Development of High Performance Stainless Steel Powders

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Abstract. Advanced melting technology is now being employed in the manufacture of stainless steel powders. The new process currently includes electric arc furnace (EAF) technology in concert with Argon Oxygen Decarburization (AOD), High Performance Atomizing (HPA) and hydrogen annealing. The new high performance processing route has allowed the more consistent production of existing products, and has allowed enhanced properties, such as improved green strength and green density. This paper will review these processing changes along with the potential new products that are being developed utilizing this technology. These include high strength stainless steels such as duplex and dual phase as well as stainless steel powders used in high temperature applications such as diesel filters and fuel cells.

Introduction

Stainless steel powders have been made via induction furnace technology since the 1960's. Relatively low volumes of stainless steel powders had dictated that small induction furnaces (typically 1 to 2 ton in capacity) are commonly used. The raw materials are melted in the induction furnace and atomized using high- pressure water and a V-Jet configuration. The chamber in which the powder is atomized is normally purged with nitrogen to prevent excessive oxidation of the powder. After atomizing the material is screened to the desired particle size distribution.

This method of manufacturing stainless steel powders was sufficient to meet the early demand for stainless steel powder. However, the recent growth in stainless powder metallurgy has led to the development of a high volume, high performance, processing route. The new processing route is shown in Figure 1. A twenty-five ton electric arc furnace is used in conjunction with an argon-oxygen decarburization unit to melt and refine stainless steel to the required composition and temperature. The steel is then transferred by a bottom pour ladle to the High-Performance Atomizer where it is converted into powder. Ferritic grades are then annealed in the hydrogen atmosphere, annealing furnace. Powders are then screened and premixed according to customer specifications.

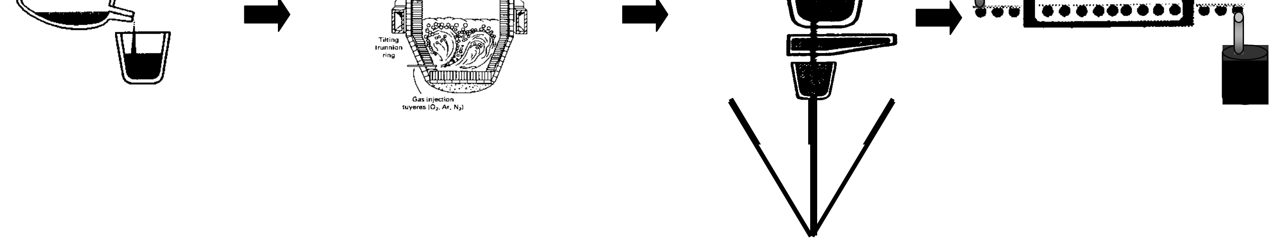

Figure 1: High Performance Stainless Processing Route

One of the most obvious advantages of this EAF/AOD/HPA process is the size. The EAF can produce 20 tons of powder; this is compared to 1 to 2 tons typically melted in an induction furnace. The larger heat size associated with the EAF allows for truckload quantities to be shipped from one batch. Needless to say, the properties such as apparent density, flow, green and sintered properties are much more consistent when 20 tons of powder are made from one batch as opposed to multiple heats required by induction melting. Other advantages of the new processing route include lower and more consistent carbon and nitrogen levels which lead to improved compressibility. Both the high performance atomizing and annealing have provided improvements in green strength and green density.[1]

New Grade Development

The use of the high-performance processing route has allowed the development of some new grades of P/M stainless steel, such as dual phase stainless and duplex stainless.

Traditionally, when stainless parts producers have needed high strength and hardness, graphite has been added to a ferritic grade to promote martensite, or a more highly alloyed material, such as 17-4PH has been used. In applications that require abrasion resistance, hardness, ductility and high strength, wrought producers of stainless steel have developed a dual phase stainless steel consisting of a microstructure of martensite and ferrite. The level of martensite is controlled according to a chemical balance:

$$K_m = Cr + 6 \times (Si) + 8 \times (Ti) + 4 \times (Mo) + 2 \times (Al) - 2 \times (Mn) - 4 \times (Ni) - 40 (C + N) - 20 \times (P) - 5 \times (Cu)$$

In this equation, chromium, silicon, titanium, molybdenum, and aluminum are used to stabilize the ferrite. Manganese, nickel, carbon, nitrogen, phosphorus and copper promote formation of high temperature austenite, which transforms to martensite during cooling. By adjusting elements in real time in the AOD, a consistent value of K_m can be maintained.

Table I shows the chemical composition of a newly developed dual phase stainless steel along with the two high strength options discussed earlier. The chemistry of the dual phase stainless steel has been optimized leading to a microstructure consisting of ferrite and martensite. Table II shows the physical properties of the aforementioned grades. Using conventional sintering (typically 1260 ^{o}C in hydrogen) 17-4PH is a poor option. The high alloy content is not only costly but leads to poor green and sintered density. The lower sintered density leads to mechanical properties that are lower than expected for the level of alloy content. The precipitation-hardening grade also requires secondary heat treatment to achieve its high strength.

Table I. Chemical composition of high strength-stainless grades.

Type	**C** (%)	**S** (%)	**O** (%)	**N** (%)	**P** (%)	**Si** (%)	**Cr** (%)	**Ni** (%)	**Cu** (%)	**Mn** (%)	**Mo** (%)	**Cb (%)**
410L + C	0.060	0.008	0.30	0.018	0.013	0.85	12.50	0.09	0.08	0.15	0.02	---
Dual Phase	0.015	0.007	0.21	0.009	0.014	0.84	11.60	1.03	0.03	0.10	0.34	---
17-4PH	0.018	0.010	0.300	0.020	0.025	0.85	17.00	4.00	3.55	0.15	0.03	0.25

The graphite addition to the 410L increases the formation of chromium carbides and leads to sensitization. The net effect is the depletion of chromium in solution and the lowering of corrosion resistance. Graphite also reduces the compressibility of the powder and requires strict atmosphere control in the sintering furnace for optimum carbon control. Even with the higher carbon levels, hardness and tensile properties of the 410L + C are inferior to the dual phase stainless steel.[2]

Table II. Mechanical propety data for high strength stainless steels.

	Pressure		Sintered Density	D.C.	TRS		Hardness	UTS		0.20% OFFSET		Elongation
Material	(tsi)	(MPa)	(g/cm^3)	(%)	(ksi)	(MPa)	(HRA)	(ksi)	(MPa)	(ksi)	(MPa)	(%)
410L + C	50	690	7.05	-2.17	181	1248	49	92	633	52	358	4.9
Dual Phase	50	690	7.15	-2.99	238	1641	56	119	819	89	612	2.5
17-4PH	50	690	6.67	-1.80	206	1421	53	110	757	91	627	1.4

.75% Acrawax C used as lubricant and sintered at 2300°F (1260°C) in 100% Hydrogen.

Note: 17-4PH was heat treated at 900 °F (482 °C) for 30 minutes.

While dual phase stainless steels provide high strength and corrosion resistance slightly better than typical ferritic stainless steels, its use in highly corrosive environments is somewhat limited. Duplex stainless steels display a corrosion resistance equal to or better than that of the austenitic grades while their mechanical properties range between ferritic and austenitic. A typical chemistry for 2205 (duplex stainless steel) is shown in Table III.

Table III. Chemistry of Duplex Stainless Steel

Type	**C** (%)	**S** (%)	**O** (%)	**N** (%)	**P** (%)	**Si** (%)	**Cr** (%)	**Ni** (%)	**Cu** (%)	**Mn** (%)	**Mo** (%)
Duplex 2205	0.009	0.004	0.23	0.076	0.028	1.00	22.20	5.50	0.04	0.16	3.43

The microstructure of a duplex stainless steel is a mixture of austenite and ferrite with optimum properties normally achieved within a range of 30% to 70% ferrite. An advantage of P/M duplex stainless steels is the availability of nitrogen during sintering as an alloy element. Nitrogen is a strong austenite former and can replace nickel, thus lowering the cost. By varying amount of nitrogen in the sintering atmosphere (as shown in Table IV) the properties of the duplex stainless steel can be improved.

Generally when nitrogen is introduced into stainless steels there is a concern for the formation of chromium nitrides, which may adversely affect the corrosion resistance of the alloy. However, in duplex stainless steels, the high nitrogen content promotes austenite which has a high solubility for nitrogen and significantly reduces the formation of chromium nitrides. In this sense, the use of nitrogen in duplex stainless steels increases pitting and crevice corrosion resistance. Since nitrogen is a very effective solid-solution strengthening element, duplex stainless steels have excellent strength. However, the presense of austentite in the microstructure also allows the alloy to have good toughness and ductility.[3]

Table IV. Mechanical property data for varoius sintering atmospheres of dulpex stainless.

	Pressure		Sintered Density	D.C.	TRS		Hardness	UTS		0.20% OFFSET		Elongation
Material	(tsi)	(MPa)	(g/cm^3)	(%)	(ksi)	(MPa)	(HRA)	(ksi)	(MPa)	(ksi)	(MPa)	(%)
100% Hydrogen	50	690	7.2	-5.33	202	1390	50	84	578	62	427	10.8
50% Hydrogen/ 50% Nitrogen	50	690	7.2	-4.6	197	1356	52	81	558	61	420	7.6
10% Hydrogen/ 90% Nitrogen	50	690	6.79	-2.70	214	1473	55	96	661	67	461	5.3

.75% Acrawax C used as lubricant and sintered at 2300°F (1260°C).

High temperature alloys which provide strength and oxidation resistance at elevated temperatures (300 °C to1200 °C) will be critical in new applications such as fuel cell technology and diesel engines. These materials are generally used in the presence of combustion gases that may be generated from exhaust and pollution control equipment. The opportunities for these materials are on the rise. These components will be exposed to high tempertures and various service atmospheres such as superheated steam, hydrogen, and air. Particulate filters for capturing soot and ash from the exhaust of diesel engines are being used to meet the European environmental regulations. The ease of which shapes can be made from P/M products make them extremely attractive for this application.

Table V. Chemistry of oxidation resistant alloys.

Type	Si (%)	Cr (%)	Ni (%)	Mo (%)	Cb (%)	W (%)	Co (%)
409Cb	0.85	10.80	0.08	0.08	0.50	---	---
430CB	0.85	18.00	0.08	0.03	1.00	---	---
310L	1.50	26.50	21.10	0.02	---	---	---
Super Ferritic	0.90	24.20	0.05	0.03	---	---	---
Hastelloy X	1.20	22.00	49.00	9.00	---	0.60	1.30

The alloy selection must be based on both cost and performance. Certainly high levels of nickel and chromium will aid in performace (Table V) but the cost must be justfied. Figure 2 shows the TGA results of several stainless compositions. The weight gain of various powder compositions was measured in air while increasing the temperature from ambient to 1200 °C. The alloys tested ranged from a 409Cb which is commonly used for exhaust flanges to Hastelloy X, which has been used for industrial applications (furnaces) because it has unusual resistance to oxidizing, reducing and neutral atmospheres. In general, as the alloy content increased (in particular nickel), the oxidation resistance increased. The super ferritic alloy, which contained 24% chromium, is especially resistant to oxidation. In the wrought industry, this grade is used in the manufacture of parts which must resist scaling at high temperatures. This AOD processing of this alloy, which produces low carbon and nitrogen levels, improves its relative corrosion resistance and mechanical properties. The high temperature-mechanical properties of this alloy are far less than Hastelloy X.[3]

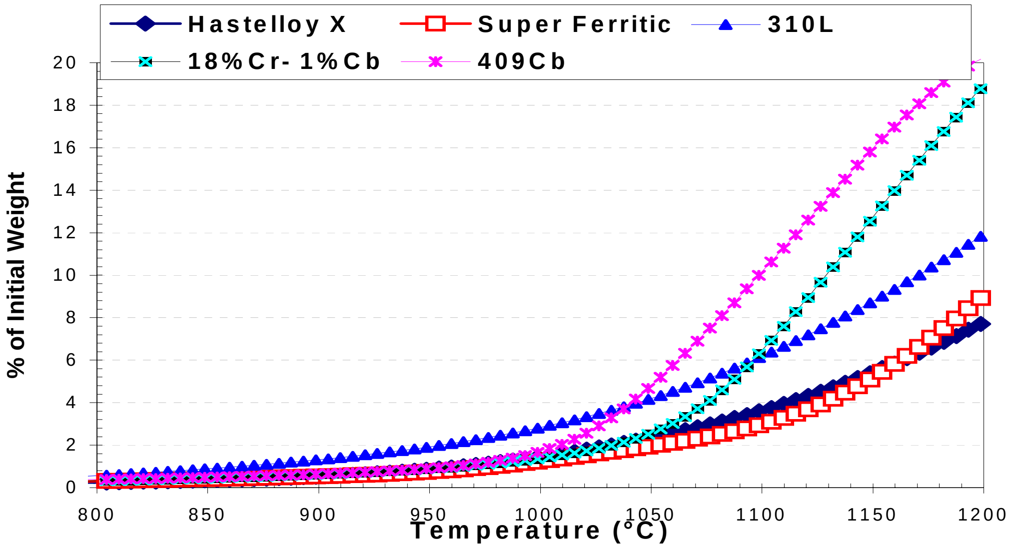

Figure 2. Oxidation rate of alloys measured in air.

Summary

A new high performace processing route for the manufacture of stainless steel powders has been developed that allows for the improved properties of existing powder grades while providing opportunities to develop new grades of stainless steel powders to meet the increasing demands of the marketplace.

References

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