Austenitic Stainless Steels with Enhanced Mechanical Strength

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ABSTRACT
The commonly used grades of austenitic stainless steels (303L, 304L and 316L) exhibit modest levels of mechanical strength, when sintered in a 100% hydrogen atmosphere. Hydrogen sintering is essential for the achievement of good corrosion resistance. Hence, despite having good corrosion and oxidation resistance, the usage of PM austenitic stainless steels is limited to applications that are less demanding from the mechanical strength point of view.

The present work is aimed at enhancing the room and elevated temperature mechanical strengths of austenitic stainless steels, without compromising their corrosion resistance. These enhancements are achieved via modification of alloy composition and sintering practice.

INTRODUCTION
Among the various families of wrought stainless steels, the austenitic family commands the highest volume of usage despite its high material cost. This is because alloys of this family offer excellent corrosion resistance, combined with adequate mechanical strength and good formability. They also exhibit remarkably good toughness and are readily hardenable by cold work. In the wrought form, their high rate of work hardening is frequently put to use to help achieve a wide range of mechanical properties. The alloys of the ferritic family, in comparison, are significantly lower in cost and offer only a moderate level of corrosion resistance. As a result, the ferritic alloys are selected in many high volume applications which can tolerate a modest level of corrosion resistance. In addition, the ferritic alloys are preferred in applications involving cyclic heating and cooling as they exhibit greater resistance to thermal fatigue when compared to the austenitic alloys. The precipitation hardenable (PH) and the martensitic families of stainless steels offer significantly higher strengths compared to both the austenitic and the ferritic alloys. The usage of the PH family of alloys is limited primarily due to its high processing (thermo-mechanical) cost. The alloys of the martensitic family suffer from poor fabricability, as well as from their relatively low corrosion resistance.

The PM processed austenitic stainless steels do not enjoy the same degree of success as their wrought counter parts do. This is because it is difficult to achieve both good corrosion resistance and a moderately high mechanical strength in these alloys when processed under the most commonly used sintering practices. In the PM processing of stainless steels it is essential to employ a 100% hydrogen sintering atmosphere in order to avoid chromium nitride precipitation in the material and thereby retain the alloy's corrosion resistance. In addition, the use of a high sintering temperature (above 1230°C) is often preferred for achievement of a relatively higher sintered density as well as for reduction of surface oxides. Reduction of surface oxides leads to enhanced corrosion resistance and good ductility.

Sintering of an austenitic stainless steel in dissociated ammonia (DA) atmosphere (75% hydrogen/25% nitrogen) invariably results in the formation of chromium nitride precipitates in the matrix, which leads to deterioration of corrosion resistance. Despite this drawback a significantly large volume of austenitic stainless steels are currently sintered in DA, as their corrosion and other properties are acceptable in many of the 'less demanding' applications. Nevertheless, it is

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imperative that in order to open up more applications for PM austenitic stainless steels these materials do need to combine high mechanical strength with good corrosion resistance.

Strengthening by cold work is not an option in PM. In consideration of this, one needs to look for other means to enhance mechanical strength. These may include:
(a) Solid solution strengthening by substitutional alloying elements
(b) Solid solution strengthening by interstitial alloying elements
(c) Dispersion strengthening via introduction of sub-microscopic hard phase particles
(d) Matrix reinforcement by introduction of hard particles or fibers
(e) Grain refinement

This work examines the effectiveness of three of the above options (a, b, and d) in enhancing mechanical strength of PM austenitic stainless steels.

Two alloys were used in this study. One of these was 316L, which is a highly popular grade of austenitic PM stainless steel and the other alloy was 310L, which contains higher levels of Cr and Ni than 316L. The latter was selected as the test alloy for the determination of the effects of alloy composition (solid solution strengthening) on the mechanical properties. Alloy 310L is a well established wrought austenitic alloy which offers superior oxidation resistance combined with relatively high elevated temperature strength. Although 310L contains higher amounts of Cr and Ni compared to 316L, in the powder form of the alloy does offer adequate compressibility and consequently is suitable for PM processing. The 100% hydrogen sintered 316L was considered to be the 'reference' material.

In the wrought processing of austenitic stainless steels, it is possible to enhance the mechanical strength of the alloy by injecting nitrogen into the molten metal prior to ingot casting. Presence of nitrogen atoms at interstitial sites in the matrix leads to strengthening of the alloy. In PM processing this approach can be utilized only in limited way, since it requires extra care to prevent chromium nitride precipitation in the matrix during sintering. Avoidance of chromium nitride precipitation requires careful control of the amount of nitrogen absorbed during sintering, as well as the employment of rapid cooling following sintering to suppress nitride precipitation.

Effect of matrix reinforcement was investigated by admixing with a hard alloy powder. HB 400 alloy powder was used as the reinforcement agent. This concept has been investigated earlier by other researchers for improvement of wear resistance of 316L [1]. However, no mechanical properties data are available in the literature for this composite material.

Fatigue strength of an alloy is a critical material property for components subjected to cyclic loading. Unlike wrought steels, it is not easy to predict fatigue strength of PM steels based on static mechanical properties. This study includes a comparative evaluation of fatigue performance of PM 316L and PM 310L sintered in 100% hydrogen.

MATERIALS

Stainless steel 316L and 310L powders were used in this study. Both powders were nominally minus 149 microns in particle size, and were produced by water atomization using commercial production equipment at North American Hoganas. Chemical compositions and physical properties of the powders are listed in Table 1.

Tests aimed at evaluating the effect of a hard phase additive utilized HB 400 gas atomized powder. The additive amount was 20% by mass. The nominal particle size range of HB 400 powder was 15 to 45 microns and its apparent density was 4.74 g/cm^3. It comprised of 29.7% Mo, 9.8% Cr, 2.75% Si, 1.0% Ni, 0.75% Fe, 0.02% C, and balance Co.

Alloy	Cr	Ni	Mo	C	Si	Mn	P	S	O	N	A D g/cm^3	<45μm %
316L	16.7	13.4	2.2	0.029	0.87	0.10	0.012	0.010	0.176	0.039	2.88	48.4
310L	24.7	20.0	0.0	0.029	1.03	0.11	0.008	0.010	0.205	0.047	2.79	50.3

Table 1. Chemical compositions (mass %) and physical properties of powders used

EXPERIMENTAL PROCEDURE

(1) Static Mechanical Properties Evaluation:

All powders used in this study were lubricated with 1.0% Acrawax. Test samples employed were in the form of Transverse Rupture Strength (TRS) bars and 'dog bone' tensile test specimens (MPIF Standard 35). All green compacts were prepared using a double acting die in a hydraulic press. The green densities of all samples used in the study were kept at 6.60 g/cm^3. All green compacts were delubricated in a laboratory pusher furnace in an atmosphere of dissociated ammonia at a temperature of 600°C. All sintering was carried out in a programmable batch furnace having a work zone of one cubic foot. The heat up and the cool down profiles were kept the same for all sintering runs. For all sintering runs the sintering temperature was held at 1316°C and the sintering time was kept at 45 minutes. Sintered densities of all samples in this study ranged from 7.00 to 7.07 gm/cm^3.

The first group of tests was designed to determine the effect of nitrogen content on the mechanical properties of 316L and 310L. Four different sintering atmospheres were employed: 100% hydrogen, 90% hydrogen/10% nitrogen, 85% hydrogen/15% nitrogen, and 80% hydrogen/20% nitrogen. Gas cylinders containing the specified gas compositions were procured from (and certified by) an industrial gas supplier. Cooling of samples from the sintering temperature to room temperature was carried out in the same gas composition as was used for sintering. The cooling rate from the sintering temperature to 800°C was 1.1°C/sec. In each test, samples from the two test alloys were sintered in the same sintering run.

The second group of tests focused on the effect of HB 400 addition on the mechanical properties of 316L and 310L. Here, only two sintering atmospheres were employed: 100% hydrogen and 90% hydrogen/10%nitrogen. For these tests 316L and 310L powders were admixed with 20%, by mass, HB 400 powder and compacted into TRS bars and 'dog bone' tensile specimens. The compaction, delubrication, and sintering parameters were kept the same as used for the first group of tests.

Sintered TRS bar specimens were tested for sintered density, dimensional change, and microstructure. Sintered 'dog bone' test specimens were used for determination of UTS, 0.2% yield strength, elongation, and hardness. Elevated temperature mechanical testing was conducted at 650°C under a shroud of argon gas. All mechanical testing was carried out by Westmoreland Testing and Research Laboratory, Youngstown, PA 15696. The broken room temperature tensile test specimens were used for determination of oxygen, nitrogen and carbon contents. LECO Model TCC 436 analyzer was used for determination of oxygen and nitrogen contents, while a LECO Model CS 244 analyzer was used for determination of carbon contents.

(2) Determination of Fatigue Properties

Only the dispersoid-free, 100% hydrogen sintered 310L and 316L materials were tested for fatigue strength. The test specimens were prepared from the same blends of 316L and 310L as used for the other tests. Test specimens were in the form of 90 mm long, ISO 3928 un-notched test bars, modified with a small chamfer (Fig. 1). The compaction and sintering parameters were kept the same as used for static mechanical testing. The sintered densities of the fatigue test specimens were 7.05 g/cm^3.

Plane four point bending displacement controlled fatigue tests were performed using fully reversed load ratio (R = -1) at 25 – 30 Hz. Before testing the corners of the test bars were carefully ground to remove burr. The load determinations were based on the staircase method, per MPIF Standard 56, with a run out limit of 2 million cycles. Fatigue survival limits for 50% and 90% probability (σ_{50} and σ_{90}) and respective standard deviations (*s*) were determined.

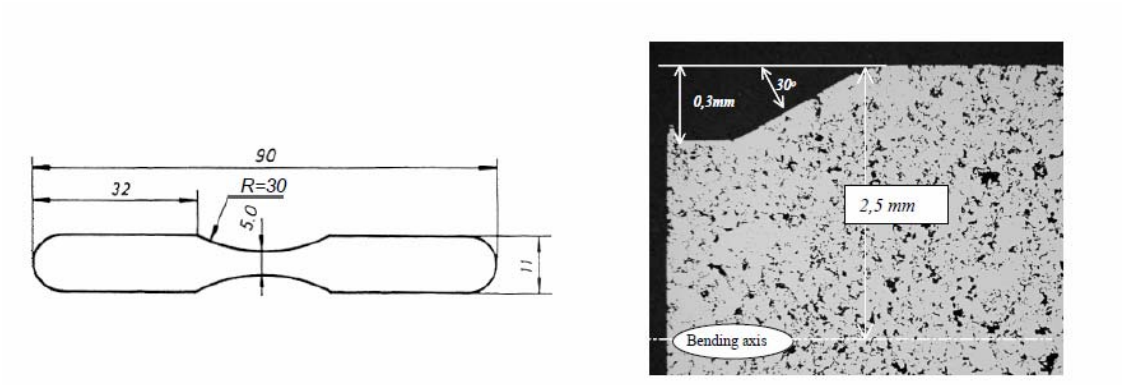


Figure 1. Modified ISO 3928 Fatigue test specimen with chamfered edges

RESULTS AND DISCUSSION

(1) Static Mechanical Properties

The room temperature mechanical strength, ductility, and hardness results are presented in Table 2, along with the interstitial contents of the tested samples. Figure 2 is a plot of yield strength as a function of the nitrogen content of sintering atmosphere. The UTS and yield strength of 310L are considerably higher than those of 316L for each combination of sintering atmosphere and HB 400 modification. Typically, 310L samples exhibit 25% higher yield strength compared to similarly processed 316L. HB 400 modified 316L and 310L show typically 12% higher yield strength over HB 400-free samples of the same alloy when sintered in 100% hydrogen. However, no such benefit is seen from HB 400 addition when sintering is carried out in the 90% hydrogen/10% nitrogen atmosphere.

Microstructures of 100% hydrogen sintered 316L and 310L samples are shown in Figure 3. Both microstructures show fully austenitic grain structure with well rounded porosity. The grain interiors and grain boundaries are free of carbides and nitrides.

Alloy	Density	Sintering Atmosphere	UTS	Y S	Elon	Hard.	Oxygen	Nitrogen	Carbon
	gm/cm^3	% H_2/%N_2	MPa	MPa	%	HV10	ppm	ppm	%
316L	7.03	100/0	334	134	20.5	80	860	67	0.021
310L	7.07	100/0	389	183	27.5	94	2363	115	0.018
316L	7.05	90/10	419	239	18.0	106	1859	1475	0.024
310L	7.07	90/10	499	298	19.0	131	3186	2363	0.022
316L	7.04	85/15	431	262	15.0	118	1716	2117	0.020
310L	7.05	85/15	524	328	17.0	138	2912	2844	0.022
316L	7.03	80/20	457	276	16.5	120	1949	2212	0.020
310L	7.05	80/20	532	330	17.0	138	3069	3170	0.023
316L+HB400	7.02	100/0	341	177	14.0	101	1067	22	0.020
310L+HB400	7.07	100/0	365	204	13.5	109	1834	39	0.022
316L+HB400	7.00	90/10	349	237	8.0	113	1766	1311	0.021
310L+HB400	7.02	90/10	441	287	10.0	129	2607	1945	0.023

Table 2. Room temperature mechanical properties and interstitial contents

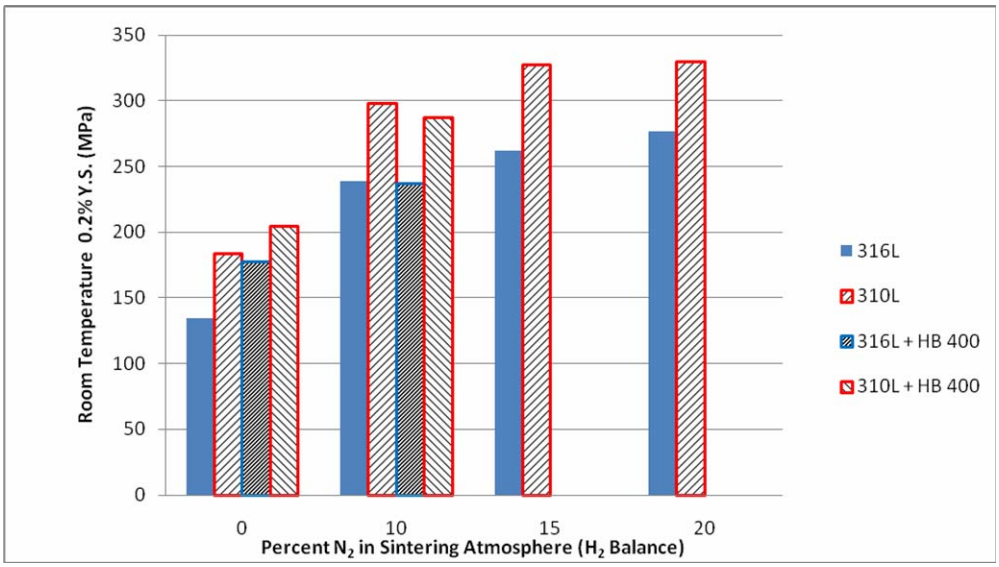


Figure 2. Room temperature Y.S. as a function of N_2 content of sintering atmosphere

The 100% hydrogen sintered samples from both alloys contained very small amounts of residual nitrogen. Hence, the higher yield strength and U T S of 310L sintered in 100% hydrogen over similarly processed 316L can be attributed entirely to solid solution strengthening from the 50% higher chromium present in the alloy. It has been reported in literature that Ni does not contribute to solid solution strengthening in stainless steels [3].

As expected the hydrogen/nitrogen mixed gas sintered samples contained significant amounts of nitrogen. Also, the residual nitrogen contents in the two alloys increased with the nitrogen content of the sintering atmosphere. The 310L samples absorbed greater amounts of nitrogen compared to the 316L samples. This can be attributed to the higher chromium content in the 310L alloy. Significant strengthening is seen in both steels from alloying with nitrogen. However, it is important to keep in mind that the nitrogen content should not be so high that it results in the formation of chromium nitrides in the alloy matrix during cooling. If chromium nitride formation occurs in the sintered stainless steel, chromium will be depleated from the matrix and corroision resistance of the material will deteriorate. Chromium nitride formation is also influenced by the cooling rate (from the sintering temperature to about 800°C); a rapid cooling rate supresses chromium nitride formation and also minimizes any additional nitrogen absorption at intermediate temperatues. Several researchers have determined, for specific cooling rates, the critical nitrogen level necessary for avaoidance of chromium nitride formation in 316L. (Although no such data is available in the literature for 310L, the solubility limit of nitrogen in 310L is expected to be higher than that of 316L due to its higher Cr content, and the critical nitrogen level is also expected to be somewhat higher.) Frisk et al. have determined the critical nitrogen content for 316L to be 4000 ppm for a cooling rate of 1.0°C/sec [4]. Zitter et al. have indicated that corrosion resistance of 316L is unaffected if the nitrogen content is less than 3000 ppm [5]. Samal et al. have reported deterioration of corrosion resistance of 316L when nitrogen content was 2400 ppm. for a cooling rate of 1.1°C/sec [6]. Based on these data, it can be said that the use of a 90% hydrogen/10% nitrogen sintering atmosphere is definitely safe for both alloys under most normal sintering conditions. Considering this, the combined effect of selecting 310L and utilizing a 90% hydrogen/10% nitrogen leads to a two fold increase in yield strength over that of a 100% hydrogen sintered 316L. The 85% hydrogen/15% nitrogen sintering atmosphere is considered safe to use only for 316L. The use of 80% hydrogen/20% nitrogen atmosphere is not recommended for either alloy. Relative enhancements in the mechanical strength become smaller and smaller as the amount of nitrogen in the sintering atmosphere beyond 10%.

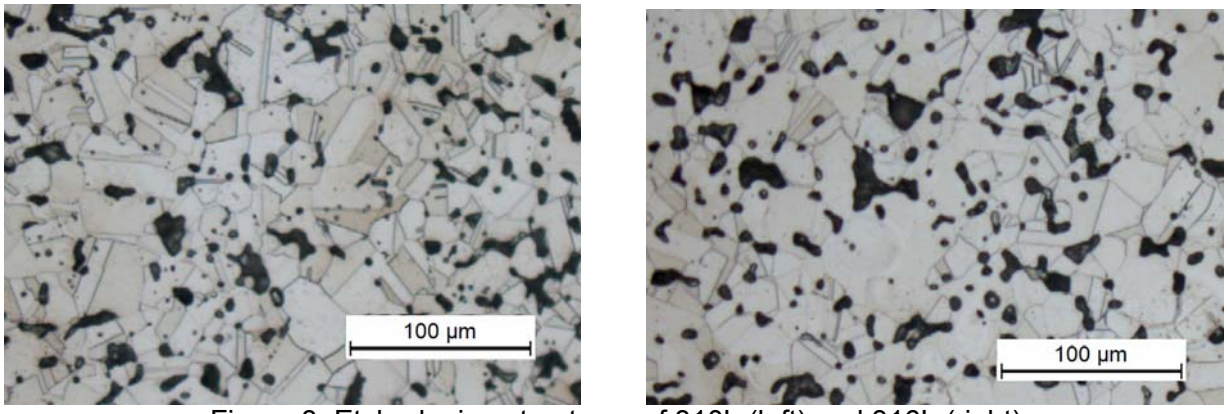


Figure 3. Etched microstructures of 310L (left) and 316L (right)

Table 3 and Figure 4 present the elevated temperature mechanical properties of 316L, 310L, and the HB 400 modified versions the alloys sintered in 100% hydrogen and 90% hydrogen/10% nitrogen atmospheres. In 100% hydrogen sintering 310L shows approximately 10% higher yield strength over similarly processed 316L. In the 90% hydrogen/10% nitrogen sintering 310L samples typically shows 25% higher yield strength over their 316L counterparts. HB 400 modification enhances mechanical strength under both sintering atmospheres and for both alloys. Hence, enhancements in the elevated temperature yield strength can be achieved by all three means - solidsolution strengthening, nitrogen alloying and hard phase addition.

Alloy	Density	Sintering Atmosphere	UTS	Y S	Elon.	Oxygen	Nitrogen	Carbon
	gm/cm^3	% H_2/%N_2	MPa	MPa	%	ppm	ppm	%
316L	7.05	100/0	187	84	10.5	860	67	0.021
310L	7.06	100/0	192	92	12.5	2363	115	0.018
316L	7.03	90/10	229	124	8.5	1859	1475	0.024
310L	7.03	90/10	244	157	9.0	3186	2363	0.022
316L+HB400	7.04	100/0	200	118	9.0	1067	22	0.020
310L+HB400	7.04	100/0	242	128	9.0	1834	39	0.022
316L+HB400	7.00	90/10	207	143	5.0	1766	1311	0.021
310L+HB400	7.00	90/10	232	188	13.0	2607	1945	0.023

Table 3. Elevated temperature (650^0C) mechanical properties and interstitial contents

HB 400 modification of these two austenitic stainless steels may be characterized as non-continuous reinforcement of their matrices by the hard particles, similar to that of a metal matrix composite (MMC). SEM examination of the fracture surfaces of the HB 400 modified 310L sample showed that there was no de-cohesion at the hard particle/matrix interface; and that the HB 400 particles had undergone fracture along with the matrix. SEM/EDS analyses of the fracture surface of HB 400 particles also indicated that a modest amount of chromium had diffused into the HB 400 particles during sintering. These observations indicate that there was a limited degree of sinter bonding between the matrix and the HB 400 particles, and this may account for the minimal reduction in ductility compared to the HB 400-free materials, at both room and elevated temperatures.

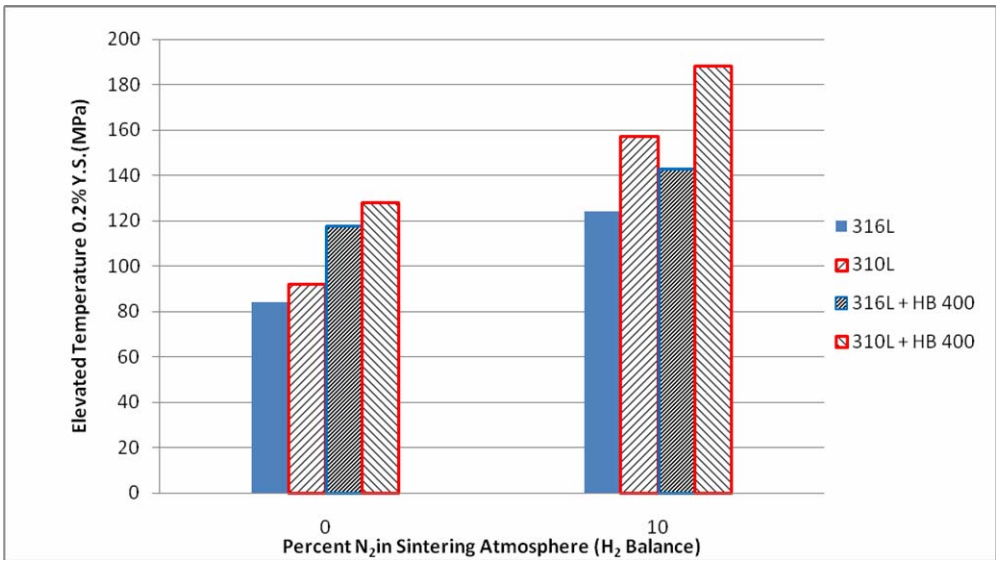


Figure 4. Elevated temperature Y.S. as a function of N_2 content of sintering atmosphere

(2) Fatigue Properties

The results of the fatigue testing are presented in Table 4 and the corrsponding SN-curves are shown in Figure 5. The fatigue limits with 50% and 90% survival rates are denoted as σ_{50} and σ_{90}, respectively. The measured standard deviation is denoted as '*s*'. It is noted that fatigue limit of 310L is around 8% higher than that of 316L. In both cases the scatter in the data is small.

As seen in Fig. 5, both materials have several failed specimens between 10^6 and $2x10^6$ cycles. This means that it is unclear if a plateau in the SN-curve has been reached and the run out limit should be set higher than $2x10^6$ cycles to verify the measured fatigue limit. This was not possible for practical reasons and the results must therefore be used with some caution.

The fatigue properties obtained here translate to fatigue endurance ratios (F.E.R.) of 0.36 for 310L and 0.40 for 316L. This is based on mean fatigue life (σ50). Using the same criteria (σ50), Sanderow et al. had determined the F.E.R. of 6.90 g/cm^3 density, nitrogen free 316L to be approximately 0.34. Their study was based on rotating beam fatigue testing of machined impact bar specimens [2].

Material	σ_{50} [MPa]	*s* [MPa]	σ_{90} [MPa]
310L	144	<7.5	134
316L	134	<7.5	124

Table 4. Summary of fatigue properties

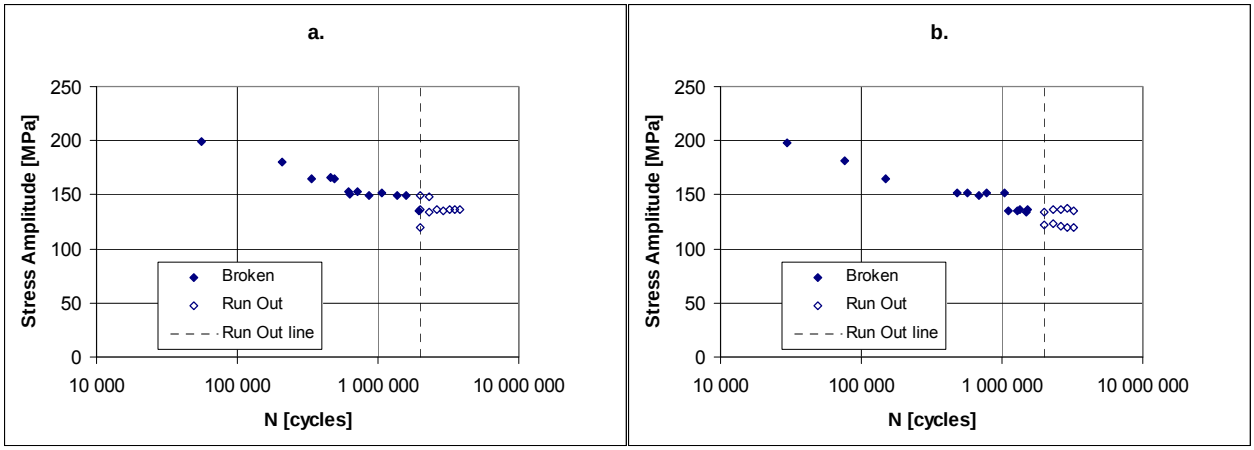


Figure 5. SN-curves for 310L (a) and 316L (b)

CONCLUSIONS

1. Significant strengthening can be achieved in both 316L and 310L by sintering in a 90% hydrogen/10% nitrogen atmosphere, when compared to 100% hydrogen atmosphere.
2. Use of 310L in the place of 316L can provide higher room and elevated temperature mechanical strengths, for both 100% hydrogen and 90% hydrogen/10% nitrogen, sintering atmospheres.
3. Alloy 310L offers 8% higher fatigue strength compared to 316L for the 100% hydrogen atmosphere sintering.
4. Admixing of HB 400 powder to 316L and 310L does lead to enhancements of their mechanical strengths at both room and elevated temperatures (650°C), with minimal reduction in ductility.

ACKNOWLEGEMENT

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