Characterization of Martensitic Stainless Steels in PM Components

Amber Neilan, Roland Warzel III & Dr. Bo Hu
North American Höganäs
111 Höganäs Way
Hollsopple, PA 15935

Roger Neyman, & Joe Hinchliffe
SMC Power Metallurgy
1251 Route 6 West
Galeton, PA 16922

ABSTRACT

Martensitic stainless steels are widely used for their superior mechanical properties and moderate corrosion resistance. Martensitic 400 series stainless steel can be heat treated to a wide range of hardness and strength levels. There are many different variations of martensitic 400 series stainless steel, each with its own unique property characteristics for corrosion resistance, mechanical and physical properties as well as surface aspects. Selecting the right martensitic stainless steel grade for a specific application is very important in order to achieve a workable solution. This paper will evaluate properties of common 400 series stainless grades to determine the optimum material and processing methods for required properties. As a comparison, properties of a precipitation-hardened (PH) steel were also examined.

INTRODUCTION

Powder metallurgy (PM) stainless steels are a popular manufacturing choice for applications that require superior corrosion resistance, high temperature resistance and durability. The stainless steel family can be divided into numerous categories, which are defined by their alloying elements, areas of application or their metallurgical structures. [1]

Ferritic stainless steel are the most basic of stainless grades, due to their simple composition of iron and chromium. The ferritic stainless steels consist of 10.5-18% chromium, carbon levels below 0.05%, and, unlike austenitic stainless steels, normally contain no nickel. They are superior in oxidation and corrosion resistance compared to martensitic stainless steels, but generally inferior when compared to austenitic stainless steels. They are also resistant to stress corrosion cracking, and provide high scaling resistance at elevated temperatures.[2] While ferritic stainless steels are useful for their corrosion properties, they generally have only moderate levels of strength. [3] Targeted applications for the ferritic stainless steel PM grades include automotive exhaust flanges and hot exhaust gas oxygen (HEGO) sensor bosses. By adding carbon and nitrogen to ferritic stainless steels, the higher strength martensitic stainless steels can be achieved.

Martensitic stainless steels were developed as a group to provide a steel with a moderate level of corrosion resistance but with the ability to be hardened by heat treatment. They are generally composed of iron, nitrogen, chromium, and carbon, but may be combined with various alloys such as molybdenum, nickel, manganese or copper to expand the materials' property range. [4] It is the addition of carbon and/or nitrogen that allows martensitic stainless steels to be heat-treated and develop progressively improved mechanical properties. [5] Compared to ferritic stainless steels, martensitic stainless steels offer significantly higher strength, hardness and wear resistance. Tempering after heat treatment can provide a mild level of ductility to martensitic steel. [6] Martensitic stainless steels are also ferromagnetic. They are generally resistant to corrosion in relatively mild environments, but are poorer in corrosion resistance compared to both ferritic and austenitic stainless steels. Martensitic stainless steels are ideal for applications such as wear resistant bushings and wear plates.

Common PM martensitic stainless steel grades include the 410HT and 420HT grade steels. The most basic grade of martensitic stainless steel is 410HT, which uses 410L as a base powder. The410HT stainless steel grade commonly contains approximately 12.5% chromium with carbon additions below 0.15%. Carbon and nitrogen-free 410 remains ferritic at all temperatures throughout the sintering process. The addition of carbon and/or nitrogen to the 410 grade is used to stabilize the austenite during sintering, and transform the austenite to martensite during cooling. [7] The martensitic transformation consequently increases the achievable mechanical properties and decreases corrosion resistance. The 410HT grade of steel is mildly compressible, making it a popular choice for components that require higher sintered densities.

The 420HT stainless steel grade is a high carbon version of 410HT. It consists of 12.5% chromium and carbon levels between 0.15-0.3%. The increase in carbon level provides improved strength and wear resistance compared to 410HT. The 420HT grade is generally quite brittle in the hardened condition, and must be tempered to reach a useful toughness level. [4] It is similar in compressibility and corrosion resistance to the 410HT grade, as it also uses the 410L stainless steel grade as a base powder.

A secondary branch of the martensitic stainless family are known as precipitation-hardened (PH) steels. The PH steels are chromium-nickel alloys that contain elements such as copper, titanium or aluminum that enhance the precipitation hardening process. [4] PH steels offer superior strength with a moderate level of ductility, as opposed to the 410HT and 420HT grades that are very brittle. The enhanced mechanical properties of PH grades occurs through a specialized heat treat process. This includes a solution annealing treatment where the alloy is heated to a high temperature and rapidly quenched. The steel is then heated and held again at an intermediate temperature, allowing submicroscopic precipitates to form in the martensitic matrix. These precipitates further strengthen the martensitic matrix while also retaining some ductility. [8] This process of precipitating is also known as age hardening. One advantage of PH stainless steels is that full martensite transformation can be achieved at relatively low temperatures, which in turn reduces distortion. [9] Due to the high alloy content of chromium and nickel, the PH grades also exhibit improved corrosion resistance compared to the martensitic stainless steels, and are comparable in corrosion resistance to the austenitic series stainless. [3] Due to poor compressibility, PH grades have seen little use in powder metallurgy despite their high strengths. [8] The preferred processing route for precipitation-hardened grades is by metal injection molding. However studies conducted by Reinshagen and Witsberger have proved the feasibility of using precipitation-hardened grades in powdered metal processing.[8] The precipitation-hardened PM grades are most often seen in areas where corrosion resistance, high strength, high fatigue and low distortion are required. These applications include the medical, dental and other components that need high strength with good corrosion performance. [9]

The most common precipitation-hardenable stainless steel is known as 17-4PH. The 17-4PH is a high chromium-nickel alloy that uses prealloyed copper additions to enhance the age hardening process. The 17-4PH grade has a typical composition of 17% chromium, 4% nickel and 4% copper. [10] Despite the outstanding mechanical properties and resistance to corrosion, there are many processing challenges that have hindered development of 17-4PH in the PM industry. Sensitivity of the alloys in 17-4PH requires heightened control of temperatures and cooling rates during the sintering and age hardening processes, increasing the chance of component inconsistency if control is not achieved.[3] The addition of secondary age processing also increases overall fabrication costs compared to its single operation sintering counterparts.

The martensitic and precipitation hardened grade steels offer a wide range of powder, mechanical and corrosion properties through various alloy additions and heat treat cycles. This paper examined common martensitic and precipitation- hardened PM Steels. The results from the investigation can be used to determine the benefits and challenges each has in respect to powder and compaction properties, sintering, mechanical properties, and corrosion resistance. The purpose of the paper is to categorize these advantages and disadvantages to determine the optimum material and processing methods for required properties.

EXPERIMENTAL PROCEDURE

A commercially available 400 series stainless steel grade and a precipitation-hardened (PH) steel grade were chosen as the base powder for this study. The alloy compositions are shown in Table 1.

Table 1. Composition of Stainless Steel PM Alloys (w/o)

Base Powder	Cr	Ni	Cu	Nb	C
410L	11.5-13.5	-	-	-	0.02
17-4PH	15.5-17.5	3.0-5.0	3.0-5.0	0.15-0.45	0.02

Mixes were manufactured from the base powder grades to achieve three grades of 400 series martensitic stainless steel and one PH steel. Various lubricants were chosen in order to maximize powder performance. Table 2 shows the material systems used in the evaluation.

Table 2. Material Systems

	Base Powder	Graphite (%)	Lubricant (%)
410	410L	0	1% Amide Wax
410HT	410L	0.15	1% Intralube® F
420HT	410L	0.30	1% Intralube® F
17-4PH	17-4PH	0	1% Lithium Stearate

Each mix was evaluated for flow and apparent density. The mixes were then compacted into 12.7 mm (0.5 inch) height transverse rupture strength (TRS) specimens at compaction pressures of 400 MPa, 550 MPa, and 690 MPa (30, 40, 50 tsi) respectively. The green density was measured at each compaction pressure to generate a compressibility curve. Based on the compressibility data of each mix, a green density was chosen for mechanical property evaluation. The mixes were then compacted at the chosen green density into standard 6.4 mm (0.25 inch) height TRS specimens and 10 mm (0.39 inch) x 10 mm (0.39 inch) x 75 mm (2.95 inch) charpy impact specimens. The charpy impact specimens were also used to prepare round tensile specimens. All specimens were prepared in accordance with MPIF standards. [11] The green specimens were delubed at 870 °C (1600 °F) in a dissociate ammonia (DA) atmosphere for the 410L based material in a 100% Hydrogen atmosphere for the 17-4PH material. After machining the tensile round specimens, all of the specimens were sintered at the conditions shown in Table 3.

Table 3. Sintering Parameters

	Temperature	**Atmosphere**	**Cooling Rate**	**Temper**
410	1230 °C (2250 °F)	DA	2 °C/sec (4 °F/sec)	204 °C (400 °F)
410HT	1230 °C (2250 °F)	DA	2 °C/sec (4 °F/sec)	204 °C (400 °F)
420HT	1230 °C (2250 °F)	DA	2 °C/sec (4 °F/sec)	204 °C (400 °F)
17-4PH	1270 °C (2320 °F)	100% H_2	2 °C/sec (4 °F/sec)	204 °C (400 °F)

The sintered 17-4PH specimens were heat-treated according to the conditions shown in Table 4.

Table 4. Precipitation Hardening Parameters

	Solution Annealing		**Age Hardening**	
	Temperature	**Cooling Rate**	**H900**	**H1025**
			Temperature	**Temperature**
17-4PH	1065 °C (1950 °F)	2 °C/sec (4 °F/sec)	480 °C (900 °F)	552 °C (1025 °F)

The heat-treated tensile and impact specimens were tested for ultimate tensile strength, yield strength, elongation and impact energy. The transverse rupture strength specimens were evaluated for dimensional change, sintered density, hardness, and microstructure.

Corrosion resistance was also evaluated with the transverse rupture strength specimens according to ASTM B895. [12] The specimens were submersed in 5% NaCl solution and rated on an A-F grading scale at timed intervals.

In order to understand the material performance in a manufacturing setting, a production trial was conducted at SMC Powder Metallurgy (Galeton, PA). Steering column components were compacted from each material to their designated densities previously determined by the compaction properties. One hundred components were compacted, processed and sintered according to the conditions shown in Tables 3 and 4. The component and specifications are shown in Figure 1.

	Flange Thickness	Body Length	ID Bevel Length
Spec	5.48-5.58 mm (0.216-0.220 in)	3.5-3.6 mm (0.138-0.142 in)	0.005-0.015 mm (0.0001-0.006 in)

Figure 1. Steering Column Component and Specifications

RESULTS

The Hall flow and apparent density rate for each mix are shown in Figure 2. The 410HT and 420HT mixes with Intralube ®F as a lubricant showed improved hall flow rate compared to the 410 and 17-4PH mixes using Amide Wax and Lithium Stearate respectively. The 410HT and 420HT materials with Intralube ®F lubricant also measured the highest apparent densities.

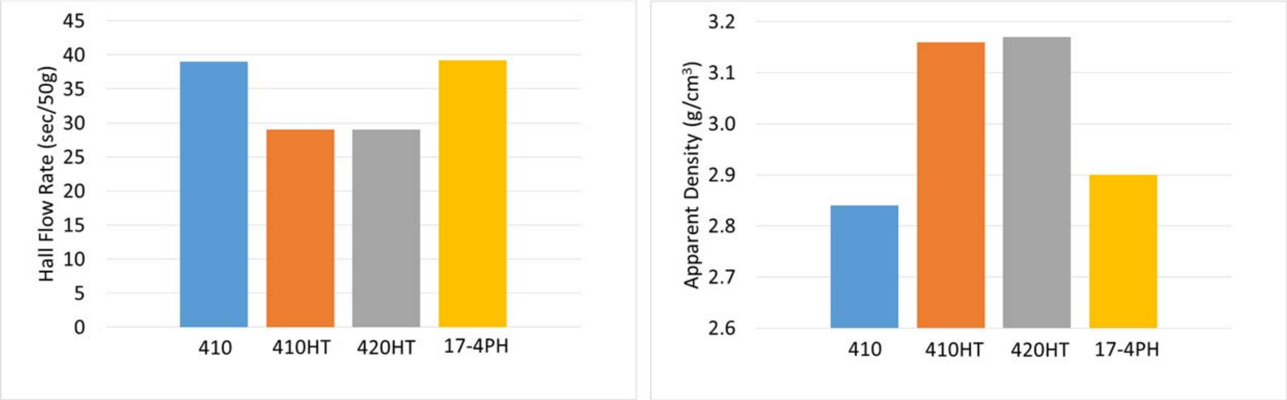

Figure 2. Flow and Apparent Density

The compressibility curve at compaction pressures of 400, 550 and 690 MPa is shown in Figure 3. The material grades using 410L as the base iron exhibited superior compressibility compared to the higher alloyed 17-4PH grade. The green densities of 6.4 g/cm^3 and 6.0 g/cm^3 were chosen respectively for the 410L based materials and the 17-4PH material for mechanical property testing.

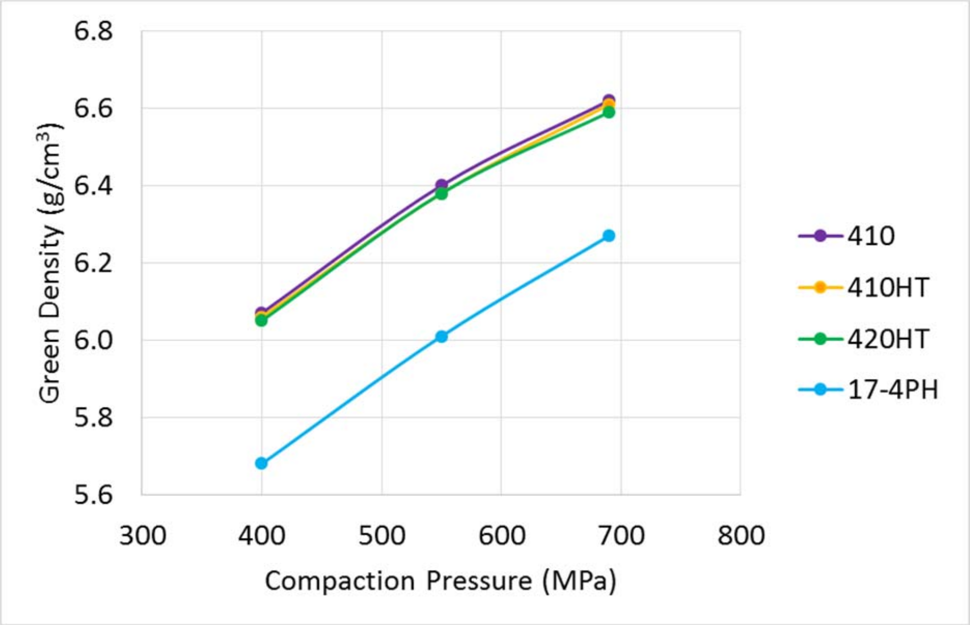

Figure 3. Compressibility

The mechanical properties are shown in Table 5. The dimensional change decreased with the addition of carbon in the 410L based material grades. The reduced shrinkage by the addition of carbon also played a factor in the final sintered density achieved. The 410 material was able to achieve similar apparent hardness levels compared to the 410HT and 420HT materials by achieving a higher sintered density.

Table 5. Mechanical Properties

	Green Density (g/cm^3)	**Sintered Density (g/cm^3)**	**Apparent Hardness (HRC)**	**Microhardness ($HV_{0.1}$)**	**Dim. Change (%)**
410	6.4	6.78	31	529-584 (563)	-2.05
410HT	6.4	6.57	29	584-637 (611)	-1.03
420HT	6.4	6.55	33	696-736 (723)	-0.98
17-4PH *H900	6.0	7.27	31	428-561 (444)	-4.89
17-4 PH **H1025	6.0	7.26	28	388-410 (398)	-4.70

*Processed at 480 °C (900 °F)

**Processed at 552 °C (1025 °F)

The chemistry of each sintered material is shown in Table 6.

Table 6. Chemistry

	C (%)	**S (%)**	**N (%)**	**O (%)**
410	0.02	0.003	0.289	0.180
410HT	0.09	0.002	0.387	0.017
420HT	0.17	0.001	0.399	0.015
17-4PH H900	0.06	0.003	0.005	0.218
17-4 PH H1025	0.07	0.002	0.004	0.208

The ultimate tensile strength and yield strength is shown in Figure 4. The 17-4PH H900 material exhibited the highest ultimate tensile and yield strengths. The tensile strength of the 410L based grades slightly decreased as the carbon content increased. The 410L based grades did not yield.

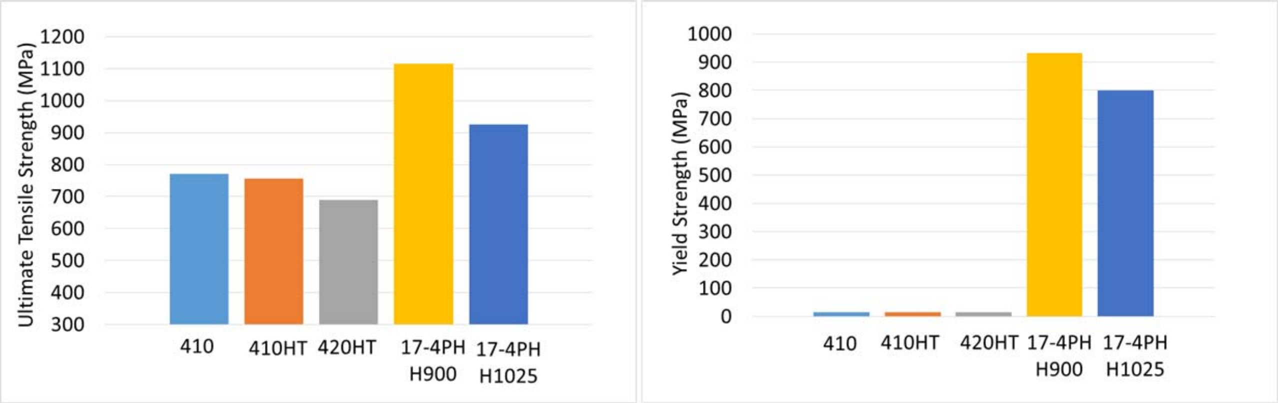

Figure 4. Ultimate Tensile Strength and Yield Strength

The impact energy and elongation is shown in Figure 5. The 17-4PH H1025 material grade exhibited the highest impact and elongation properties. The 410L based material grades did not elongate.

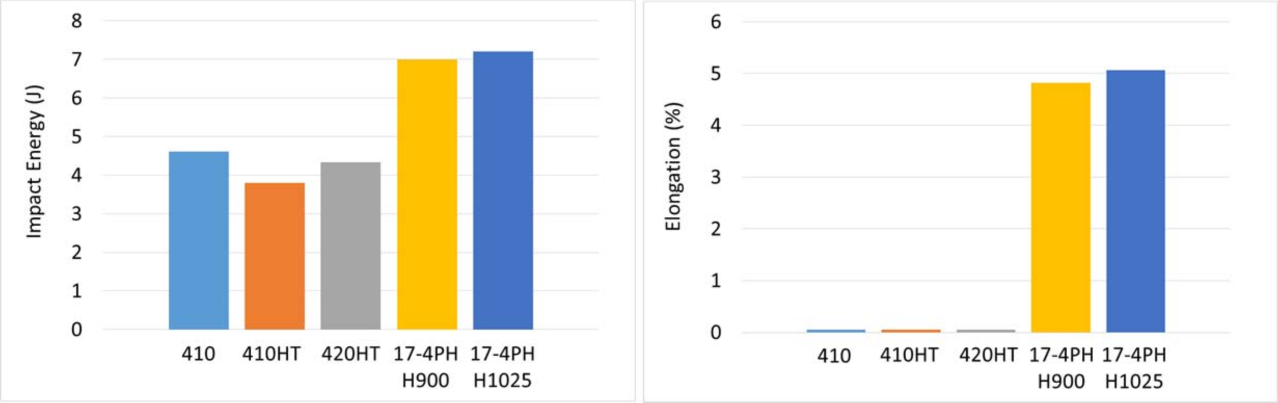

Figure 5. Impact Energy and Elongation

The microstructure of the 410 grade is shown in Figure 6. The material exhibited a martensitic microstructure. Nitrogen content in combination with a rapid cooling rate was capable of achieving martensite transformation without any carbon addition.

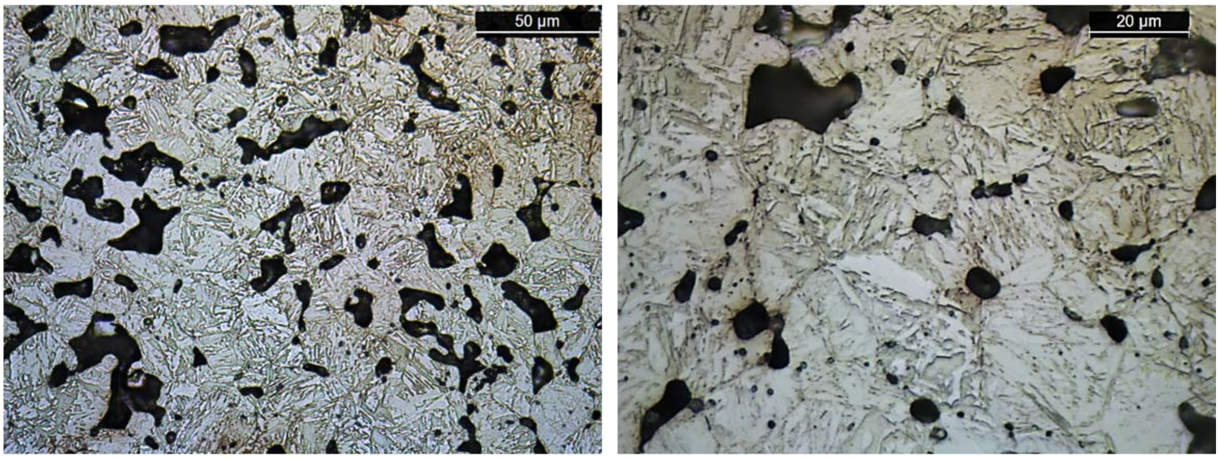

Figure 6. Microstructure of 410

The microstructure of the 410HT grade is shown in Figure 7. The material exhibited a martensitic microstrcuture. The carbon addition in the 410HT grade provides a denser martensite microstructure compared to the 410 grade with no carbon. This was reflected in the microhardness results. Carbide formation was observed in the grain boundaries of the structure.

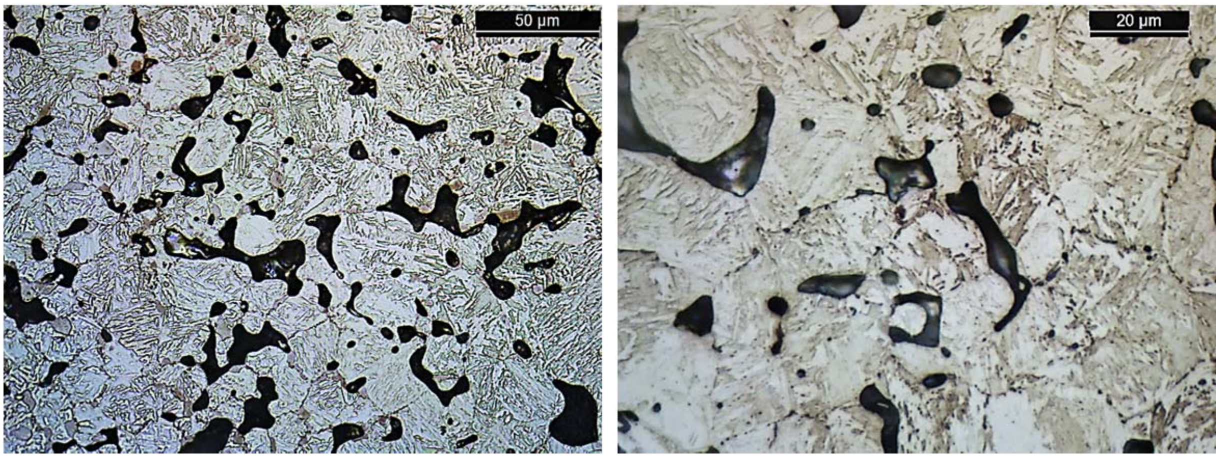

Figure 7. Microstructure of 410HT

The microstructure of the 420HT material grade is shown in Figure 8. The microstructure exhibited martensite. The martensite formation of the 420HT grade showed a denser martensite structure than the 410HT grade. This was reflected in the microhardness results. More carbide formation was observed in the grain boundaries of the 420HT grade structure compared to the 410HT grade structure.

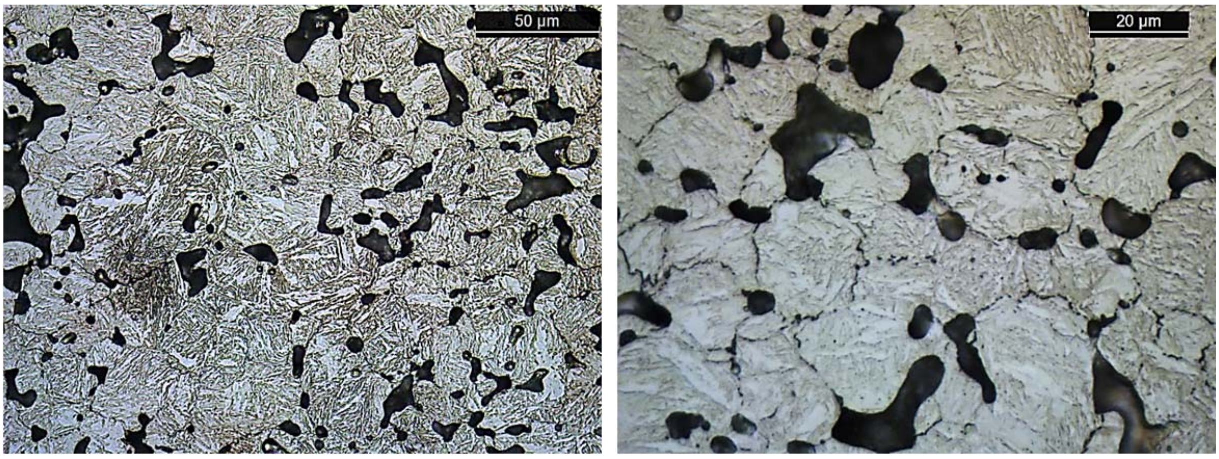

Figure 8. Microstructure of 420HT

The microstructure for the 17-4PH material grade aged at 480 °C (900 °F) is shown in Figure 9. The 17-4PH H900 material exhibited a martensitic microstructure. Very dense areas of martensite were observed throughout the structure. No precipitates were observed in the grain boundaries.

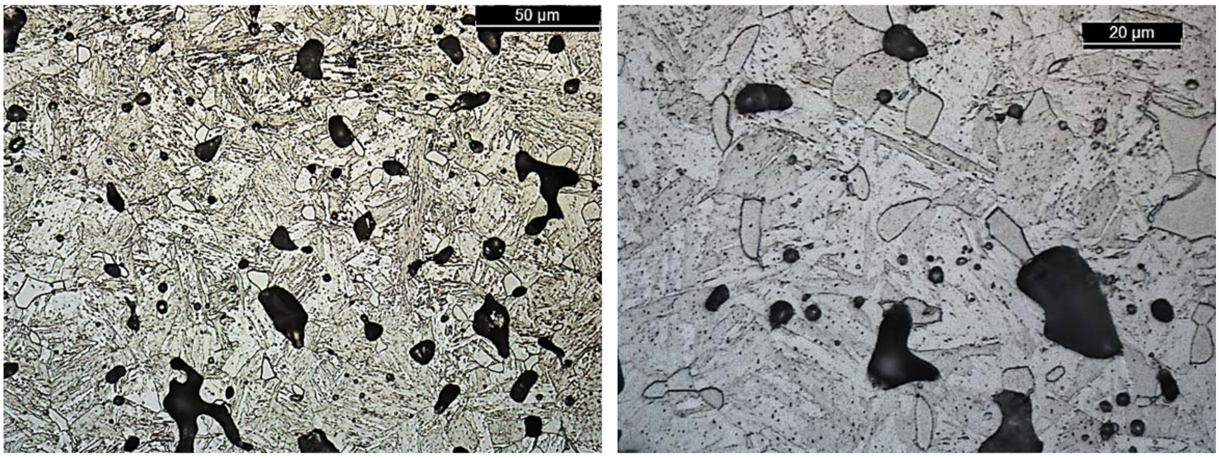

Figure 9. Microstructure of 17-4PH aged at 480 °C (900 °F) - H900

The microstructure for the 17-4PH material grade aged at 552 °C (1025 °F) is shown in Figure 10. The 17-4PH H1025 material exhibited a martensitic microstructure. Very dense areas of martensite were observed throughout the structure. Precipitate formation was observed in the grain boundaries.

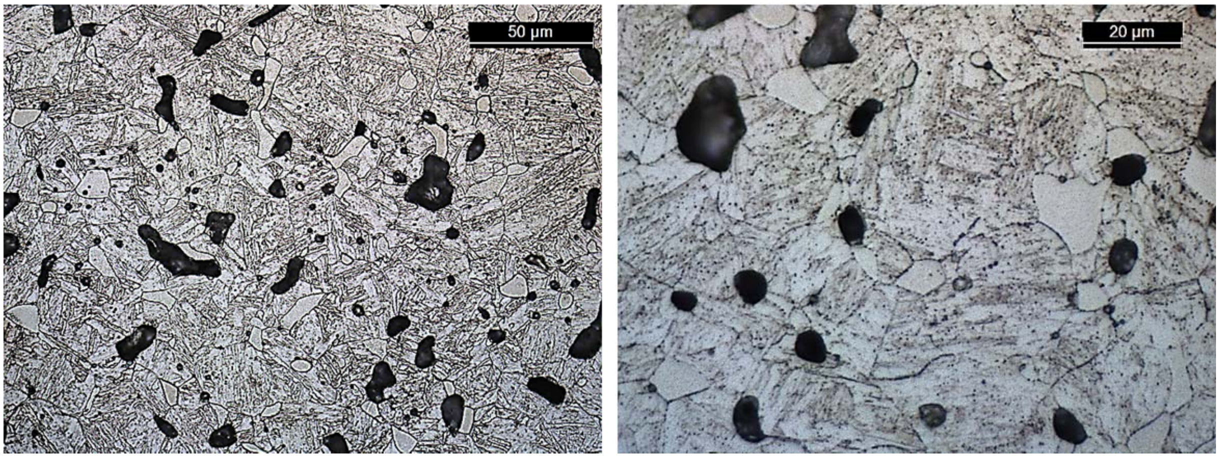

Figure 10. Microstructure of 17-4PH aged at 552 °C (1025 °F) - H1025

The results of the specimens saturated in 5% NaCl for 96 hours are shown in Figure 11. The 410L base grades were severely corroded after 96 hours.

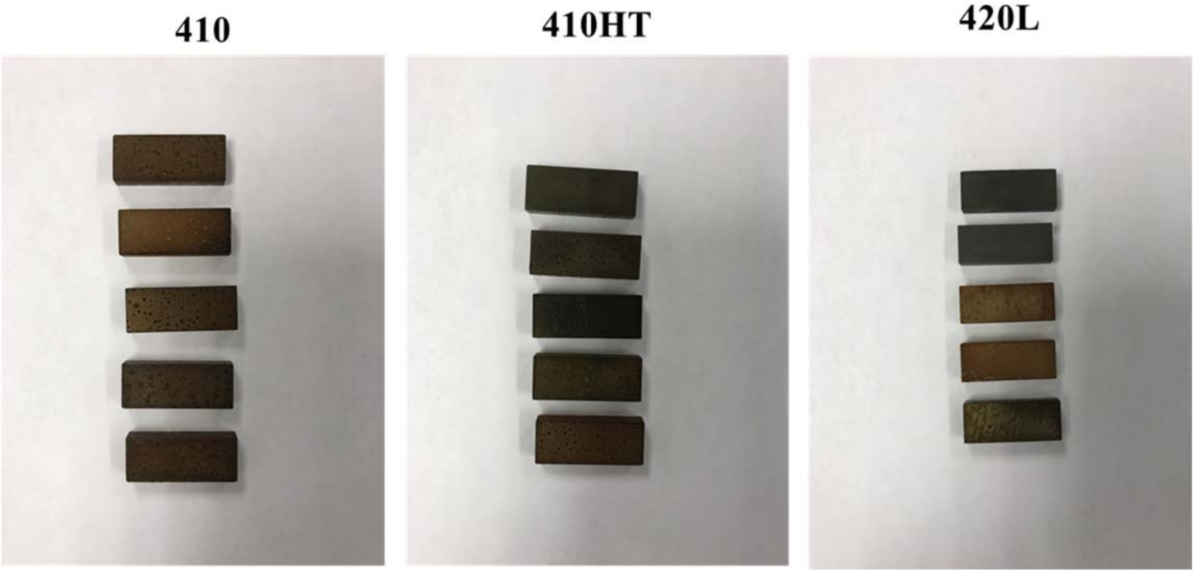

Figure 11. Corrosion specimens of 410, 410HT and 420HT after 96 hours in 5% NaCl solution

The 17-4PH grades saturated in 5% NaCl for 96 hours are shown in Figure 12. The 17-4PH material at both age hardening levels (H900, H2015) maintained their corrosion resistance after 96 hours.

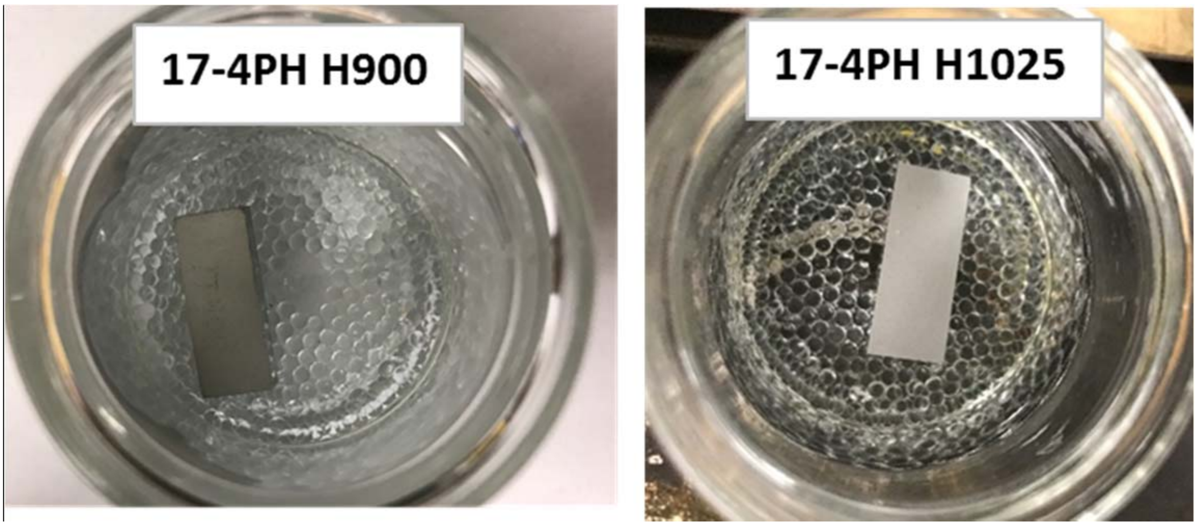

Figure 12. Corrosion specimens of 17-4PH age hardened at 480 °C (900 °F) and 552 °C (1025 °F) after 96 hours in 5% NaCl solution

The production trial of steering column components observed no difficulties during the compaction process. All materials demonstrated proper flow into the die, and resulted in no scoring of the tooling.

DISCUSSION

The production trial of steering column components was used to identify the benefits and challenges of each material in a production setting. Perspective from a production standpoint on the compaction, sintering, and achievable mechanical properties is important to understand the behavior of each material outside of laboratory testing. Individual material grades and processing conditions can provide their own unique benefits and challenges during production processing.

The 410HT and 420HT material grades were considered the most workable martensitic PM stainless steel compared to the 17-4PH grade. The low alloy content allowed for easy compaction and the ability to achieve high densities at lower sintering temperatures than its higher alloy counterpart did. Documented studies have shown that the addition of carbon has the advantage of boosting mechanical performance and martensite development as the carbon level increases. [3, 10] In this study, carbide formation in the 410HT and 420HT grain boundaries had a detrimental effect on the mechanical properties and resulted in premature fracture of the test specimens. The formation of carbides throughout the 410HT and 420HT structure are considered to be a result of insufficient cooling.

The 17-4PH material obtained superior mechanical properties of the martensitic stainless steels evaluated. However, this material proved to be challenging to compact from a compressibility and ejection standpoint. The laboratory compaction trials experienced tool scoring, low compressibility and high ejection forces during the compaction process. The production trial observed similar compressibility challenges, however did not observe the same tool scoring as the laboratory trial. This may be due to a difference in tooling clearances.

The main benefit of using martensitic stainless steel PM is that components can be sinter-hardened and tempered to achieve desired strength properties without secondary processing steps. However, one of the most reoccurring challenges seen during production of any 400 series stainless PM grades are the intermittent flow issues. These issues are attributed to powder settling and environmental factors. Seasonal flow issues are seen during extreme humidity as well as extreme cold. Additive additions such as graphite can also lead to flow problems. Powder flow issues require more adjustments during production runs, which can cause shifts in weight and OAL dimensions. Utilizing advanced lubricant systems specifically designed for stainless steel powders can help alleviate these issues and offer improvement in powder properties. The Intralube °F lubricant system utilized in this investigation showed its capability in improving the powder properties of powdered metal stainless steels. The evaluated material properties showed improved flow and increased apparent density compared to a similar material system that used industry standard Amide Wax. Standard flow data for a 410HT material grade with 1% Amide wax averages a flow of 39 seconds per 50 grams of powder. The same 410HT material grade with 1% Intralube ®F improved the flow to 29 seconds per 50 grams of powder. Standard apparent density data for a 410HT material grade with 1% Amide wax averages an apparent density of 2.84 g/cm^3. The same 410HT material grade with 1% Intralube ®F increased the apparent density to 3.16 g/cm^3. The Intralube ®F lubricant system was chosen for this investigation in order to maximize powder performance.

CONCLUSION

- The 410HT and 420HT materials using Intralube ®F were able to achieve improved flow and higher apparent density properties compared to a similar material system using Amide wax.
- The 410L based materials exhibited higher compressibility compared to the 17-4PH material grade.
- The 410L based material grades exhibited reduced shrinkage as the carbon content increased.
- The 17-4PH material grades exhibited the highest mechanical properties. The H900 age hardened temperature exhibited higher tensile strength compared to the H1025 age hardened temperature, while the H1025 age hardened materials exhibited slightly higher elongation and impact strength compared to the H900 age hardened material.
- Carbide formation was observed in the grain boundaries of the 410HT and 420HT material grades.
- The 17-4PH material showed superior corrosion resistance compared to the 410L based grades.

REFERENCES

1. "The Stainless Steel Family" International Stainless Steel Forum, Belgium (n.d) www.worldstainless.org
2. "Types of Stainless Steel" Southern Africa Stainless Steel Development Association (n.d) http://sassda.co.za/about-stainless/types-of-stainless/
3. K. Prasan Samal, Nagarjuana Nandivada, Ingrid Hauer, "Properties of 17-4PH Stainless Steel Produced Via Press and Sinter Route" (2008) North American Höganäs, USA, Höganäs AB, Sweden
4. ASM Specialty Handbook: Stainless Steels, First edition (1994)
5. "Handbook of Stainless Steels" (2013) Outokumpu Stainless AB, Sweden
6. Chris Schade, John, Schaberl, Alan Lawley "Stainless Steel AISI Grades for PM Applications" (n.d) Hoeganaes Corporation, USA, Ancor Specialties, USA, Drexel University, USA
7. H.D. Ambs, M. Svilar "P/M Martensitic Stainless Steels: Processing and Properties" (1990) SMC Metal Products Inc.
8. Chris Schade, Alan Lawley "Precipitation Hardening PM Stainless Steels" (n.d) Hoeganaes Corporation, USA, Ancor Specialties, USA
9. K. Srinivasa Vadayar, S. Devaki Rani "Characterization of Precipitation-Hardenable Stainless Steels" (2014) International Journal on Theoretical and Applied Research in Mechanical Engineering, Volume -3 Issue -1
10. E. Klar, P. Samal, "Power Metallurgy Stainless Steel – Processing Microstructures and Properties", 2007, ASM International, Materials Park, OH.
11. Standard Test Methods for Metal Powders and Powder Metallurgy Products, 2016 Edition, Metal Powder Industries Federation, Princeton, NJ
12. ASTM International Standard B895-16 "Standard Test Methods for Evaluating the Corrosion Resistance of Stainless Steel Powder Metallurgy (PM) Parts/Specimens by Immersion in a Sodium Chloride Solution" ASTM International (2016)