AN INVESTIGATION INTO THE PROCESSING AND PROPERTIES OF GAS ATOMIZED HIGH NITROGEN AUSTENITIC STAINLESS STEELS

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Abstract

The addition of nitrogen to stainless steels can dramatically improve properties. Using rapid solidification processing with its increased chemical homogeneity makes further improvements possible. To enable the optimization of properties, predictive models, developed from the results of previous work, were used to guide the selection of compositions and processing conditions for a new series of alloys. These alloys were then fabricated and tested to determine their mechanical properties, pitting corrosion resistance, and stress corrosion cracking resistance. This approach also resulted in alloys with a reduced quench rate sensitivity that will enable production of thicker cross sections or as thermal spray coatings.

Introduction

Nitrogen containing steels have been investigated for the better part of the last century (1, 2). Significant advances were made through the development of the Nitronic⁻ alloys¹ in the 1970's with specific alloys designed for either high strength, wear resistance or improved corrosion properties (3). Many significant advances were reported at the five previous international conferences on high nitrogen steels (4-8). Among the most significant were studies on nitrogen solubility (2, 9-11), thermodynamics (2, 9), mechanical properties (12, 13), corrosion properties (14), and the precipitation of intermetallics (9, 15). While many of these studies demonstrated improvements in properties, they also identified several limitations of these alloys including: a) the formation of brittle, stable nitrides and intermetallics, such as Cr₂N, sigma, and chi phase,(16) b) the formation of casting defects and macrosegregation which can render these highly alloyed materials unworkable by conventional wrought processing techniques (12, 13, 17) and c) the difficulty in producing predictable nitrogen levels during both conventional and pressurized casting methods (11, 12, 17). Collaborative research between the National Institute of Standards and Technology (NIST) and Crucible Research Corporation has shown that casting defects can be eliminated by melting High Nitrogen Stainless Steels (HNSS) under an ambient nitrogen atmosphere, atomizing with N₂ gas, and Hot Isostatic Press consolidation (HIP). It was also found that atomizing with N2 gas eliminated the hollow spheres normally associated with inert gas atomization and that HIP processing produces dense material with less porosity than typically found in castings (12, 13, 18).

The beneficial effects of nitrogen on the properties of HNSS have been reported previously (2, 9, 11, 14-16, 18). For example, research has shown that the Yield Strength (YS), Ultimate Tensile Strength (UTS), Charpy V-notch Impact Energy (CVN), corrosion resistance and wear resistance can all be improved by increasing the nitrogen content (2, 9, 13, 16). Nitrogen is an austenite stabilizer and it suppresses the formation of deformation induced martensite during cold work (13, 16). The benefits of nitrogen alloying can be augmented by the microstructural refinement, enhanced chemical homogeneity, and increased solubility of constituents that results from Powder Metallurgy (PM) and Rapid Solidification Processing (RSP). This approach (RSP, PM, and HIP consolidation) also provides the opportunity for near-net shape fabrication of the alloys, minimizing machining time and scrap. The alloys described in this study were prepared by N₂ gas atomization in the NIST Supersonic Inert Gas Metal Atomizer (SIGMA) followed by HIP consolation (13, 19, 20).

The goal of this research was to produce a single phase HNSS alloy with the following mechanical properties: UTS = 1050 MPa, tensile elongation = 50 %, and CVN = 120 J. In addition, a pitting and stress corrosion cracking resistance that exceeds that of implant grade 316L stainless steel was desired (19, 20). To accomplish these goals with a minimum of expense and effort, a predictive model was developed by assembling a database of results generated by 60 prior atomization experiments and then analyzing the database with a multiple regression analysis. This resulted in a set of regression coefficients that represented the influence of each constituent on nitrogen solubility, mechanical properties, and corrosion resistance. Analysis of the ferrite contents measured by Rechsteiner (9) provided coefficients for estimating the single phase (austenite) boundary for these alloys. This predictive model was then used to estimate the properties of a number of different alloy compositions from which 6 were selected to be produced.

¹References to commercial trademarks are for identification purposes only and in no way constitute endorsement or evaluation of the relative merits of these products.

Experimental

The design objectives for these alloys imposed a number of constraints on the compositions. The minimum N mass fraction was fixed at 0.8 % to ensure high strength and austenite stability, but was not allowed to exceed 0.95 % to preclude the formation of stable nitrides (e.g. CrN and Cr₂N). The Cr mass fraction was set at 28 % to 30 % to ensure a high nitrogen solubility for the alloy (11) and the Mo mass fraction was set at 2 % to increase corrosion resistance. Higher mass fractions of Mo were not considered due to both its high cost and its tendency to segregate, thus greatly enhancing the formation of the brittle sigma and chi-type phases. According to Speidel (16), "these phases in turn can embrittle highly alloyed manganese austenitic stainless steels..., thus resulting in a severe reduction of the impact toughness". Mn concentration was limited to a mass fraction of 15 % to minimize both its detrimental effect on corrosion properties and its tendency to stabilize ferrite (9, 16). For good corrosion resistance, the mass fraction of Mn should be kept lower than this, but Mn increases the solubility of N so the Mn content was set at 15 % to reach the minimum 0.8 % N solubility requirement (9, 12, 13). Finally, Ni, although relatively high in cost and detrimental to N solubility (2), was maintained above 12 % to ensure austenite stability.

The experimental alloys were produced by melting Fe, Cr, Mn, Ni and Mo by a vacuum induction melting technique, back filling the melt chamber with N_2 gas at the onset of melting, and atomizing in SIGMA. In an earlier study (18), it was shown that absorption of nitrogen from the atomizing gas is minimal (most absorption occurs during melting) and that the hollow particles found in Ar and He atomized powders are eliminated by atomizing with N_2 gas, apparently the trapped N_2 dissolves in the alloy (9, 18).

Particle size analysis was performed by first spin riffling the complete batch of atomized powder (typically 22 kg) to obtain a representative 5 g specimen, followed by sonic sifting for final particle size analyzes. The average particle size measured was between 30 μ m and 40 μ m for these alloys (21). Fully dense specimens were produced by HIP consolidation from -60 mesh (250 μ m) powder. Decarbonized mild steel cans were filled with powder, degassed, evacuated, sealed by electron beam welding and HIP processed at 1180 °C and 200 MPa (30 ksi) for two hours. The compositions of the consolidated specimens were determined using wet chemistry for metallic elements and a commercial gas analyzer for C, S, 0 and N. The 305 mm long consolidated HIP cans were cut into 76 mm long x 51 mm diameter sections. These sections were then used to prepare specimens for tensile, yield, impact, metallographic, hardness, corrosion, solution-treating, and X-ray diffraction tests.

While corrosion can cause failure of materials through a number of different mechanisms, the two failure modes of most concern for stainless steels are pitting corrosion and stress corrosion cracking. Electrochemical polarization tests (ASTM G61-86) and critical pitting temperature tests (ASTM G48-97) in several standard solutions² failed to induce pitting over the range of temperatures examined (25 °C to 95 °C) in samples of the previous batches of these alloys, hence these experiments were not attempted on the alloys produced for this study. Instead these alloys were evaluated by conducting potentiodynamic polarization experiments in a 10 mol/L LiCl solution that had proven capable of inducing pitting in the earlier alloys at (65 ± 0.5) °C. A AgCl reference electrode was developed for use in the LiCl solution and immersed in the solution at 65 °C (22). In addition, since one potential application of these alloys is as biomedical implants,

²The test solutions were (a) 3.5 % by mass NaCl, (b) 6 % by mass FeCl₃, (c) "green death" (10 g FeCl₃ + 10 g CuCl₂ + 0.062 L of 18 mol/L H₂SO₄ + 0.028 L of 11.6 mol/L HCl + 0.834 L H₂O), and (d) "yellow death" (1 g Fe₂(SO₄)₃ + 40 g NaCl + 0.008 L HCl + 0.950 L H₂O).

electrochemical polarization tests were also conducted in an artificial physiological solution (Hanks solution) at (37 ± 0.5) °C. For the Hanks solution, a commercial saturated calomel reference electrode was used at room temperature and connected to the solution via a salt bridge. These experiments were conducted essentially in accordance with ASTM G5-94 with two exceptions. A 250 mL double walled glass cell was used for the environmental chamber enabling better control of temperature. The samples were held using a Pt electrode holder of the type first used by Brauns and Schwenk (23, 24), after initial experiments confirmed that use of this type of holder would not significantly influence the results. For the potentiodynamic experiments, a series of initial experiments at different scan rates indicated that a scan rate of 1 mV/s was a good compromise between testing time and reproducibility.

The stress corrosion cracking (SCC) resistance of the alloys was evaluated with the slow strain rate (SSR) tensile test technique (ASTM G129-95). In this technique, cylindrical specimens are slowly loaded in tension until failure occurs. By comparing the strain to failure in an aggressive environment to that in an inert control environment, a measure of the relative susceptibility of an alloy to SCC can be obtained (25-27). The SSR technique has proven to be a relatively reliable indicator of SCC susceptibility (28). The SSR experiments were performed in a 500 ml PTFE-lined cell with closed-loop control of temperature (140 ± 1) °C. These tests were conducted on a computer controlled SSR testing system that was configured to record applied load, cross head displacement, elapsed time, and electrode potential at a constant cross head speed of 0.025 µm/sec $(1 \times 10^{-6} \text{ in/sec})$. The specimen preparation technique and other procedures used for SSR experiments are detailed elsewhere (25-27). While the SSR tensile tests were designed to be consistent with ASTM Standard Practice G129-95, this standard does not specify a testing environment. Boiling MgCl₂ at (155 ± 1) °C is a commonly used testing environment for the evaluation of SCC in statically loaded stainless steel samples (i.e. ASTM G38-94), but experience in our laboratory indicates that LiCl yields similar results, but can be used over a wider range of temperatures with less corrosion damage to the fracture surfaces. These two factors, plus the fact that the electrochemical experiments were being conducted in saturated LiCl, lead to this solution being selected for the SSR tests as well. After failure, the samples were promptly removed from the cell, rinsed in flowing water and alcohol, dried, and then stored in a vacuum desiccator until examined in the scanning electron microscope to verify the failure mechanism. The data from the experiments conducted in LiCl were compared to the intrinsic mechanical properties determined at 140 °C for each alloy through tests conducted in dry nitrogen gas.

Results and Discussion

The alloys in this study are compared to alloys from a prior study which were derived empirically from nitrogen solubility data (2, 13, 15, 16). In HNSS alloys, Mn in mass fractions below about 10 %, assists in the absorption of nitrogen and helps stabilize the austenite.(9,13) As Mn concentrations were increased, the nitrogen content in the alloys also increased. Also, increasing N content improved the mechanical and corrosion properties. Table I shows measured compositions of the alloys examined in this study. Uncertainties (3 σ) in reported values are $\pm 0.04 \cdot (\text{value})^{\frac{1}{2}}$. Table II shows N content predicted by a regression analysis (N_R) using the following formula:

$$N_{R} = const + \sum_{i} (C_{1i}E_{i} + C_{2i}E_{i}^{2})$$
(1)

Where const = -6.898E-01, and C_{1i} , C_{2i} , and E_i are shown in Table III. Equation (1) must be solved iteratively because of the recursive dependence on N content. Table II also shows the measured hardness, strength, elongation, corrosion pitting potential (PP), and volume fraction γ values. The volume fraction γ values were estimated from X-ray diffraction peak intensities associated with the

Table I Two Phase Allov Compositions (mass fraction %)

		- · ·	-		- 5		L	()	
Alloy #	Fe	Cr	Ni	Mn	Mo	Ν	Si	0	С	S	V	Cu
NSS.059	64.95	24.74	5.00	2.10	2.67	0.49	<.005	0.029	0.015	0.004	0.005	<.005
NSS.057	62.59	24.97	4.84	4.06	3.00	0.50	<.005	0.019	0.016	<.003	<.005	<.005
NSS.054	60.10	25.37	5.01	6.01	2.85	0.58	0.030	0.026	0.026	0.003	<.005	<.005
NSS.053	58.39	24.14	4.79	7.99	3.01	0.60	0.030	0.026	0.021	0.003	<.005	<.005
NSS.050	57.51	24.76	4.98	10.03	2.02	0.64	<.005	0.040	0.015	0.004	<.005	<.005
NSS.047	56.26	24.79	4.62	12.11	1.46	0.67	0.005	0.043	0.040	0.004	<.005	<.005
NSS.056	53.68	24.88	5.08	14.04	1.53	0.70	0.020	0.048	0.019	0.005	<.005	<.005
NSS.060	51.69	24.80	4.88	16.15	1.58	0.81	0.014	0.042	0.022	0.004	<.005	0.005
NSS.020	48.42	25.36	5.11	18.36	1.31	0.88	0.310	0.090	0.024	0.014	<.005	0.120
NSS.028	47.98	22.00	5.01	21.97	2.05	0.78	0.020	0.042	0.012	0.008	0.130	<.005
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Table	e II	Two	Phase	Allo	эy F	Properties
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	N _R	N _M	hardness	YS	UTS	%	PP	γ
Alloy #	(%)	(%)	(HV) ₀₀₀	(MPa)	(MPa)	elong.	V(SCE)	vol.fr.
NSS.059	0.46	0.49	318	577	924	39	-0.160	0.80
NSS.057	0.51	0.50	312	602	956	32	-0.218	0.67
NSS.054	0.58	0.58	317	593	961	34	-0.229	0.72
NSS.053	0.61	0.60	319	611	977	42	-0.177	0.79
NSS.050	0.64	0.64	319	644	1009	41	-0.212	0.82
NSS.047	0.69	0.67	337	620	1001	42	-0.298	0.94
NSS.056	0.74	0.70	331	655	1016	42	-0.311	0.92
NSS.060	0.78	0.81	354	679	1064	41	-0.259	0.97
NSS.020	0.86	0.88	347	657	1042	46	-0.308	0.94
NSS.028	0.78	0.78	339	651	1041	38	-0.329	0.98

 α -ferrite and γ phases and is shown only to indicate the relative proportions of α and γ within these alloys. (Due to limitations of the software and calibration standards used to calculate these values absolute concentrations with error limits cannot be determined).

Figure 1 shows representative microstructures of the alloys produced in a prior study (13). Due to slow cooling in the HIP (similar to slow cooling in ingot castings) σ and Cr₂N intermetallic phases precipitate in the alloys necessitating treatment (ST) solution (as described by Rechsteiner (9) and Orida (15)) to dissolve these brittle phases. Microstructures and X-ray diffraction patterns were compared between as-HIP and HIP + ST conditions to verify that the brittle dissolved. Figure 1(a) is a micrograph of the alloy with a Mn mass

Table III Regression Coefficients

$E_i (\frac{\text{mass}}{\text{fraction}})$	C_{li}	C_{2i}
% Cr	4.913 E -02	-1.298 E -04
% Ni	-6.398 E -03	0.000 E+00
% Mn	2.310 E -02	-8.494 E -05
% Mo	-6.103 E -05	0.000 E+00
% N	2.216 E -02	-5.110 E -02
% Cu	5.702 E -01	-1.057 E+00
% Si	-9.740 E -03	0.000 E+00
% P	-2.370 E -01	0.000 E+00



intermetallic phases were fully Figure 1: Micrographs of alloys (electrolytic 10 mol/L KOH: 3V, 3s). (a) 4 % Mn, 0.50 % N (as-HIP). Small dark structures are intermetallics, larger gray phase is α -ferrite.

- fraction of 4 % before ST, clearly (b) 4 % Mn, 0.50 % N (HIP + ST). Darker phase is α -ferrite.
- showing α -ferrite (larger grav (c) 10 % Mn, 0.62 % N (HIP + ST). Darker phase is α -ferrite.
- phase) and intermetallics (dark (d) 18 % Mn, 0.88 % N (HIP + ST). Darker phase is α -ferrite.

structures). The micrographs in Figure 1(b, c, d) show the alloys with Mn mass fractions of 4 %, 10 % and 16 % respectively after ST. Note that no intermetallic phases are present in any of these microstructures. The relative proportions of γ and α -ferrite are also apparent in this series of micrographs.

Figure 2 shows a typical X-ray diffraction pattern of these alloys in the as-HIP and HIP + ST condition. Although these diffraction patterns are for the alloy with a Mn mass fraction of 10 % (Figure 1(c)), it is representative of all the experimental alloys discussed in this earlier study. In the lower trace of Figure 2, showing the as-HIP condition, evidence is given of σ and Cr₂N intermetallics. The upper trace of Figure 2 indicates the absence of the intermetallics and an α -ferrite peak can be seen in the HIP + ST diffraction pattern. Thus the undesirable brittle phases are removed during ST and subsequent water quenching. The photomicrographs in Figure 1 clearly exhibit the benefits of rapid solidification processing, which are fine grain size and microstructural refinement.

It is necessary to recognize that the nitrogen content ultimately determines the properties of the alloy. That is, as N increases in these alloys, all of the other properties increase. According to Speidel and Uggowitzer (16), nitrogen is the most potent solid solution hardening element known in austenitic stainless steels. They attribute this effect to the additional interactions between moving dislocations and the stress fields that surround the nitrogen atoms which occupy the interstitial sites in the fcc crystal lattice. In addition, they show that the yield strength in these materials increases with the square root of the nitrogen concentration (16).



Figure 2: X-ray diffraction data showing the effect of solution treatment. Intensity is plotted as a function of diffraction angle (2θ) .



Figure 3: Strength vs. nitrogen content



Figure 4: Measured micro-hardness and estimated strength vs. cold reduction.

A strong correlation between N and strength is supported by the measured tensile and yield strength data (Table II and Figure 3). These alloys display a range in UTS from 924 MPa (134 ksi) to 1064 MPa (154 ksi) and a range in YS from 577 MPa (84 ksi) to 679 MPa (98 ksi) as the N mass fraction varies from 0.485 % (Mn mass fraction >2.1 %) to 0.807 % (Mn mass fraction = 16.15 %). HNSS alloys are known to have a high work hardening coefficient (16, 29, 30). Figure 4 describes an estimate of the UTS and YS following cold work. A specimen with a Mn mass fraction composition of 18.36 % was subjected to increasing amounts of cold work (10 % to 95 % reduction) in a laboratory rolling mill. Microhardness was measured after each level of reduction.

A model for estimating the YS and UTS from hardness values was derived from the data in Table II along with several tests on other high strength, high hardness HNSS alloys. Actual tensile test data at 50 % reduction has been plotted in Figure 4 to demonstrate the validity of this estimate. The measured values reveal that the estimated values are conservative. This leads to the conclusion that by cold working the alloys, YS and UTS values could be enhanced.

Table IV shows the measured compositions of the HNSS alloys most recently produced. The alloys numbered NSS.082 to NSS.087 are the experimental alloys that resulted from the predictive model previously mentioned. Alloy NSS.057 from an earlier study is included for comparison and represents a typical HNSS alloy where reduced Cr, Mn, and N resulted in a two phase microstructure seen as in Figure 1(b, c, d). Table V shows N_R (calculated with Equation (1)), measured N content, (N_M), hardness, YS, UTS, % elongation, strain-hardening exponent (SHE), and impact energy. Measurements

Table IV Single Phase Alloy Compositions (mass fraction %)

	-	-		-	-			`		
Alloy #	Fe	Cr	Ni	Mn	Мо	Ν	Si	0	С	S
NSS.057	62.59	24.97	4.84	4.06	3.00	0.50	0.00	0.019	0.016	<.003
NSS.082	40.79	29.82	13.93	11.99	1.94	0.97	0.48	0.059	0.017	0.002
NSS.083	42.56	29.90	13.91	10.29	1.95	0.94	0.37	0.055	0.021	0.003
NSS.084	39.27	27.42	14.94	15.07	1.93	0.84	0.46	0.045	0.019	0.003
NSS.085	43.81	29.65	15.13	8.03	1.96	0.86	0.50	0.046	0.014	0.003
NSS.086	46.33	29.35	15.02	5.96	1.94	0.83	0.51	0.044	0.016	0.003
NSS.087	45.29	29.49	12.85	9.00	1.92	0.88	0.50	0.042	0.020	0.004

Table V Single Phase Alloy Properties

	N	N ₄	hardness	YS	UTS	%		impact
Alloy #	(%)	(%)	$(HV_{1})_{00}$	(MPa)	(MPa)	elong.	SHE	ener.(J)
NSS.057	0.51	0.50	312	602	956	32.30	0.181	25
NSS.082	0.84	0.97	303	642	1096	55.70	0.214	69
NSS.083	0.79	0.94	298	635	1089	59.35	0.218	115
NSS.084	0.81	0.84	293	565	1034	57.85	0.231	126
NSS.085	0.73	0.86	296	609	1066	57.80	0.221	140
NSS.086	0.69	0.83	275	591	1066	53.90	0.225	132
NSS.087	0.77	0.88	300	642	1100	53.10	0.213	129

were made using methods described in ASTM E8 for UTS, YS and elongation, ASTM E646 was used to calculate SHE values, and ASTM E23 was used to calculate impact energy. The measured uncertainties (2σ) for UTS and YS values are ± 17 MPa, ± 1.3 % for elongation values, ± 0.003 for SHE, and ± 4 J for impact energy. Volume fraction . was found to be in excess of 0.99 for all the alloys listed (as determined by X-ray diffraction analysis and optical metallography).

Although solution treatment can be effective in eliminating the brittle phases, the duplex matrix was still a source of some concern. Ferrite is known to affect certain mechanical properties. Ferrite can cleave and fail catastrophically when rapidly loaded (e.g. when struck by a projectile). Under similar conditions, however, austenite does not cleave, it fails by a ductile mode (30, 31). Ferrite also reduces corrosion resistance, and the ferrite crystal structure has a much lower N solubility than austenite (32). Therefore, in this new set of alloys the chemistry was adjusted with the intent of producing a 100 % austenite material. The photomicrograph shown in Figure 5 (NSS.085 after



Figure 5: Micrograph of consolidated HNSS Figure 6: X-ray diffraction data from single showing a equiaxed single phase . grain structure. phase austenite atomized powder.





Figure 7: Plot of hardness vs. nitrogen content Figure 8: Plot of YS vs. nitrogen content data data from Table IV.

from Table IV.

HIP consolidation) is typical of the austenitic alloys in this latest study. Fine equiaxed grains $(\approx 25 \,\mu\text{m})$ of austenite are accompanied by small precipitates of manganese silicate amounting to less than 1 % of the volume. Figure 6 is a typical X-ray diffraction pattern exhibited by these alloys. No evidence of secondary phases was found in any of these newer alloys, either in the as atomized powder or after HIP. The relatively high CVN-s (exceeding 100 J in all but alloy NSS.082) are further evidence of the elimination of these undesirable second phases. These new austenitic HNSS chemistries can reduce production costs by reducing or eliminating the need for costly solution treatments. In addition, the absence of these phases will allow the fabrication of thicker sections (quench sensitivity in the previous alloys limited specimen thickness). This in turn will allow designers greater flexibility while taking advantage of the outstanding properties found in these alloys. In addition, the absence of the intermetallics in both the atomized powder and the HIP material strongly suggests that these powders could be used as feed stock for wear and corrosion resistant thermal spray coatings as a replacement for toxic hexavalent chromium. The data in Table IV demonstrates that, in general, as the N content is increased, mechanical properties are improved. As the nitrogen mass fraction varies from 0.83 % to 0.97 % the Vickers hardness varies from 275 HV₁₀₀₀ to 303 HV₁₀₀₀, the YS varies from 565 MPa to 642 MPa and UTS varies from 1034 MPa to 1100 MPa. The microhardness and YS data are plotted in Figures 7 and 8.

Figure 9 shows the results of the electrochemical experiments used to evaluate the pitting resistance of these alloys. In these experiments, pitting is identified by a monotonic increase in current as the potential of the electrode with respect to the reference electrode increased and the pitting potential is defined as the potential where this increase starts. Pitting was confirmed by visual examination in all cases. This type of experiment uses a high-gain closed-loop amplifier (a potentiostat) to control the potential of the sample with respect to a reference electrode. Since the potential of the reference electrode is fixed by thermodynamic equilibrium for an electrochemical reaction, controlling the potential of the sample with respect to this electrode amounts to controlling the thermodynamic conditions on the surface of the sample (or more precisely, control of the weighted average thermodynamic conditions). Then, slowly increasing the potential of the electrode at 1 mV/s amounts to increasing the force driving corrosion reactions in a manner similar to the addition of an oxidizing agent, but without requiring the mixing of solutions. In addition, since potential is linearly related to Gibbs free energy by the relationship $\Delta G = -nFE$, where F=Faraday=s constant and n=coulombs/mol, linearly scanning potential amounts to linearly scanning the free energy driving corrosion reactions. On the other hand, the relationship between Gibbs free energy and concentration is logarithmic ($\Delta G = -RT \ln(K)$). As a result, a 60 mV difference in the pitting potentials between two alloys indicates that an order of magnitude more oxidizer is required to



Figure 9: Pitting potential for alloys in : (a) Hanks Solution and, (b) 10 mol/L LiCl.

cause pitting in the alloy with the higher pitting potential $(2.3 \cdot \text{RT/F} = 0.061 \text{ V} \text{ at } 37 \text{ °C})$. By examining Figure 9, it can be seen that the pitting potential of the alloys exceeded that of 316 stainless steel by more the 600 mV. This value exceeds any uncertainties in these measurements. Since pitting reactions may be catalyzed by different environmental constituents, experiments should be conducted in a specific environment before utilizing any alloy. However, these results indicate that these alloys meet and exceed the performance of 316L SS in all applications.

The results of the SCC evaluation indicated that all of the alloys demonstrated good ductility in the 140 °C nitrogen reference environment. The average strain to failure (STF) value for the NIST HNSS alloys in this environment was (45.0 ± 9.7) %. The performance of each HNSS alloy far exceeded the 13.3 % value recorded for the 316L under the same experimental conditions. The ratios in Figure 10 compare the performances of the alloys in LiCl and nitrogen at 140 °C. As shown, most of the HNSS alloys demonstrated both good retention of ductility and resistance to SCC in the LiCl environment. However, the NIST alloys 053, 060, 085, and 087 did not perform as well in this environment. The fracture surfaces of these specimens consisted



Figure 10: STF ratios for experimental alloys.

primarily of intergranular-SCC, although some transgranular-SCC was observed on the surface of 087. The reduction in the ductility for NIST alloy 059 may be an indication that this alloy is susceptible to SCC. This was confirmed by fractographic analysis which showed a mixture of both intergranular and transgranular cracking, and ductile failure modes. No evidence of SCC was observed in any of the other HNSS alloys included in this study.

Applications

Considering the outstanding mechanical and corrosion properties of HNSS alloys, they have the potential to replace nickel based superalloys in many applications where the highest corrosion resistance is required (32). The industries where this potential resides are chemical, petrochemical, oil and gas production, pharmaceutical and offshore technologies. In addition these new HNSS with their simultaneous high strength, high hardness, ductility, impact strength and corrosion resistance have the potential to impact aerospace (engine cowlings and landing gear), marine (shafts and

propellers), military (personal and heavy armor), medical (hip and knee prostheses, angioplasty stents), and electric power generation (retaining rings) industries.

Conclusions

This study introduced a new processing technique for producing HNSS: gas atomization/HIP consolidation. This technique conveys the added benefits of microstructural refinement (5 μ m to 20 μ m grain sizes), enhanced chemical homogeneity, and fully dense near-net-shape fabrication to the already outstanding strength and corrosion resistance of these alloys. A previously developed model was used that accurately predicts phase stability, nitrogen solubility, and properties of HNSS. This model allowed a more rational approach to the production of a series of alloys with excellent mechanical and corrosion properties by avoiding much of the costly trial and error procedures that otherwise would have been required.

The measured mechanical property data provides confidence in an expected high reliability in structural components made from these alloys. In particular, the high ductility (> 50 % elongation), relatively high SHE (≈ 0.2), and good impact properties of these alloys are evidence of resistance to brittle failure and expected good wear properties. In addition, the alloys produced using the predictive model have, thus far, not given any indication of the presence of intermetallic. The lack of these brittle intermetallic phases in these alloys strongly suggests that they can be used for thermal spray coatings and that thicker sections can be produced due to a lower quench rate sensitivity.

The objective with respect to the corrosion properties of these alloys was to meet or exceed the corrosion resistance of 316L. The pitting corrosion experiments demonstrated that the alloys produced in this study are significantly more resistant to pitting attack than 316L. Since the well known improvement in pitting resistance offered by 316L over 304L amounts to an improvement in pitting potential that is typically less than 60 mV, the 600 mV improvement over 316L observed for these alloys is evidence of a dramatically superior pitting resistance. The slow strain rate tensile test technique employed here to detect SCC susceptibility uses a constantly increasing strain to impose stress on the sample. As a result, higher yield strength materials will be exposed to higher stresses during the experiment. Even though the new alloys produced here had dramatically higher yield strengths than 316L, not all of the alloys demonstrated susceptibility to SCC while 316L failed with reduced ductility and fractographic evidence of SCC. Therefore, it is concluded that alloys that did not exhibit susceptibility to SCC are more resistant to SCC than 316L, and even those that did fail by SCC may have done so at higher stress levels than those that caused cracking in 316L.

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