Influence of Nitrogen/Hydrogen Atmospheres on Sintered Properties of P/M Components

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Abstract

The effect of individual gas constituents in a sintering atmosphere is examined to optimize the sintered properties of Iron-Carbon P/M components. The influence of sintered properties is reviewed as a function of hydrogen percentages and dew point in the sintering zone. Microstructures, porosity, pore morphology and dimensional changes are the subject of this review. The effects of CO containing atmospheres are compared against the non CO atmospheres in terms of hardness, carbon control and dimensional changes.

Introduction

Since the late 1970’s the use of Nitrogen/Hydrogen systems has become the atmosphere of choice for sintering of iron and steel p/m 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 and better economics and increased reliability became the reasons for the adoption and popularity of the nitrogen based atmospheres. 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 be changed as a function of time, during the sintering process thereby influencing the final properties.

The sintering mechanisms and sub processes taking place inside the furnace in the presence of an atmosphere include:

- Reducing Specific Surface Area
- Increasing Number and Strength of Inter-metallic Bonds
- Decreasing Pore Volume-Increasing Density
- Rounding of Pores
- Alloying and Homogenization
- Eliminating/Reducing Lattice Defects

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 some 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 P/M parts. Flow control panels can precisely monitor and control the mixing of different gases that make up the required atmosphere system.

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
- Densification, Carbon Control, Microstructure Control,
- Prevention of Oxidation and 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 such as atmosphere composition, flow rates, flow distribution, atmosphere pressure and exit curtain design.

In the Pre-heat 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 we need to maintain this ratio as high as possible at the lowest costs. 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.

Effect of Hydrogen on Dimensional Change:

Garg¹ 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 a linear dimensional growth from 0.24% to 0.32% as the hydrogen concentration in the N2/H2 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%.

Dew Point and Carbon Control
Maintaining the desired carbon level in the P/M part is essential to obtain consistent part properties. Properties such as hardness, dimensions and yield strength are subject to changes if there is carburization or de-carburization occurring either in the surface or in the core of the P/M part. In carbon neutral atmospheres, such as Nitrogen based with H2 or dissociated ammonia, the atmosphere control parameter is the hydrogen to moisture ratio. In such atmospheres (5 to 10% hydrogen,) maintaining a dew point below -30F will be reducing to the iron oxides yet be carbon neutral.

In carbon rich atmospheres such endothermic gases, the control parameter is the CO to CO2 ratio and dew point. In these atmospheres it is essential to control the carbon potential, using natural gas as the controlling gas, because of the inherent variations in CO and CO2 content of the atmosphere resulting from air and natural gas composition 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, changes in the cooling water temperature

Harb studied the effect of CO containing and non-CO containing 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 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 and also variations could be observed as deep as 30 mills into the surface of the P/M part.

Other Causes for Property Variations:
Atmosphere related problems such as improper delubrication, and oxidation at the front end or exit end of a furnace are also causes for variations in the properties of the final 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 titled “Trouble Shooting Guide for Sintering Furnace Atmospheres”.

References