

## CHARACTERIZATION OF ATOMIZED HIGH NITROGEN STAINLESS STEEL AS A POSSIBLE IMPLANT MATERIAL

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High Nitrogen Stainless Steel (HNSS) can simultaneously have high strength (ultimate and yield) high hardness, high ductility, and outstanding corrosion properties. These properties can be further improved if these HNSS materials are produced from Hot Isostatic Press (HIP) consolidated, gas atomized powder due to the resulting microstructural refinement and increased chemical homogeneity that this Rapid Solidification Processing (RSP) imparts. This unusual combination of properties and the additional advantages of RSP near net shape manufacturing should make HNSS an excellent candidate for hip and knee prostheses, as well as other body implant devices. For this study HNSS alloys were produced that significantly exceed previously reported results. The high nitrogen solubility was achieved using alloy chemistry modifications and atmospheric nitrogen pressures. Strength, hardness, and corrosion properties are presented that support the opportunities HNSS materials offer as biocompatible materials.

### 1. INTRODUCTION

The evolution of joint arthroplasty has shown itself as a successful and cost-effective solution for musculoskeletal articular disorders. Over 500,000 hip and knee procedures were performed in the United States in 1995. Device usage in the younger, more active patient is placing greater demands on the materials of fabrication.<sup>1</sup> A limiting factor in realizing successful long term clinical outcome is material deficiency of the articulating surfaces. According to H. Wagner and M. Wagner,<sup>2</sup> wear particles, chiefly polyethylene from the articulating surfaces, are the primary cause of aseptic loosening (370,000 polyethylene particles are generated per step) and are the most important late complication of total hip replacement.

These events are leading to a renewed interest in other materials as a substitute for

polyethylene in hip articulation. Aluminum-oxide ceramic is one option. It has excellent sliding properties, but it is also brittle. Another option is metal alloys. Notable clinical experience with various metal articulation (McKee-Farrar, Ring, etc.) was obtained more than 30 years ago.<sup>1,2</sup> In these earlier studies device failure was found to result from improper manufacturing practice, often the result of mismatched articulating components. However, in instances when the proper design tolerances were met, some of these prostheses are still performing quite adequately 25 years later.<sup>2</sup> A possible explanation of these good results with properly manufactured metal prostheses is the enhanced tribological performance. Particle discharge has been measured to be 100 times less with metal articulations than with polyethylene pairings.<sup>2</sup> These findings have led to the application of over 400 metal articulations with good results over the past four years. (No macroscopically discernible metal abrasion and no metallosis of the soft tissues was observed following histologic examination.)<sup>2</sup>

Currently the application of metal alloys in mechanically stressed biomedical implants is limited to a small number of alloy systems. Cobalt-chromium-molybdenum alloys, e.g. Crucible Materials' Biodur™ CCM Plus™ alloy\* with 68.65 % Co, 26.00 % Cr, 5.00 % Mo, 0.20 % C, and 0.15 % N (mass fractions), is used extensively for the repair of stressed members and articulating joints due to its superior corrosion and mechanical properties. The Ti-6Al-4V alloy with 90.00 % Ti, 6.00 % Al, and 4.00 % V (mass fractions), has also been applied for numerous repairs where reduced weight and biocompatibility are needed (however, the surface of the Ti-6Al-4V alloy is usually protected by applying a wear resistant coating).<sup>3</sup> Finally, austenitic stainless steels (316 and 304) are used for less demanding applications due to their moderate mechanical properties and reduced corrosion resistance.

Recently, increasing interest has been shown in a new class of austenitic stainless

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

steels with strength and corrosion improvements resulting from the addition of nitrogen to the alloy.<sup>4,5,6</sup> This study will explore a new class of High Nitrogen Stainless Steel (HNSS) alloys fabricated from gas atomized, HIP consolidated rapidly solidified powders. These new HNSS alloys, compared to the previously mentioned metal alloys, provide better combinations of strength, corrosion resistance, hardness, ductility, impact strength, and cost factors and could, therefore, excel in biomedical implant applications.

## 1. EXPERIMENTAL

The alloys described in this study were prepared by N<sub>2</sub> gas atomization in the National Institute of Standards and Technology's (NIST) Supersonic Inert Gas Metal Atomizer (SIGMA) followed by HIP consolidation. This technique and its benefits have been described more extensively elsewhere.<sup>7</sup> Several important features of this processing route are enhanced chemical homogeneity, increased microstructural refinement, greatly reduced grain size, increased solubility of the constituents and 100% theoretical density. HIP consolidation also lends itself well to producing near net shapes, thus reducing machining time and scrap-recycling problems. A series of measurements of the microstructural, mechanical, and corrosion properties of these materials has indicated outstanding characteristics.

In these HNSS, as the nitrogen content increases, the alloys get stronger, and more corrosion resistant. However, as the nitrogen mass fraction approaches about 1 %, stable nitrides (e.g. Cr<sub>2</sub>N) are formed. In addition, these essentially austenitic ( $\gamma$ ) alloys are prone to the formation of  $\delta$  ferrite and  $\sigma$  phase. All of these secondary phases tend to degrade mechanical and corrosion properties. To maximize nitrogen content (up to ~ 0.95 %) and to ensure a fully  $\gamma$  phase structure, the authors designed a predictive model incorporating a linear regression of their accumulated data from sixty previously successful atomization runs. This allowed the researchers to evaluate the phase stability of several hundred alloys, while only producing six, resulting in a tremendous

cost savings with far more success in meeting the design targets.

The experimental alloys were produced by melting Fe, Cr, Mn, Ni, and Mo using a vacuum induction melting technique, back filling the melt chamber with N<sub>2</sub> gas at the onset of melting, and atomizing in the NIST SIGMA facility.<sup>7,8</sup> In an earlier study by the authors it was demonstrated that absorption of nitrogen from the atomizing gas was minimal (most absorption occurs during melting) and that the hollow particles often found in Ar or He atomized powders are eliminated by using N<sub>2</sub>. Apparently any trapped atomizing gas subsequently dissolves in the alloy.<sup>8</sup>

The powder size distributions were determined 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 particle size analysis. The average particle size measured was between 30 μm and 40 μm for these alloys. Fully dense specimens were produced by HIP consolidation from -60 mesh (250 μm) powder. Decarbonized mild steel cans were filled with powder, degassed, evacuated, sealed by e-beam welding, and HIP processed at 1180 °C and 200 MPa 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, O, 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 the tensile, impact, metallographic, hardness, corrosion, solution treating, and x-ray diffraction specimens.

### 3. RESULTS AND DISCUSSION

Table I shows measured compositions of the alloys examined in this study. Table II shows predicted and measured N content (N<sub>R</sub> and N<sub>M</sub> respectively), hardness, strength, elongation, strain-hardening exponent, and impact energy. The N<sub>R</sub> values were obtained from the previously mentioned predictive model. In Table II UTS is ultimate tensile strength, YS is 0.2 % offset yield strength, and SHE is the strain-hardening exponent. Measurements 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 ( $2\sigma$ ) for UTS and YS values are  $\pm 17$  MPa,  $\pm 1.3$  % for elongation values,  $\pm 0.003$  for SHE, and  $\pm 4$  J for impact energy. Volume fraction  $\gamma$  was found to be in excess of 0.99 for all the alloys listed (as determined by x-ray diffraction analysis and optical metallography).

Prior studies by the authors<sup>9</sup> and others<sup>10,11</sup> have found it necessary to solution treat and water quench HNSS alloys to eliminate the previously mentioned  $\text{Cr}_2\text{N}$ ,  $\delta$  ferrite, and  $\sigma$  phases. However, as previously mentioned, all of the alloys produced for this study were nearly 100 %  $\gamma$ . This dramatically reduces the production cost by eliminating costly solution treatments and may improve corrosion and mechanical properties of these alloys.

The photomicrograph shown in Figure 1 (NSS.085 after HIP consolidation) is typical of all the alloys in this study. Fine equiaxed grains of austenite are accompanied by small circular specks of an as yet unidentified second phase that amounts to less than 1 % of the volume. Figure 2 is a typical x-ray diffraction pattern produced by these alloys. A relatively narrow scan ( $\Delta 2\theta = 20^\circ$ ) is shown for clarity, however, even broad  $2\theta$  scans exceeding  $100^\circ$  showed no evidence of secondary

**Table I - Alloy Compositions (mass fraction %)**

Alloy #	Fe	Cr	Ni	Mn	Mo	N	Si	O	C	S
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 II - Alloy Properties**

Alloy #	$N_R$ (%)	$N_M$ (%)	hardness (HV <sub>1000</sub> )	YS (MPa)	UTS (MPa)	% elong.	SHE	impact ener. (J)
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

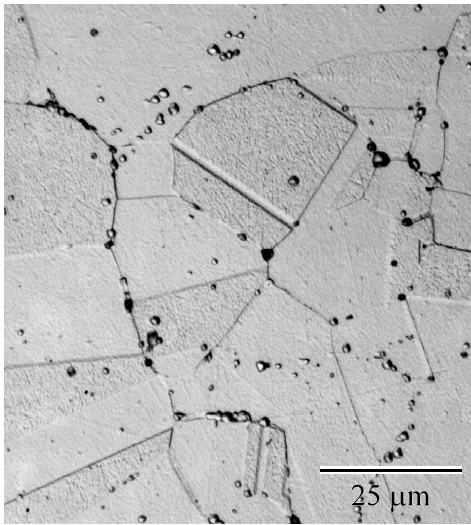


FIGURE 1

Micrograph of consolidated HNSS showing a fully dense, equiaxed grain structure.

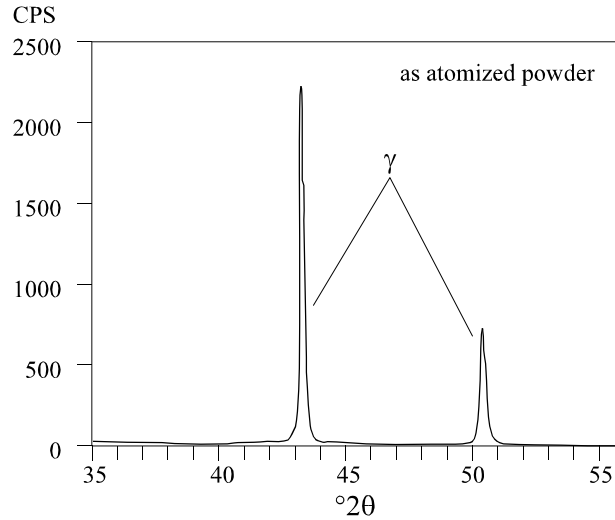


FIGURE 2

X-ray diffraction data for as atomized powder showing evidence of 100 %  $\gamma$  structure.

phases in any of the alloys either before or after HIP consolidation. The relatively high impact energies (exceeding 100 J in all but one alloy) are further evidence of the elimination of these undesirable second phases.

The data in Table II demonstrate that in general, as the N content is increased, mechanical properties are improved. As the N mass fraction varies from 0.83% to 0.97% the Vickers microhardness varies from 280  $HV_{1000}$  to 303  $HV_{1000}$ , 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 3 and 4 where error bars indicate the uncertainty in the measured values ( $\pm 8 HV_{1000}$  and  $\pm 17 MPa$  respectively).

For body implant devices such as joint replacements, tribological performance is clearly important. The increased hardness conferred by the increased nitrogen content and high SHE is expected to result in an improvement in wear resistance. Preliminary evaluation shows the coefficient of friction of these alloys, measured in dry pin-on-disk testing (HNSS against HNSS), to fall in the range  $\mu = 0.5$  to 0.6, similar to

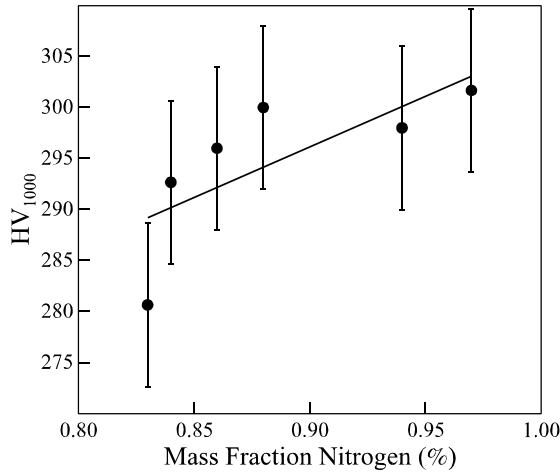


FIGURE 3

Plot of hardness vs. nitrogen content data from Table II.

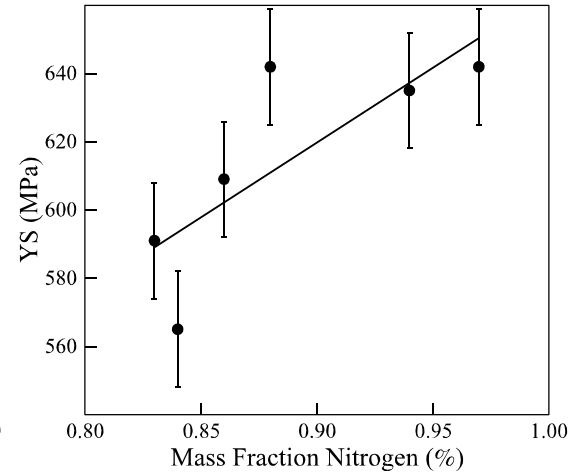


FIGURE 4

Plot of YS vs. nitrogen content data from Table II.

commercial steels. A tribological investigation for these alloys is under way and will be reported on in a future publication.

Preliminary electrochemical corrosion measurements on these alloys and on 316L in a synthetic physiological solution (Hanks solution) and in chloride solutions indicate that an implant made from one of these new HNSS will exhibit lower corrosion rates and be less susceptible to localized corrosion failure modes (pitting, crevice corrosion, etc.) than 316L and similar alloys.

#### 4. CONCLUSIONS

The mechanical property data presented for these HNSS alloys provides confidence in an expected high reliability in structural prostheses made from these alloys. In particular the high ductility (> 50% elongation), relatively high SHE ( $\approx 0.2$ ), and good impact properties of these alloys are evidence of resistance to brittle failure and expected good wear properties. Preliminary corrosion tests indicate improved performance relative to 316L and similar alloys.

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