Advanced Carbon Control in Sintering Atmospheres

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ABSTRACT

As the major driver for the Powder Metallurgy (PM) industry is the automotive industry, the sintering process now has to be more cost effective than ever. One way to success here is to combine multiple processes and to control the processes by newer technological development as well as the deployment of processes with less energy and lower consumption of resources.

The quality of PM parts is directly related to the control of process parameters of the individual production steps. The metallurgical properties and especially the microstructural changes in the case of a sintering component can only be regulated by controlling the furnace atmosphere accurately. The carbon control of the sintering process has however always been somewhat out of control since no suitable control concept was available. It is therefore a primary objective of this paper to give detailed results of successful control of carbon potential in sintering processes and leveraging the advantage of the control to produce higher quality product and at the same time to facilitate a lower production cost.

INTRODUCTION

Chromium has become more popular as an alloying element in the sintering industry in recent years because of its advantages in increasing hardenability and resistance to softening during tempering. Nickel is a more common alloying element but it is starting to be substituted by chromium because of its significantly higher price. One of the main reasons why this shift is slow is that chromium has properties that affect its performance in the sintering process, particularly its high affinity for oxygen.
In addition, the powder metal (PM) sintering industry is shifting towards sinter hardening in which two processes are combined in an effort to achieve faster, cheaper and more reliable production.

High quality sinter production should translate into a process in which all parameters are controlled to achieve all the product specifications. A failure to control the furnace atmosphere would jeopardize the total quality control. Nevertheless, it has been common practice not to control furnace atmosphere. Sintering of chromium alloys has now increased the need to control not only the carbon potential (C-Potential) but also the oxygen partial pressure. A patented furnace atmosphere control system, SINTERFLEX™, for controlling the C-Potential in sintering furnaces specifically designed through cooperation between Höganäs AB, and Linde Gas is described in this paper. Details include the results of an experimental study.

The second most important part of the sinter hardening process is to harden the alloys that have been sintered under a "C-Potential controlled atmosphere" without damage to their properties, completing the sinter production. The relevant Linde Gas technology FRIOFLEX is still under development and is reviewed in the final chapter of this paper.

FURNACE ATMOSPHERES IN THE SINTERING PROCESS

As with all furnace atmospheres used in the heat treatment of ferrous and non-ferrous metals, the type and function of the furnace atmosphere is determined by its constituents. An atmosphere can be neutral, carburizing, decarburizing, oxidizing or reducing, each of which can be a required function for different purposes in the manufacturing industry. In a sintering furnace however different functions are expected in different zones of the furnace, making sintering furnace atmospheres more challenging in terms of control and optimization.
Surface decarburization is the most common problem associated with the use of present furnace atmospheres for chromium alloys such as Astaloy CrM. The composition of Astaloy CrM is given in Table-1 below.

Table-1: The composition of the component prepared using Astaloy CrM in weight percent

Alloy	**C**	**Cr**	**Mo**	**Fe**
Astaloy CrM	0.45	3.0	0.5	Bal.

The decarburization problem is therefore that the use of PM sintered parts in manufacturing is restricted because of their increased sensitivity to fatigue cracks [*4 & *3]. Malas et al [*1] discussed the problems associated with existing furnace atmospheres, including endothermic atmospheres and nitrogen-hydrogen mixtures.

Increasing the C-potential at sintering temperature by adding fixed flows of hydrocarbons to conventional atmosphere types has been shown to be impractical, as well as producing a high carbon potential at lower temperatures, leading to sooting and excessive carbide formation. This experimental study and development have therefore focused on a new gas mixture as the furnace atmosphere and a new measurement method to control carbon in the mixture. The real problem for C-Control in fact is the lack of a satisfactory on-line system for measuring the exact conditions inside the furnace. Therefore monitoring of, and intervention in, the furnace atmosphere for any undesired condition is rather slow and too late in the process timeframe. Current industrial practice in monitoring furnace atmospheres gives insufficient indication of the carbon potential. A new approach is needed to address the issue.

DEVELOPMENT OF A NEW SINTERING CONTROL SYSTEM: SINTERFLEX™

1. What is SINTERFLEX™
   SINTERFLEX™ is a new and patented C-Potential control technology developed by Linde Gas and Höganäs AB for sintering furnaces. The system uses the simple gas sampling principle of the sintering furnace and a newly designed oxygen probe and internal analysis furnace arrangement to give exact C-Potential readings in the sintering zone of the furnace. The system controls the gas composition, particularly its carbon enrichment, to maintain a healthy C-Potential to produce sintered products of chromium alloys such as Astaloy CrM that are free of decarburization.

2. EXPERIMENTAL PROCEDURE

Knowledge of the oxygen partial pressure in the sintering zone tells the operator the actual conditions during sintering. It can be measured by an oxygen sensor, which determines whether the processed metal is oxidized or whether a metal oxide is reduced*2.

The development study has focused on two areas: a new furnace atmosphere to introduce carbon into the sintering zone that can be controllable and responds to any changes; and a new measurement and monitoring system with an oxygen probe to control this carbon containing atmosphere. The new furnace atmospheres used are mainly mixtures of CO, hydrogen and nitrogen with addition of propane, in proportions controlled by the new sintering atmosphere control system SINTERFLEX™.

2.1 INITIAL TESTS

First tests were carried out in a lab unit consisting of a heating chamber to generate the sintering furnace temperatures.

Synthetic gas mixtures similar to sintering furnace atmospheres were introduced into the system through the flange arrangement at the top of the probe unit. This work focused on the control of oxygen via an oxygen probe. The maximum limit of pO_2 is $5.5xE^{-18}$ for Astaloy CrM. A new zirconia probe was developed that could measure such very low oxygen partial pressures and meet C-potential control requirements. This probe worked well for low levels of oxygen measurements in the lab scale furnace in the first set of trials. It was then decided to demonstrate that the system could work in an industrial furnace up to 1160 °C (2100 °F). This temperature is limited only by the maximum heating capability of the internal heating element inside the heating chamber of the analyzer.

Direct addition of CO to the furnace atmosphere and CO produced by the decomposition of hydrocarbons such as methane and propane provided the required conditions to control the carbon content via reaction [1] and this CO value is measured by a CO analyzer.

$$CO = \underline{C} + \tfrac{1}{2} O_2 \qquad [1]$$

2.2 FURTHER DEVELOPMENTS

A new approach was needed to adapt the idea for industrial scale furnaces leading to further developments of the probe in the more convenient and compact design.

The newly designed system is shown in Figure-1, with the oxygen probe and its Al_2O_3 cover surrounded by a small electrically heated chamber, which would be heated to sintering temperatures. Gas sampled from the sintering zone passes through the encapsulated area where it interacts with the zirconium probe. The gas sample is also analyzed for its CO and H_2 content. These readings are used in the C-potential calculations. The probe readings are continuously monitored and recorded.

The system can be set to the C-Potential required by the process and the SINTERFLEX™ system then maintains this set value by means of regulating the flow of the enrichment gases.

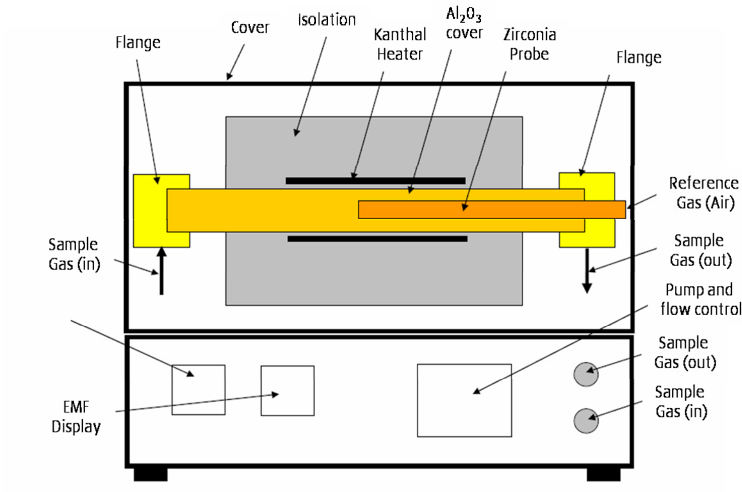


Figure-1: Schematic illustration of SINTERFLEX™ ACS mini.

The complete SINTERFLEX™ system as shown in Figure-2 comprises an analyzer and a FLOWTRAIN® allowing operators to control the sintering furnace atmosphere completely.

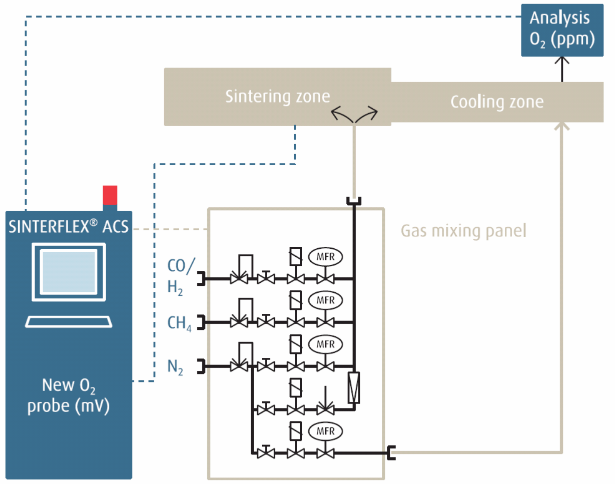


Figure-2: SINTERFLEX™ System

The oxygen sensor works on the same principle as a regular oxygen probe to make its measurements but within a small scale furnace. The sensor chamber would be filled with fresh furnace atmosphere providing an on-line measurement of oxygen in an mV- signal. The sample gas also provides on-line analysis of the furnace atmosphere. Input data is processed by a EUROTHERM 3504 controller and the C-Potential is calculated as an on-line measurement. Operators can control the furnace atmosphere parameters and correct any undesired condition immediately it occurs.

ATMOSPHERE CONSIDERATIONS AND RESULTS OF FINAL TESTS

1. Measurements during the recent tests have shown that the C-Potential could be regulated with propane (C_3H_8) added to the carrier gas as the controlling parameter. The trials were performed in Höganäs AB’s pilot scale furnace.

2. As stated above, sintering furnace atmospheres consist of mixtures of nitrogen, hydrogen, carbon monoxide and propane. Trials compared results with atmospheres with and without hydrogen. The trials aimed to provide an atmosphere with a neutral C-Potential to the parts at sintering temperatures thereby ensuring that carburization would be achieved during cooling. The importance of preventing decarburization is evident especially when considering the dynamic properties as shown in figure 6. Decarburization causes residual tensile stress at the surface. In figure 6 the residual stress obtained is 150MPa giving a bending fatigue strength of 200 MPa. A carburized surface removes tensile stresses and creates residual compressive stresses. The positive carbon gradient gives bending fatigue strengths of 450 to 520MPa, depending on the achieved stress levels.

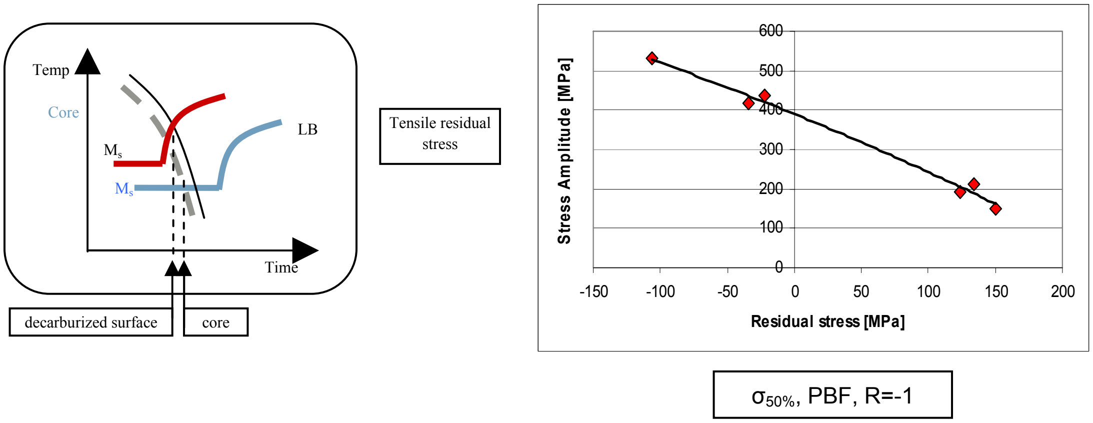


Figure 3 a. CCT diagram surface core microstructure b. Residual stress effect on bending fatigue strength.

3. The carbon potential setting of the furnace atmosphere is decided from calculations of the amount of oxygen and CO in the furnace. The carbon content of the components will differ depending on the chemical composition of the material being sintered. Their carbon content can be calculated by using Gunnarssons' formula [2] and the carbon potential of the atmosphere.

$\text{Log } Cp / C = 0.055\ (\%\ Si) – 0.013\ (\%\ Mn) – 0.040\ (\%\ Cr) + 0.014\ (\%\ Ni) – 0.013\ (\%\ Mo)\ C.$ [2]

The new oxygen probe successfully maintained the required atmosphere conditions and C-Potential. Figure-4 shows a 3-hour measurement window of a test where the C-potential was set to 0.38 at 2% H_2 atmosphere.

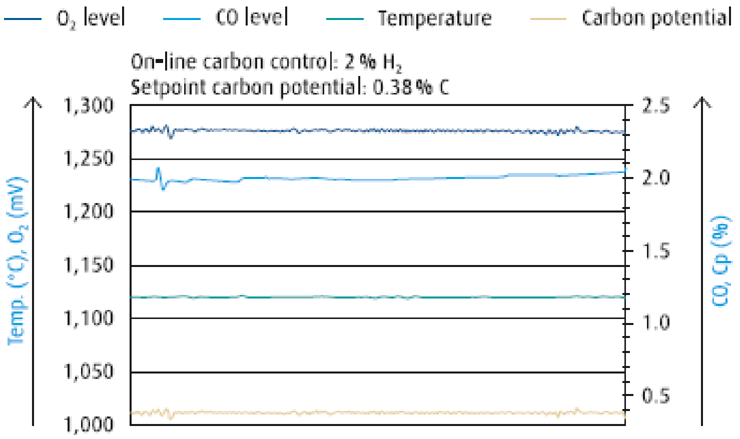
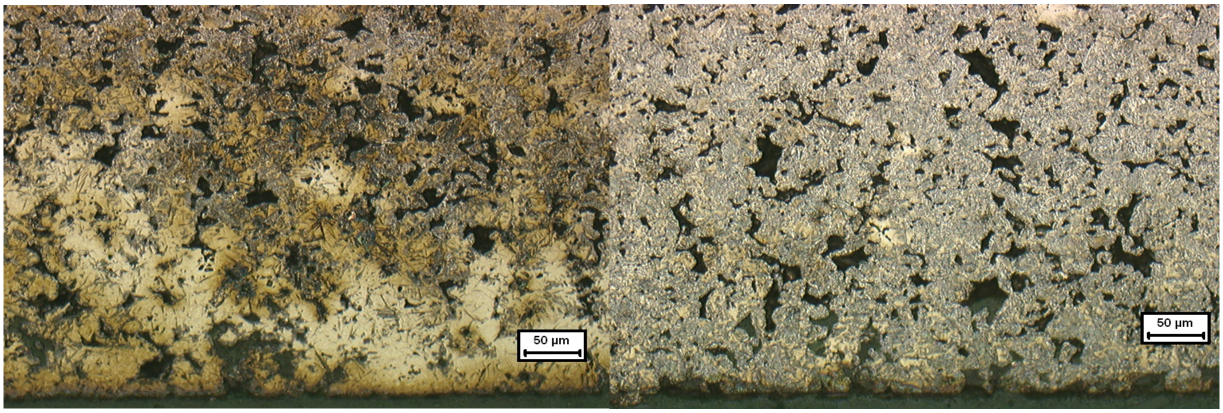


Figure 4 – Record of SINTERFLEX-controlled atmosphere parameters over a 3h production period

4. In a further investigation, an atmosphere containing N_2 - 2% H_2- 2% CO and additions of C_3H_8, was tested to carburize the surface to 0.45% carbon where the carbon content in the centre is 0.38%. The results showed a positive carburizing gradient approximately ~150µm thick for CrM material. The same material however showed no carbon profile in a dry atmosphere of N_2 – 10% H_2. Figure- 5 illustrates a comparison of these two studies. It has also been observed that at a constant atmosphere mixture, the carbon potential increases as the temperature falls.



Astaloy CrM treated with CO atmosphere *Astaloy CrM treated with N2/H2 Atmosphere*

Figure-5: Comparison of CrM Microstructures in different atmosphere conditions

EFFICIENT COOLING FOR SINTER HARDENING

Malas et al *1 have achieved cooling rates of 2.5 – 4.5 °C/sec in an industrial furnace where many operational and constructional limitations affected the results, including the impingement time, distance and flow rates. It was therefore decided to go one step back and undertake pilot tests to optimize the process for industrial application. Linde Gas FRIOFLEX™ technology, which is being developed for sinter hardening furnaces, is now under full scale test as this paper is being published.

The recently updated system now consists of a series of top and bottom nozzles that will allow the parts to cool down until they reach the temperature where transformations stop at the hard structures required by the specifications. The system will be available as a separate or a retrofit unit.

CONCLUSIONS

The newly developed oxygen probe offers the following advantages:

1. Use of and quantitative control of carbon neutral or carburizing atmospheres to avoid surface decarburization giving higher quality parts and increased product performance.
2. Potential to replace a subsequent case hardening operation by means of tailored surface carbon gradients during sintering, leading to lower total cost and better dimensional tolerances.
3. Provision of valuable information on the quality of sintering along with traceability through the optional process data storage system which will help avoid scrap and increase overall equipment effectiveness.
4. Any disturbances to the process and potential atmosphere problems (gas flow/-rate and draughts) are detected quickly and adjusted easily through on-line control which will again reduce the costs of lost production and scrap.

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