

# Controlling Properties of Sintered Steel Powder Metal Components Using Atmosphere Composition as a Variable

Thomas Philips, John J. Dwyer, Jr. and Zbigniew Zurecki

**Air Products and Chemicals Inc.**

7201 Hamilton Boulevard  
Allentown, PA 18195-1501

# Controlling Properties of Sintered Steel Powder Metal Components Using Atmosphere Composition as a Variable

Thomas Philips, John J. Dwyer, Jr. and Zbigniew Zurecki  
Air Products and Chemicals, Inc.  
7201 Hamilton Boulevard  
Allentown, PA 18195

## **ABSTRACT**

The role of gas constituents in a sintering atmosphere is re-examined in order to optimize sintered properties of iron-carbon powder metal (PM) components. Property variations in sintered products are related to hydrogen concentration and dew point inside sintering zone. Discussed properties include microstructure, porosity, pore morphology and dimensional stability. Effects of CO containing atmospheres are presented in terms of hardness, carbon control and dimensional changes. It is shown that sintering atmosphere control is critically important in the case of sinter-hardenable, alloyed products.

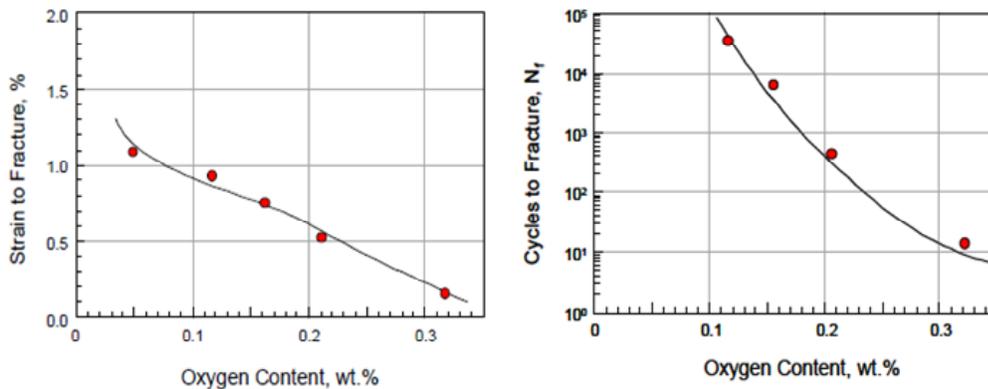
## **INTRODUCTION**

Since the late 1970's the use of Nitrogen/Hydrogen systems has become the atmosphere of choice for sintering of iron and steel powder metal (PM) parts. The original motivation for the switch from conventional natural gas based endothermic atmosphere was due to the natural gas shortages of the late 70's, however with time the additional benefits of inherent safety, higher properties, better economics and increased reliability became the reasons for the adoption and popularity of the nitrogen based atmospheres. With increasing demands on the properties of sintered components used in the automotive industry, it was not sufficient just to obtain better properties, but imperative to obtain the same properties consistently. The final properties of sintered components is determined by a multitude of processing variables such as powder size and size distribution, powder composition and purity, and the carbon content. Additional variables that influence the end results include, type and amount of lubricants, compaction densities and furnace parameters (temperature, time at temperature, cooling rates and belt loading.). Often overlooked is the sintering atmosphere as a variable. While most of the variables mentioned earlier are determined during the design stage of the component, it is the atmosphere that can change or can be made to change as a function of time, during the sintering process thereby influencing the final properties and their consistency. The sintering mechanisms and sub processes taking place inside the furnace in the presence of a controlled atmosphere include:

- reducing specific surface area and rounding of pores
- increasing number and strength of inter-metallic bonds
- decreasing pore volume-increasing density
- alloying and homogenization
- eliminating/reducing lattice defects

The advent of sinter-hardened materials presents additional challenges to controlling the property variations. The surface densification, oxidation and carbon control in the sintering zone can enhance or decrease the cooling rates in the accelerated cooling zones and consequently lead to additional property variations. To increase the density, strength, hardenability and service performance, sinter-hardenable powders contain easily oxidizable elements such as chromium and molybdenum in addition to nickel, manganese, and/or copper. Sigl and Delarbre<sup>1</sup> in a study on the impact of oxygen on the microstructure and fracture morphology of iron (chromium, molybdenum) PM steels have concluded that the ductility of chromium-PM steels is seriously deteriorated by high oxygen contents.

## Effect of oxygen pick-up during sinter hardening of Cr/Mo-alloyed, structural steel compacts



L.S. Sigl and P. Delarbre, "Impact of Oxygen on the Microstructure and Fracture Morphology of Fe (Cr,Mo)-PM Steels", Proc. of the 2003 Int. Conf. on Powder Metallurgy & Particulate Materials, PM2TEC 2003, June 8-12, Las Vegas, MPIF

**Figure 1.**

In another study, Fillari<sup>2</sup> et al demonstrated the significant effect cooling rates have on the tensile and yield strength of steels containing 0.69% carbon.

### **ATMOSPHERE SYSTEMS FUNDAMENTALS**

In blended nitrogen-based atmospheres the incoming composition is relatively stable, but the gas chemistry within the furnace can vary depending on the integrity of the furnace and external factors such as room pressures and exhaust systems. It is also important to be aware that new species of gas may be formed within the furnace, even though they were not part of the original supply system. It is not uncommon to produce small amounts of ammonia in a nitrogen+ hydrogen atmosphere. This ammonia can then dissociate within the furnace and the atomic nitrogen can lead to nitriding of stainless PM parts. Flow control panels can precisely monitor and control the mixing of different gases that make up the required atmosphere system.

The table below summarizes individual roles of different atmosphere constituents in the sintering process.

## Role of Atmospheres Constituents

- N<sub>2</sub>** – inert, can nitride (SS, Ti, Ta)
- H<sub>2</sub>** – reducing, decarburizing can hydride (Al, Ti)
- CO** – carburizing, reducing
- CO<sub>2</sub>** – decarburizing, oxidizing
- O<sub>2</sub>/AIR** - oxidizing
- H<sub>2</sub>O** – oxidizing, decarburizing
- Ar** - inert
- C<sub>x</sub>H<sub>y</sub>** - ( hydrocarbns) carburizing, H<sub>2</sub> source
- He** – inert
- NH<sub>3</sub>** – (Ammonia) nitriding

It is useful to understand the role that the atmosphere system plays in the whole sintering process. The principal atmosphere functions in a sintering furnace are:

- delubrication
- oxide reduction
- sintering, bonding, and densification
- carbon control
  - surface carbon
  - core carbon
- microstructure control
- prevent oxidation
- heat transfer

Since atmosphere plays a critical role in the final quality and properties of the sintered part, it is also important to be able to control the atmosphere through direct or indirect control of the variables of an atmosphere system. The primary variables in an atmosphere system are:

- **atmosphere composition**
  - H<sub>2</sub>O (dew point)
  - H<sub>2</sub> %
  - CO %
  - CO<sub>2</sub>%
  - CH<sub>4</sub>%
- **atmosphere flow rates and distribution**
  - turbulent vs. laminar flow
- **atmosphere pressure inside the furnace**
- **atmosphere exit velocity**
- **atmosphere stability (external influences)**
- **door opening (part height)**
- **furnace curtain design**

The key atmosphere reactions taking place in the three main zones of the furnace are represented below in Figure 2.

## Key Atmosphere Reactions in Furnace

### Preheat Zone:

#### Lubricant Removal

#### Dry Atmosphere



#### Humidified atmosphere:



#### OXIDE REDUCTION – A FUNCTION OF H<sub>2</sub>/H<sub>2</sub>O RATIO:



ENDO (4OH <sub>2</sub> , 0.8 H <sub>2</sub> O at + 40F)	H <sub>2</sub> /H <sub>2</sub> O = 50
N <sub>2</sub> - BASED (4H <sub>2</sub> , 0.025 H <sub>2</sub> O @ -30F)	H <sub>2</sub> /H <sub>2</sub> O = 160
N <sub>2</sub> - BASED (0.5H <sub>2</sub> , 0.01 H <sub>2</sub> O @ -45F)	H <sub>2</sub> /H <sub>2</sub> O = 50

### High Heat, Sintering Zone:

#### Oxide Removal



### Cooling Zone:

#### Heat Transfer & Oxide Prevention



Figure 2.

In the pre-heating zone an oxidizing atmosphere is required to react with the hydrocarbon vapors, and prevent sooting or the formation of solid carbon. In the high heat zone the hydrogen to moisture ratio determines the oxidizing potential and one needs to maintain this ratio as high as possible at the lowest cost. The oxidation/reduction potential determines the rate at which the surface oxides of the powder particles are reduced, and this directly influences the sintering or bonding between the particles as well as hardenability and product performance – strength and corrosion resistance. The equilibrium conditions between metals and their oxides showing the effects of temperature, dew point/water content and p<sub>H<sub>2</sub></sub>/p<sub>H<sub>2</sub>O</sub> ratio is shown in Figure 3. Note that sinter-hardenable, alloyed powder blends are more sensitive to compositional variations in sintering atmosphere.

## Hydrogen/moisture for oxidation/reduction of principal sinter hardened metals and oxides

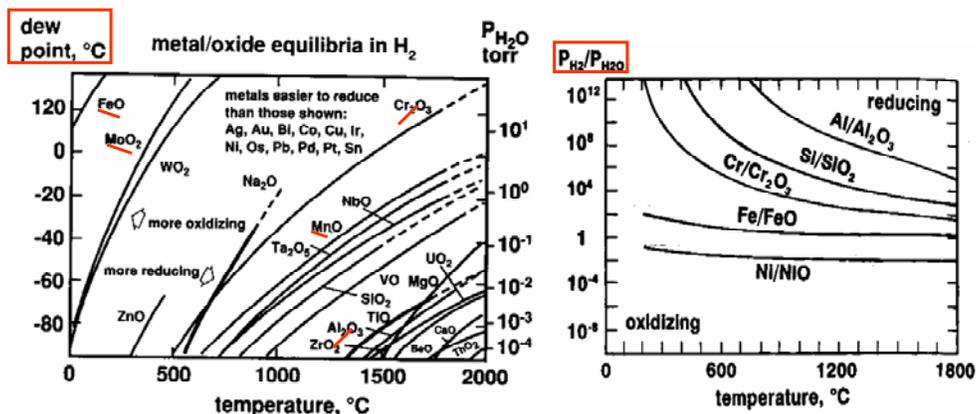


Figure 3.

In the cooling zones the primary atmosphere function is to prevent oxidation and maximize cooling rates. Generally, nitrogen by itself does an affective job of keeping oxygen out of the furnace; however, with sinter hardening considerations, we can increase the cooling rates significantly by adding hydrogen in this zone. Bowe<sup>3</sup> examined the effect of hydrogen on the heating and cooling rates and the results are shown in Figure 4.

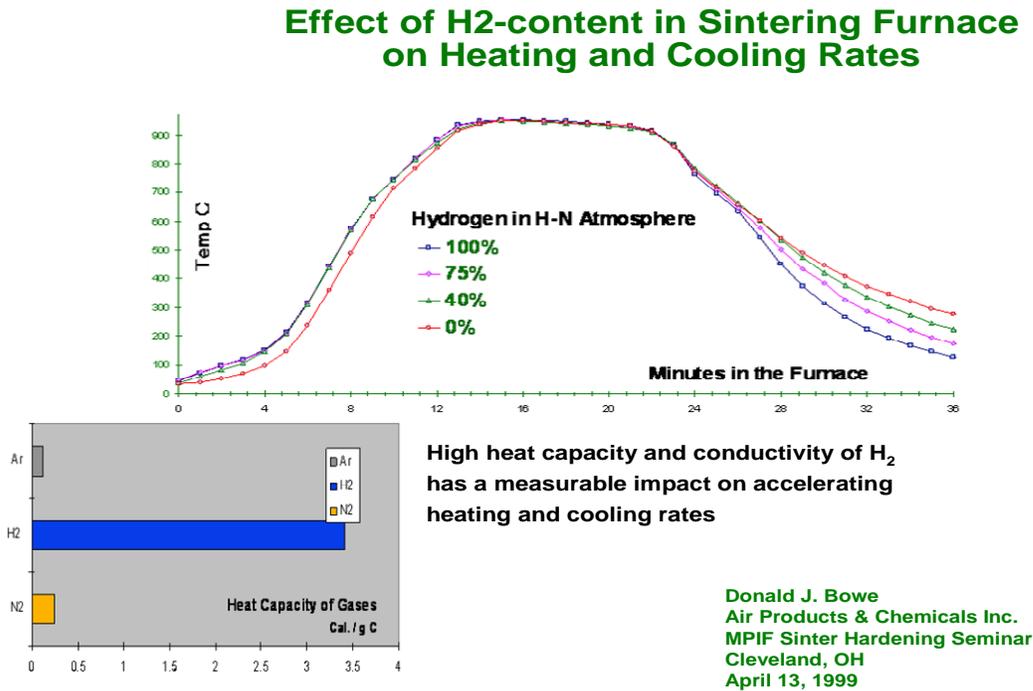


Figure 4

### EFFECT OF HYDROGEN ON DIMENSIONAL CHANGE

Garg<sup>4</sup> et al studied the effect of hydrogen and natural gas concentration on the dimensional changes in TRS bars of carbon steels. Their work showed that the linear dimensional growth from 0.24% to 0.32%, as the hydrogen concentration in the nitrogen/hydrogen atmosphere increased from 1 to 10%, followed by a decrease in growth with further increase in hydrogen concentration. They also showed that with 0.25% and 0.5 % addition of natural gas, there was no change in growth when hydrogen was increased beyond 10%. Figure 4 shows a summary of their results.

## Effect of H<sub>2</sub>% on Dimensional Change

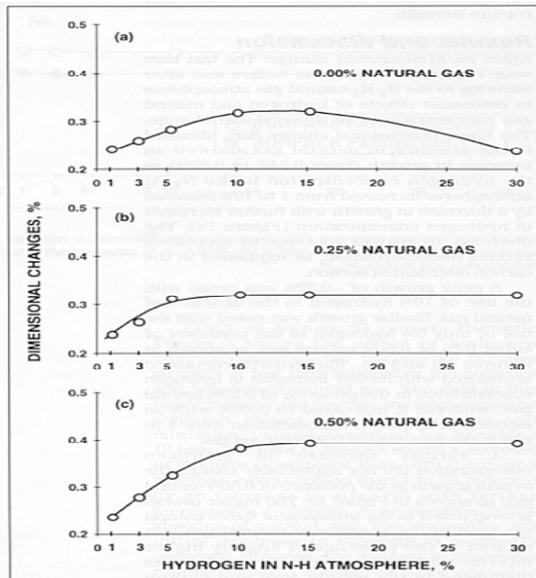


Figure 5

### References:

- Selecting N<sub>2</sub> Atmospheres for Carbon Steels, D, Garg et al, Metal Powder Report, September 1997

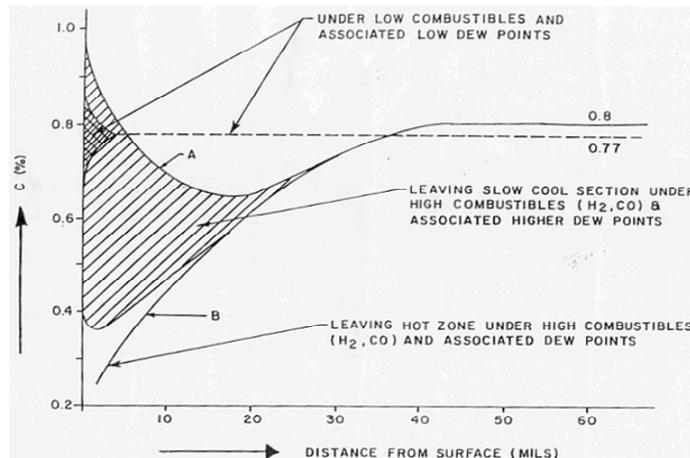
## DEW POINT AND CARBON CONTROL

Maintaining the desired carbon level in the PM part is essential to obtain consistent part properties. Properties such as hardness, dimensional stability and yield strength are subject to changes if there is carburization or decarburization occurring either in the surface or in the core of the PM part. In carbon neutral atmospheres, such as nitrogen based, with hydrogen or dissociated ammonia additions, the control parameter is the hydrogen to moisture ratio. In such atmospheres (5 to 10% hydrogen,) maintaining dew point below -30F will be reducing to the iron oxides yet be carbon neutral.

In carbon rich atmospheres such as endothermic gases, the control parameter is the carbon monoxide to carbon dioxide ratio and the dew point. In these atmospheres it becomes essential to control the carbon potential, using natural gas as the controlling gas, because of the inherent variations in carbon monoxide and carbon dioxide content of the atmosphere resulting from air and natural gas variations. Other causes for atmosphere composition variations include age and condition of the nickel catalyst, temperature control of the generator, instability of the CO in the atmosphere, and changes in the cooling water temperature.

Nayar<sup>5</sup> studied the effect of carbon monoxide containing and carbon monoxide-free atmospheres on the carbon content and concluded that in the case of atmospheres with low combustibles and low dew point, the changes in carbon level was small and limited to the first 5 mils (127 μm) from the surface of the sintered part. In the case of atmospheres with high combustibles and high dew point, the variations in carbon content was more than double; the effect could be observed as deep as 30 mils (0.76 mm) into the surface of the PM part. Figure 6 shows graphically these variations in carbon content.

## Combined Carbon Vs distance from the surface of steel P/M part in endothermic and H-N Atmospheres\*\*



Ref: H.S.Nayar, The concept of Furnace Zoning, Presented at the International P/M conf, Florence, Italy June 1982. Associazione Italiana di Metallurgia, Italy

Figure 6

One explanation for the differences in carbon content is that the PM parts undergo decarburization in the hot zone where the conventional atmospheres tend to be somewhat more decarburizing and then re-carburize in the temp range of 1700 to 1500°F, when using atmospheres with high combustibles and high dew point. In most cases, this decarburization and carburization cycle is not fully balanced and leads to inhomogeneous carbon distribution with consequent property variations.

### **OTHER CAUSES FOR PROPERTY VARIATIONS**

Atmosphere related problems such as improper delubrication procedure and oxidation at the front end or exit end of a furnace are also causes for variations in the properties of the sintered product. Depending on the type and severity of the problem, these variations can be significant. A detailed analysis of the atmosphere related problems and methodology for identifying and solving these problems was published in a paper<sup>6</sup> titled "Trouble Shooting Guide for Sintering Furnace Atmospheres."

## References

1. L.S.Sigl and P.Delarbre, "Impact of Oxygen on the microstructure and fracture morphology of Fe (Cr, Mo) P/M steels" Proc of the 2003 conf. on Powder Metallurgy &Particulate Materials. PM<sup>2</sup>TEC 2003, June 8-12 Las Vegas, MPIF.
2. George B. Fillari , R.J. Causton, Alan Lawley " Effect Of Cooling Rate In Sinter-Hardening On The Microstructure And Properties Of Hybrid P/M Steel" Proc of the 2003 conf. on Powder Metallurgy &Particulate Materials. PM<sup>2</sup>TEC 2003 , June 8-12 Las Vegas, MPIF
3. Donald J. Bowe ,Air Products & Chemicals Inc. MPIF Sinter Hardening Seminar, Cleveland, OH April 13, 1999
4. D.Garg et al, "Selecting N2 Atmospheres for Carbon Steels," Metal Powder Report, September 1997
5. H.S.Nayar, "The Concept of Furnace Zoning", Presented at the International powder metal conf, Florence, Italy June 1982. Associazione Italiana di Metallurgia, Italy
6. Tom Philips. "Trouble Shooting Guide for Sintering Furnace Atmospheres". Inter.J. Powder Met. 1990 vol26.pp 245-260.



tell me more  
[www.airproducts.com](http://www.airproducts.com)