H_2SO_4 containing 0.1M NaCl) both steels (F_{11} and F_{14}) had a negative effect against the pitting corrosion. Also, F_8 and F_{23} SSs had less pitting corrosion resistance than 304 SS in both H_2SO_4 solutions containing chloride.

Results obtained for anodic polarization behavior of type 304 SS and its alloys in deaerated HCl (0.01 M and 0.02 M) and NaCl (0.01 M and 0.02) solutions at 35°C are given in Table III. Except the plain 304 SS in 0.02 M HCl, all SSs had an anodic passive behavior. The pitting

TABLE II Corrosion and passivation behaviors in 0.1M H_2SO_4 containing two different concentrations of NaCl at 35°C

	E_{corr} (mV)		E_{pp} (mV)		E_{pit} (mV)		i_{crit} ($\mu A \cdot cm^{-2}$)		i_{p} ($\mu A \cdot cm^{-2}$)	
SS	0.1M	0.2M	0.1M	0.2M	0.1M	0.2M	0.1M	0.2M	0.1M	0.2M
304	−370	−370	−284	−287	754	368	329	483	8.0	12.0
F_8	−280	−303	−226	−246	622	273	5.7	29	6.0	8.1
F_6	−305	−335	−252	−269	872	431	40	70	6.3	8.0
F_{11}	−298	−330	−252	−271	653	499	25.3	57	6.4	7.4
F_{14}	−315	−335	−264	−267	654	497	37.2	84	5.7	7.4
F_{23}	−283	−302	−237	−246	538	296	13.7	51	7.2	7.1

TABLE III Corrosion and pitting potentials in two different chloride solutions at 35°C

	HCl E_{corr} (mV)		E_{pit}(mV)		NaCl E_{corr}(mV)		E_{pit}(mV)	
SS	0.01M	0.02M	0.01M	0.02M	0.01M	0.02M	0.01M	0.02M
304	−285	−375	440	256	−260	−195	457	390
F_8	−310	−297	396	338	−220	−255	460	403
F_6	−308	−310	490	455	−230	−252	460	480
F_{11}	−285	−298	519	452	−280	−250	505	578
F_{14}	−315	−318	606	467	−250	−290	571	593
F_{23}	−285	−338	405	390	−175	−285	468	418

TABLE IV Weight loss measurement in 2.5 M H_2SO_4 at 50°C

	304	F_8	F_6	F_{11}	F_{14}	F_{23}
Weight loss ($mg \cdot cm^{-2} \cdot day^{-1}$)	34.0	1.9	4.2	3.3	3.4	2.0

TABLE V The mechanical testing results

Steel	Hardness No. (mean value)	Max · bulge force (kN)
304	83	9.6
F_8	65	7.0
F_6	79	9.3
F_{11}	89	9.8
F_{14}	98	10.5
F_{23}	90	10.0

resistance of 304 and its alloys in HCl and NaCl solutions was less than in H_2SO_4 containing NaCl. This is may related to the pitting corrosion inhibition of SO_4^{2-} ions as explained before [9]. F_6, F_{11} and F_{14} SSs had more pitting corrosion resistance than 304 SS in both HCl and NaCl solutions. E_{pit} of F_6, F_{11} and F_{14} SSs were 50 mV, 79 mV and 166 mV, respectively, more positive than that of 304 SS in 0.01M HCl and were 200 mV, 196 mV and 211 mV, respectively, in 0.02 M. E_{pit} of F_6, F_{11} and F_{14} SSs were 3 mV, 48 mV and 114 mV, respectively, more positive than that of 304 SS in 0.01 M NaCl and were 90 mV, 188 mV and 203 mV, respectively, in 0.02 M. It is clear that improvement of pitting resistance by N addition to 304 SS more pronounced in higher chloride solution. F_8 and F_{23} SSs had a negative effect against the pitting corrosion in comparison with the plain 304 SS in 0.01 M HCl and had a minor improvement resistance among SS alloys in concentration 0.02 M. These steels had a slight or no effect in the pitting resistance in NaCl solutions.

The corrosion rate of 304SS and it alloys in 2.5 M H_2SO_4 at 50°C was measured by weight loss and the results are recorded in Table IV. The general corrosion rate decreased sharply by alloying additions to 304 stainless steel. F_8 and F_{23} SS had less corrosion rate among SS alloys, this is in agreement with anodic active dissolution measurement in H_2SO_4 solutions as shown above.

The results of the hardness number and maximum bulge force measurements are listed in Table V. The mechanical properties of the steels under study estimated from both measurements are consistent. From this table it was noticed that the measured values of the hardness and maximum bulge force in case of F_8 and F_6 was decreased in compared with that of the plain 304 SS. The measured values of F_8 was the smallest one among steels under study. The mechanical strength for the other steels F_{11}, F_{14} and F_{23} were higher than that of 304 SS. And F_{14} have the maximum values of hardness number and maximum bulge force among the steels under study.

4. Discussion

The nitrogen in stainless steel is limited by its maximum solubility in solid solution. The solubility of N

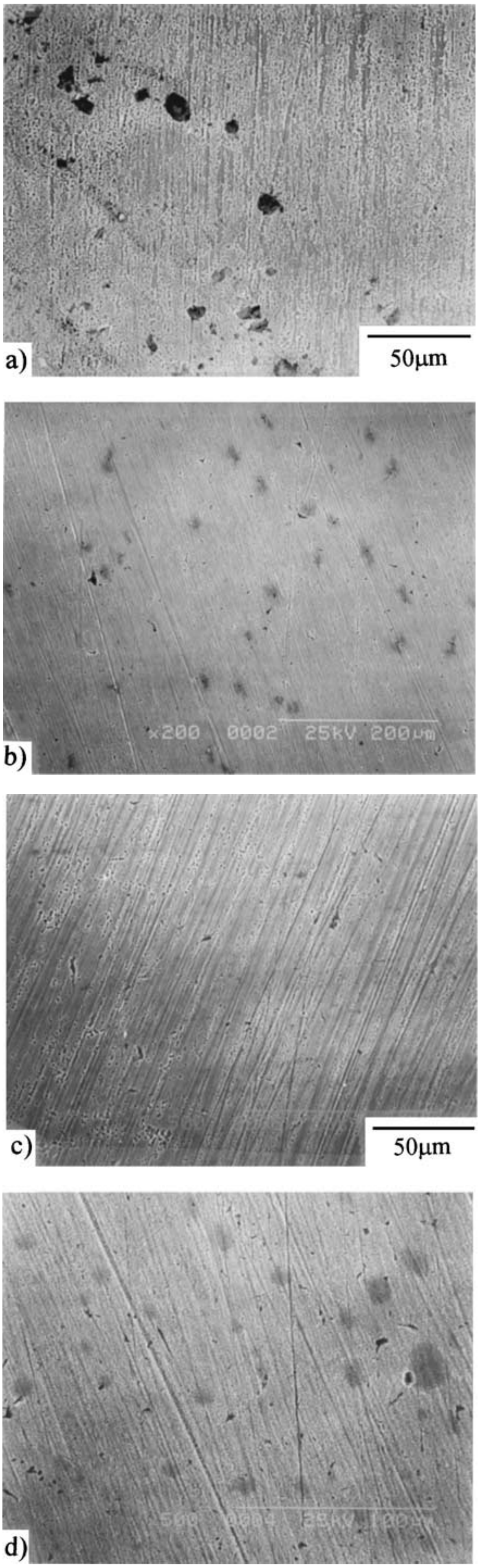

Figure 4 SEM images of δ-ferrite formed on: (a) 304, (b) F_8, (c) F_{14} and (d) F_{23} SSs.

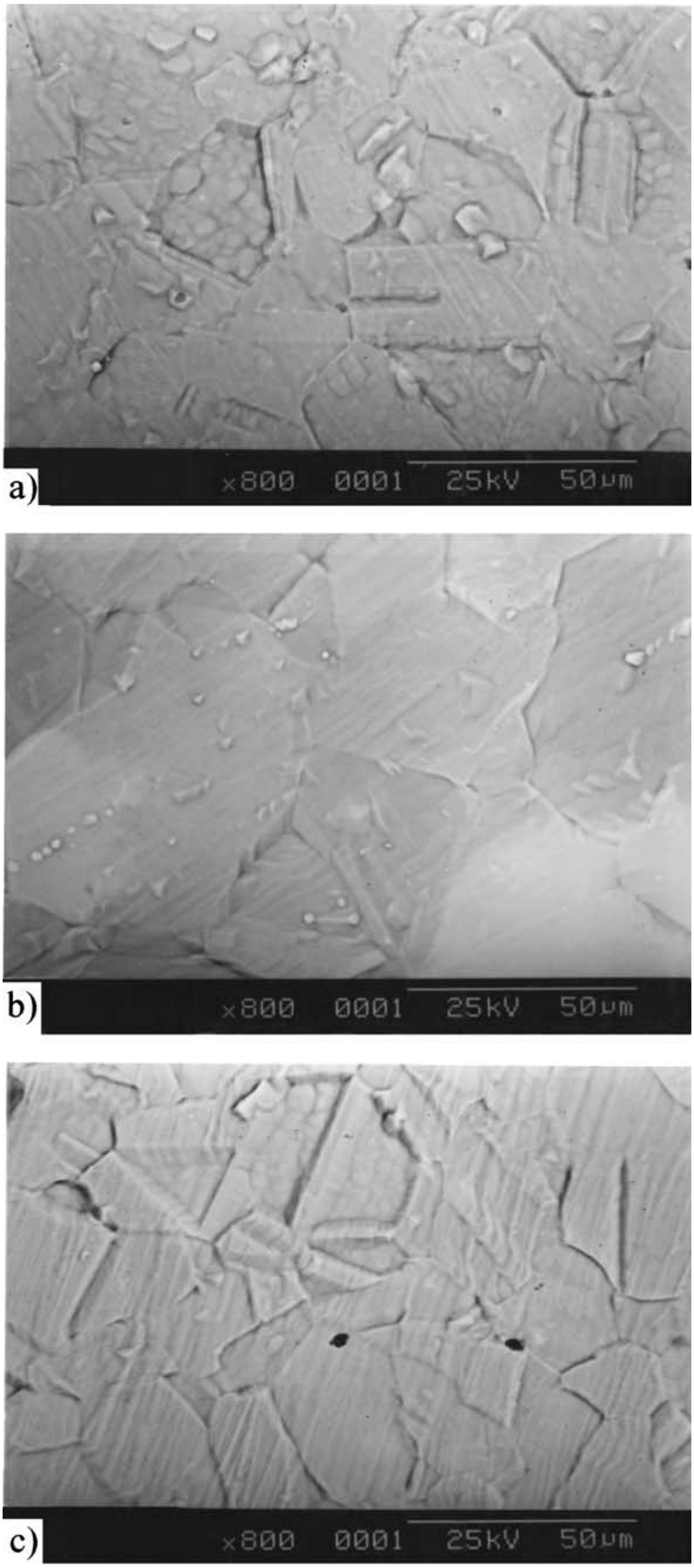

Figure 5 SEM images of microstructure for: (a) F_8, (b) F_6, (c) F_{11}, (d) F_{14} and (e) F_{23} SSs *(Continued)*.

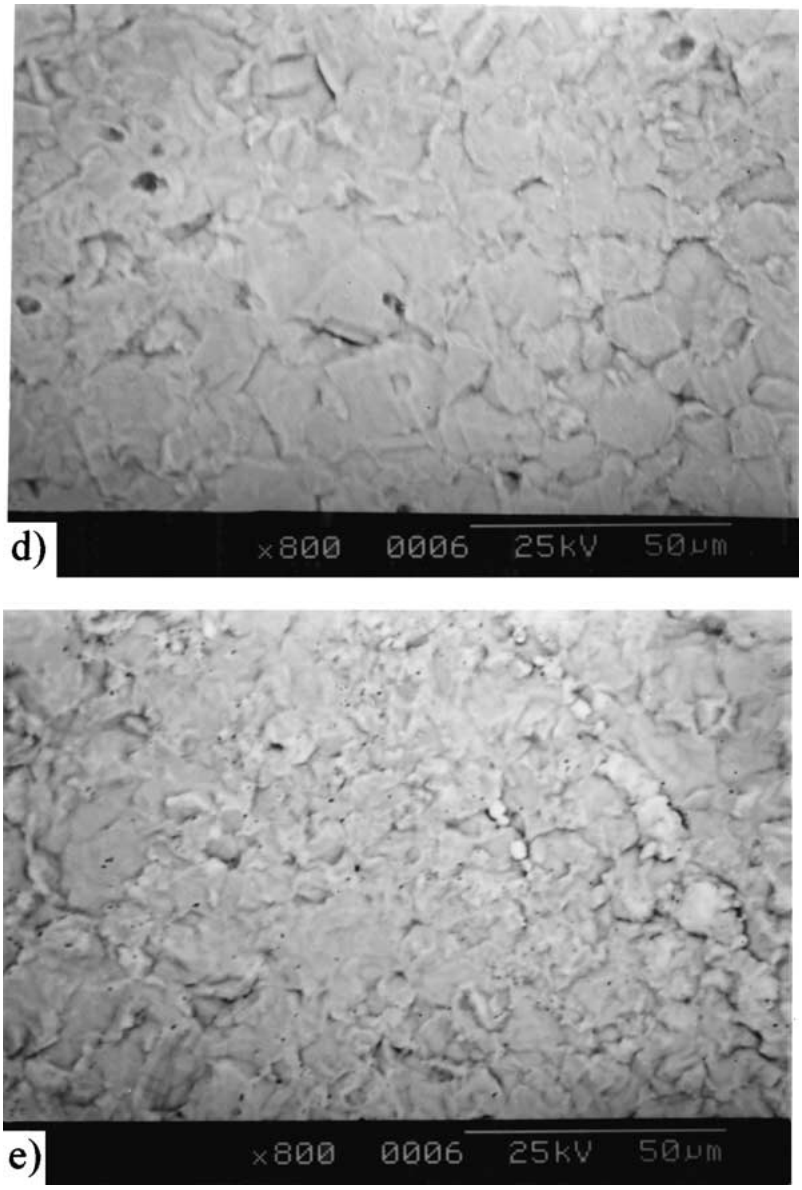

Figure 5 (Continued).

in austenite is higher than in ferrite. It is known that N solubility in steel affects greatly by alloying elements. Chromium, a ferrite stabilizer, increases the solubility of N in steel but the solubility drops when the matrix becomes ferritic. Nickel, an austenitic stabilizer, decreases the solubility of N in SS however if a suitable amount of Ni is added to a ferritic SS the matrix becomes austenitic and the N solubility is increased greatly. By more Ni addition to the austenitic steel, the N solubility decreases [4]. According to the thermodynamic studies by Omsen and Eliasson, the solubility limit of N in a solid solution of 18% Cr–8% Ni SS is a 0.22 to 0.24% [10]. Cu addition to SS decreased slightly the solubility of N but Si addition decreased greatly this solubility [4, 11]. 304 Austenitic stainless steel under study showed some ferrite phase. Although higher Ni content in F_8 SS the presence of 2% Si enhanced the ferrite information, leaving a duplex structure consisting of austenite and ferrite. But the additions of 0.086%, 0.217% and 0.336% N to 304 SS containing 2% Cu–2% Si as indicated in F_6, F_{11} and F_{14} SSs, respectively, decreased effectively the ferrite phase. F_{14} SS which contain the maximum N content has a fully austenitic structure (Fig. 4c). Nitrogen offset the ferrite-forming tendencies of Si and was more efficient than Ni as austenitizer. It commonly is used in duplex alloys as a cost-effective alternative to Ni to achieve a desired phase balance [4]. Uhlig has explained before that N does not promote the austenitic phase in 18% Cr–8% Ni SS as much as it inhibits the normally occurring transformation from the austenitic to the ferritic phase. This role of N is completely different from the function of Ni that favors austenite formation [12]. Formation of higher δ-ferrite phase in F_{23} SS indicating the drop solubility of N in the matrix as a result of higher Si and Ni contents.

SEM examination after chemical treatment of the SSs, as shown in Fig. 5, provided a significant microstructure information. The drop solubility of N in F_{23} SS led to segregation of second N-rich phases, mostly is Chromium nitride Cr_2N [13, 14], in the matrix. This means that, the second phases are rich in Cr thus they tend to deplete the surrounding matrix of Cr, resulting in poorer corrosion resistance. F_{14} SS contains higher

N (Table I) but it showed less second phases (Fig. 5d). The higher Si and Ni contents in F_{23} SS most likely decreased the limit solubility of N in the matrix [4]. This is in agreement with ferrite phase formation as explained before (Fig. 4). The N-rich phases slightly was formed in F_{11} SS and completely absent in F_6 SS. Mozh *et al.* explained that precipitation of Cr_2N in 304 SS became significant after ∼0.16% N and that N additions in excess of this not only were no longer beneficial but contributed to the extend of localized Cr depletion [13]. It is concluded that the known limit solubility of N in 304 SS (0.22% to 0.24%) is expected to decrease to slightly less than 0.2% in 304 SS containing 2% Cu–2% Si.

However, superior resistance of N-alloying 304 SS containing 2% Cu–2% Si against pitting corrosion in acidic (except in 0.01M HCl) and neutral chloride solutions under study is $F_{14} \geq F_{11} > F_6$. The improved pitting resistance of these steels were more evident in more aggressive solutions than in solutions with low chloride concentrations. Some investigators have showed before the ability of N as an alloying element to enhance the pitting resistance of SS is different in dilute and in concentrated Cl^- solutions [5, 15]. F_{23} SS exhibited less pitting corrosion resistance than 304 SS in most chloride solutions under study (Tables II and III). The higher Cr_2N precipitation in this steel reduced effectively the pitting corrosion resistance less than 304 SS.

From E_{pit} measurement in acidic chloride solution it is observed that the detrimental effect of Cr_2N precipitates in F_{23} SS containing nitrogen more evident in lower chloride concentrations. And as a result of the inhibition effect of SO_4^{2-} ions, it is possible to assume that 0.1 M and 0.2 M Cl^- ions in H_2SO_4 less aggressive than 0.01 M and 0.02 M HCl, respectively. In this case F_{14} and F_{11} which have some Cr_2N precipitates as shown in Fig. 5, exhibited less pitting resistance than 304 SS (E_{pit} of SS alloys lower by ∼100 mV) in H_2SO_4 containing 0.1 NaCl. In this solution F_6 which was free from Cr_2N (as shown in Fig. 5b) exhibited higher pitting resistance than 304 SS (E_{pit} of SS alloy higher by 118 mV).

In a pervious studies, it was found that presence of 2% Cu in 304 austenitic SS decreased corrosion rate and suppressed active dissolution in dilute [5] and concentrated [16] acidic chloride solutions. This means that the presence of 2% Cu in SS alloys played an important role in reduction of the general corrosion and I_{crit} in solutions under studies. The addition of 2% Si in all SS alloys (F_{23} SS contains 3% Si) enhanced the role of Cu. Surface analysis (AES and EDX) indicated before an enrichment of Si in the passive film of SS [6]. The beneficial effect of Si addition on the resistance to corrosion is attributed to the formation of a Si-rich film on the steel surface [1, 17]. Increasing of E_{pp} of SS alloys in sulfuric acid solution, as shown in Table II, is likely related to the presence of Cu [18]. F_8 and F_{23} SS have higher Ni content than the rest of SSs by ∼3%. The higher Ni enhanced the shift of E_{corr} and E_{pp} to noble side and reduction of I_{crit} and the general corrosion, it enhanced the role of Cu. Si was found to have no measurable effect on E_{corr} and E_{pp} [5]. The potentiodynamic measurements of F_6, F_{11} and F_{14} SSs in H_2SO_4 containing chloride indicated that nitrogen N had no effect on E_{corr}, E_{pp} and I_{crit}. Szklarska-Smialowska *et al.* found that addition of 0.07% to 0.35% N to 18% Cr–5% Ni–10% Mn SS does not significantly affected its passive behavior in 0.1N H_2SO_4 containing chloride [19]. Also, N addition had no effect on the general corrosion in pure H_2SO_4 (Table IV). Although Si improved the corrosion resistance of austenitic SS but had negative effect against the pitting resistance by creating the ferrite phase and it crackdown the positive role of N especially in higher Si contents.

It is clear that addition of 2% Si, which created δ-ferrite phase, to 304 SS as in F_8 has negative effect on the mechanical behavior, see Table V. But the addition of N to 304 SS containing 2% Si improved the mechanical strength. The improvement of the mechanical behavior increased with increasing of the N content. Steel F_{14} which contain the maximum N addition has excellent mechanical strength. It is known that N is effective solid solution strengthening element [4]. In addition, F_{23} SS has high mechanical strength as shown in Table V. This steel showed a drop in solubility of N and appearance of duplex structure as indicated above. It is likely that presence of N in solid solution and/or as intermetallic compounds improves the mechanical behavior of stainless steel.

5. Conclusions

Presence of of 2% Si in F_8 SS created ferrite phase leaving a duplex structure consisting of austenite and ferrite. But additions of 0.086%, 0.217% and 0.336% N to 304 SS containing 2% Cu–2% Si (F_6, F_{11} and F_{14} SSs, respectively) decreased this ferrite phase. Nitrogen offset the ferrite-forming tendencies of Si and was more efficient than Ni as austenitizer. Formation of higher δ-ferrite phase in F_{23} SS (0.237% N) indicated a drop solubility of N in the matrix as a result of higher Si (3%) and Ni (up to 11%) contents. This led to segregation of second N-rich phase, like Cr_2N, in the matrix. F_{14} SS has a fully austenitic structure and less N-rich phases. This steel was superior among stainless steels under study in resistance of pitting corrosion in acidic and neutral chloride solutions, while F_{23} SS was minor one (less than the plain 304 SS). The hardness number and maximum bulge force measurements showed that the superiority of mechanical strength for stainless steels under study were $F_{14} > F_{23} > F_{11} > 304 > F_6 > F_8$. Addition of Si decreased the mechanical strength while addition of N improved effectively this strength. The presence of N in solid solution or as intermetallic compounds improved the mechanical behavior of stainless steel. Although Si improved the corrosion resistance of austenitic SS but had negative effect against the pitting resistance by creating the ferrite phase and crackdown the positive role of N especially in higher Si contents.

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Received 13 June 2000
and accepted 1 February 2001