Considerations When Sintering Oxidation-Sensitive PM Steels

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Abstract

The majority of mass-produced PM steels are sintered in continuous belt furnaces operating at temperatures up to 1150°C/2100°F. The alloying elements Cu, Ni, Mo and C are normally used to obtain good material properties. However, environmental concerns and cost might restrict their use, especially Cu and Ni, as additives to PM steels, in the future. Chromium is commonly used in solid steels mainly due to low cost and good material performance, but is still rarely used for PM structural parts. One reason for this is oxidation sensitiveness. However, continuously improved sintering technology and the more frequent use of N_2-based atmospheres now makes alloying with Cr more attractive for the production of high-performance PM components at a low cost. Considerations when sintering Cr-alloyed materials in different types of furnaces are given in this paper.

1 Introduction

PM steels alloyed with oxidation-sensitive elements, such as Cr, Mn and Si, are still in restricted use in the PM industry for the production of structural parts. This is mainly because processing conditions are believed to be technically complicated for the production of consistent parts. In high-strength, low-alloyed solid steels, Cr, Mn and Si are widely used as alloying elements as these are cost-effective and result in good material performance. However, concerning PM, these elements are still mainly restricted to specific top-performance applications and for stainless steels. Production of PM structural parts alloyed with Cr, Mn and Si is in its initial stage.

In the future, it is expected that oxidation-sensitive elements will enter the market more and more as additives to mass-produced PM steel components. This is because the importance of both cutting costs and continuous improvement of material quality will increase. At present, atmospheres containing CO/CO_2 (e. g. endogas/exogas) are of great importance to the PM industry due to economic factors. There are,

however, some drawbacks of using these atmospheres, such as problems with good carbon control, sooting behaviour and the inability to sinter important alloying systems [1]. Today, N_2-based atmospheres are widely available. They are easy to control and can be used for a large variety of materials.

By knowing the dewpoint of the atmosphere and its composition, it is easy to predict the ability to use the atmosphere for processing different material compositions. In this paper some production tests for analysing the actual processing conditions in the high-heat zone were done in furnaces operating at approx. 1120°C/2050°F and 1250°C/2280°F respectively. These tests have improved on understanding of the sintering process and form the basis achieving better sintering control of all types of alloying systems in the future.

2 Sintering atmospheres

2.1 Theoretical considerations

Industry today normally uses dewpoint of sintering atmospheres to assess the processing ability when producing defined PM material compositions. Dewpoint is a well-known conception and everybody has a "sense" of how the dewpoint is related to successful component production. However, in order to be successful when producing most materials (especially those containing oxidation-sensitive elements such as Cr, Mn or Si), it is also important to understand the relevance of dewpoint for defined atmosphere compositions. The dewpoint is related to the partial pressure of oxygen in the atmosphere by the sintering temperature. It determines whether the sintering will be successful or not.

Oxygen partial pressure in the sintering zone is a conception that tells the operator the actual conditions during sintering. It can be measured by an oxygen sensor, which determines whether the processed metal is oxidised or if a metal oxide is reduced. The chemical reaction

$$Me + 1/2O_2 = MeO$$

is found in tabular form [2] and is the equilibrium pressure of oxygen when both metal and metal oxide coexist. This is the maximum oxygen pressure allowed in the sintering zone to make the metal remain in its metallic form.

Green compacts contain remainders of oxides on the surface of the metal particles. Initially, these have to be reduced to metal, either by a reducing media in the material (e. g. C) or by reducing agents in the atmosphere (e. g. H_2). Before the surfaces are clean from oxides, sintering bridges are only developed to a limited extent. Significant bridge-building between particles, being a prerequisite for material performance, occurs when the surfaces are clean from oxides. By knowing the oxygen partial pressure of the atmosphere in the sintering zone, conditions are also known for whether a defined material composition can be sintered or not. This figure can also be used for calculation of dewpoint at the sintering temperature. The maximum allowed dewpoint of defined N_2/H_2 mixes, for sintering of some Cr-alloyed PM steels at 1120°C/2050°F, are showed in figure 1.

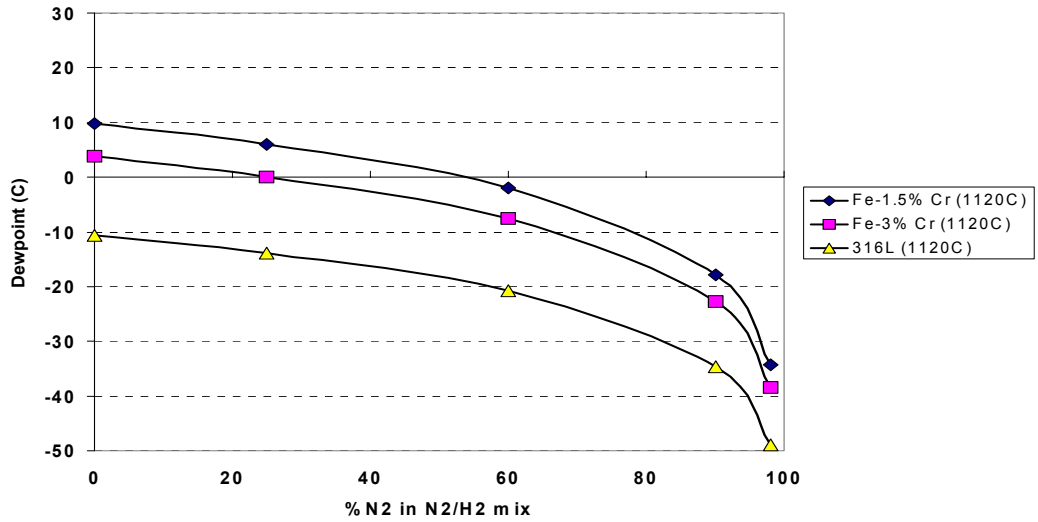


Figure 1: Dewpoint vs N_2/H_2 atmosphere composition for the sintering of Fe-1.5%Cr, Fe-3%Cr and 316L at 1120°C/2050°F (calculations according to [2] and [3])

It is important to note from the figure that the higher the relative N_2 content in the atmosphere, the higher the demand for a low dewpoint for that type of atmosphere. Theoretically, sintering in pure N_2 demands an unrealistically low dewpoint, but in practise carbon in the material and oxygen in the powder creates a protective atmosphere of CO that is sufficient for sintering of Cr-alloyed steels. Furthermore, the higher the Cr-content in the materials, the better the atmosphere conditions have to be. This is due to increased activity of Cr when the content increases.

By increasing the temperature, the sintering conditions will improve (or the maximum allowed dewpoint is increased) for a defined atmosphere composition. This is showed in figure 2 below.

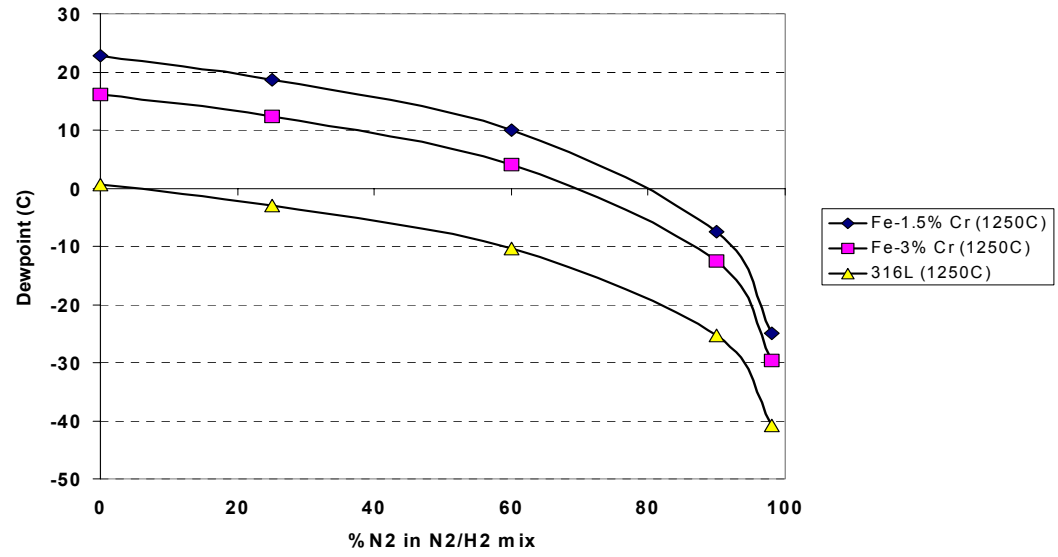


Figure 2: Dewpoint vs N_2/H_2 atmosphere composition for the sintering of Fe-1.5%Cr, Fe-3%Cr and 316L at 1250°C/2280°F (calculations according to [2] and [3])

Practically, it means that an atmosphere with a lower purity (or higher dewpoint) can be used when the sintering temperature is raised. Furthermore, the speed of bridge-building between particles increases at higher temperatures due to improved element diffusion. Therefore, the performance will improve when increasing the temperature and particularly in the case of oxidation-sensitive material, using high temperature sintering will considerably decrease the content of oxygen in the sintered material and significant improved mechanical properties

There is a negative effect from having a high relative content of H_2 in a N_2/H_2 atmosphere mix. This is the risk of decarburizing, especially at high processing temperatures. This is due to the reaction

$$C + 2H_2 = CH_4$$

having a negative figure for the formation of CH_4 and a fall in the change of Gibbs energy (delta G^0) with temperature (larger driving force of decarburizing when the temperature is increased). This means that C in the material will react with H_2 in the atmosphere and the lower the H_2 content (i. e. more relative content of N_2) the lower the risk of decarburizing.

2.2 Practical considerations

In practice, the protective atmosphere used has a defined dewpoint when entering the furnace. This dewpoint will, however, vary during the processing and depends mainly on the following factors:

1 Ability to properly control atmosphere flow
2 Flow rate of the atmosphere
3 Conditions during dewaxing
4 Air/water leakage into the furnace
5 Throughput of material or production rate
6 Material composition and type/amount of lubricant used

Therefore, in order to prevent the risk of having poor conditions in the high heat zone, the atmosphere should be selected with a good margin (see figures 1 and 2). If optimised sintering conditions are to be achieved in a production campaign, points 1, 2, 3 and 4 should be considered in particular. The atmosphere flow should be directed opposite to the transportation of the furnace load and atmospheres in the dewaxing- and sintering zones should be kept separated. The flow rate should be controlled to avoid unnecessary turbulence. Notably is also that high production rates deteriorate sintering conditions in conveyor belt furnaces, as the belt is heavily oxidised when using rapid burn off (RBO). However, in [4] it is showed that despite high production rate and by using RBO, prealloyed Cr steels can successfully be processed in conveyor belt furnaces. Proper control of protective atmosphere flow and RBO conditions was the key to success.

In mass production of components, the different zones of the sintering furnace have great significance for the achieved material performance after sintering. Controlling the sintering process is often done in the cooling zone by an oxygen sensor (lambda sond), but the conditions there are not significant for establishing the success of good bridge-building and consequently limited knowledge is gained on final part performance. Therefore, it is most significant to determine the conditions in the sintering zone. In furnaces with no double door system, there are normally some disturbances from the dewaxing part of the furnace and thus it is preferable to measure the conditions in the middle as well as at the end of the sintering zone.

An economical sintering atmosphere contains a relatively low content of H_2, but this also requires a relatively low dewpoint (see figures 1 and 2) of the N_2/H_2 mix. In practice, this is of no concern as the commercially available industrial gases of today are of good quality.

In the following, some test results under production conditions are given showing the influence of processing and how the conditions can vary in the high heat zone.

3 Experimental

In all experiments, a prealloyed Fe-3%Cr-0.5%Mo steel powder, Astaloy CrM, was used with the following chemical composition:

Table I: Chemical composition of material used in the investigation

Cr (%)	Mo (%)	C (%)	O (%)	Fe
3	0.5	<0.01	<0.25	Balance

This powder was admixed with graphite and the target value was 0.3% combined carbon after sintering (in this test material the analysed oxygen was 0.15%). 0.8% H-wax was added as lubricant.

Specimens for tensile testing and impact energy testing according to ISO 2740-1993 and ISO 5754-1978 respectively were used for the determination of tensile strength, yield strength, elongation, hardness, impact energy and chemical analysis. The impact energy specimens were also prepared for metallographic studies to reveal any carburisation/decarburisation and/or oxidation.

All specimens were compacted at 700 MPa/50.9TSI and sintered together with ordinary load in some production furnaces. During processing the sintering atmosphere was sampled at different locations in the furnace and a profile of its actual dewpoint, as well as CO content at the respective location, was monitored. The sampling of atmosphere was primarily done from the sintering zone and optionally from the dewaxing zone and cooling zone. A schematic test set-up is showed in the following figure 3.

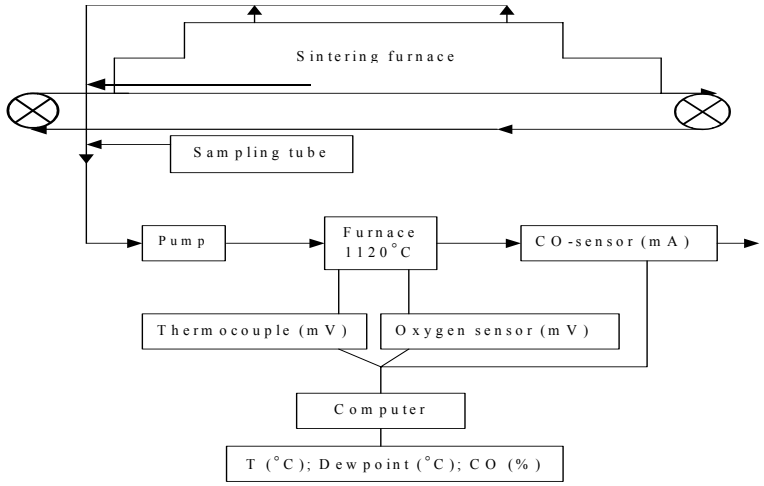


Figure 3: Test set-up for measuring actual atmosphere dewpoint and CO content in sintering furnace

In the tests performed, sampling of the atmosphere was done by introducing a 6mm stainless steel (SS) tube from the furnace entry by loosely mounting the tube by the side of the belt. When mounting the tube by the belt, atmosphere was sampled either continuously or at selected locations in the furnace. The rear end of the SS-tube was connected to a vacuum tube with a gas-tight coupling and the atmosphere was

extracted from the furnace via a pump installed in a measuring unit located outside the furnace. When the temperature was too high in the sintering zone (>1150°C/2100°F) or when sampling the atmosphere in the cooling zone, gas outlets mounted on the furnace body were used for the extraction of furnace atmosphere to the measuring unit.

The measuring unit consists of an encapsulated furnace pre-set at 1120°C/2050°F and equipped with an oxygen sensor and a thermocouple. The sampled gas passes this furnace and is further transported to a carbon monoxide sensor monitoring the CO-content.The electrical signals received from the oxygen sensor, thermocouple and carbon monoxide sensor respectively were transmitted to a data logger and then further transferred to a computer where all data were processed. An alternate way of analysing the sampled atmosphere is to cool it down to room temperature and measure dewpoint. However, in these tests an oxygen sensor was used due to its quick response to atmosphere changes.

A preset temperature of 1120°C/2050°F was selected for the small, encapsulated furnace unit as actual conditions (or close to actual conditions) of the sintered test object were to be determined. However, when measuring at temperatures other than 1120°C/2050°F, these atmospheres were calculated from the analysed 1120°C/2050°F conditions enabling a good estimation of the actual conditions at the respective sintering temperatures.

In the following chapter, some results of measured dewpoint profiles and CO-contents in furnaces under production conditions are evaluated and discussed. The dewpoint of the inlet gas compositions were in all cases approx. –35°C/-31°F. The critical dewpoints of the respective atmospheres are tabulated below in table II.

Table II: Critical dewpoint for the sintering of Astaloy CrM in the respective production test

Production test no	Atmosphere	Sintering temperature	Critical dewpoint
1	85/15 N_2/H_2	1120°C/2050°F	-20°C/-4°F
2	90/10 N_2/H_2	1250°C/2280°F	-12°C/10.4°F
3	25/75 N_2/H_2 (DA)	1120°C/2050°F	0°C/32°F
4	90/10 N_2/H_2	1120°C/2050°F	-23°C/-9.4°F

From this table it is obvious that there were good margins to sinter Astaloy CrM in all atmospheres used in the tested furnaces when considering the quality of the inlet atmosphere. However, it also assumes sufficiently good process control.

4 Result and discussion

4.1 First production test – the positive influence of good process control when using RBO

In the first test, a continuously loaded belt furnace equipped with RBO and operating at 1120°C/2050°F was assessed. The furnace atmosphere was 85/15 N_2/H_2 and no hydrocarbon was added for carbon control. Sampling of the atmosphere was initially done in the middle of the RBO zone, where the SS-tube was stopped temporarily for measuring. The next measurement was taken at the start of the high-heat zone. This was done after a sufficient interval to allow the conditions to stabilise. Later the tube was transported on to the end of the high heat zone, where the conditions were measured.

Figure 4 below shows schematically the measurement locations (a, b and c). The calculated dewpoint (from the output of the oxygen sensor) of the atmosphere during operation is on the left vertical axis and its CO-content on the right vertical axis. This figure also presents the analysed dewpoint of the inlet gas as well as the maximum allowed dewpoint for processing Fe-3%Cr-0.5%Mo at 1120°C/2050°F.

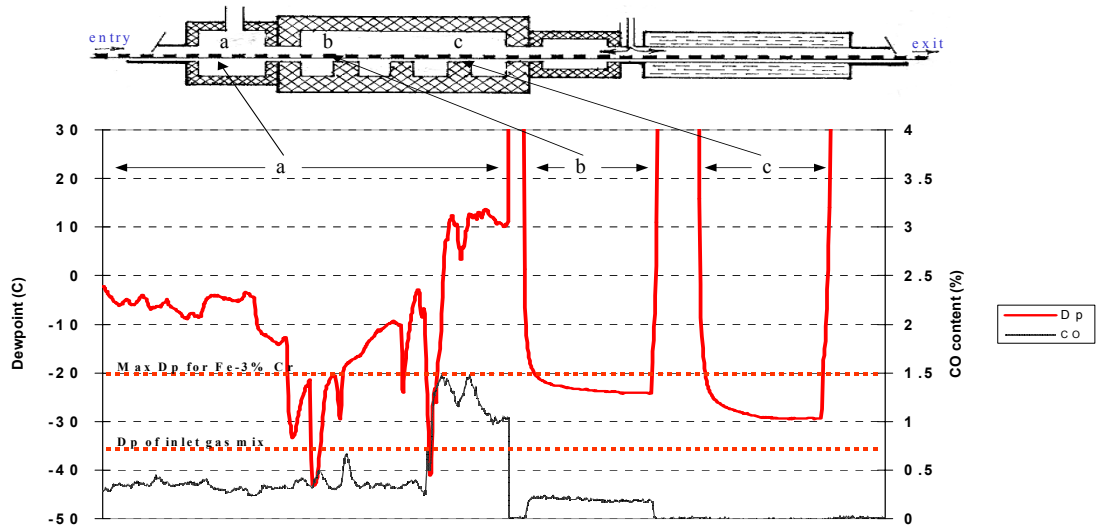


Figure 4: Dewpoint and CO measured in belt furnace operating at 1120°C/2050°F in 85/15 N_2/H_2 atmosphere (with RBO)

This is an example of controlled conditions for the mass-production of components. CO is detected in the RBO-zone (a) and is evidence of CO/CO_2 formation when lubricant from the pressed parts is vapourised/oxidised. It is typical that the atmosphere conditions vary a lot during the dewaxing stage and stabilise later in the sintering zone. Furthermore, dewaxing also oxidises the heat-resistant metallic transportation belt, which will influence the actual conditions in the sintering zone when the oxidised belt is later reduced. Although no hydrocarbon is added to the atmosphere, CO is detected at the beginning of the high heat zone (b), which reveals some of the vapours originating from the dewaxing stage (a). At the end of the high heat zone (c) no CO is detected and the atmosphere conditions have also improved.

Evaluation of the sintered test parts showed the following chemical analysis and mechanical properties (table III). These figures correspond very well with reported data [5] from good sintering of this type of Cr-alloyed PM steel.

Table III: Chemical analysis and mechanical properties of test material

Chemical analysis		**Mechanical properties**				
C (%)	O (%)	Rm (MPa/ksi)	Rp02 (MPa/ksi)	HV10	A (%)	IE (J)
0.32	0.12	860/124.7	580/84.1	240	1.4	19

A metallographic section (figure 5) shows an even carbon profile and there are no oxides present at the grain boundaries.

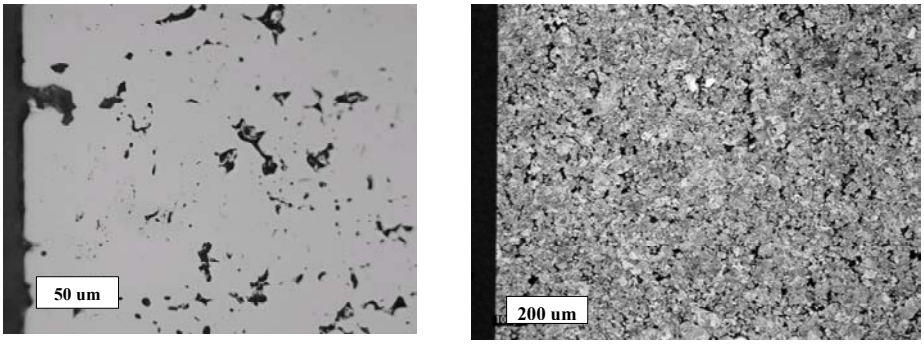


Figure 5: An unetched (left) and etched (right) section of the test material. No traces of grain boundary oxides and an even carbon profile

When the atmosphere quality is poor, grain boundary oxides are normally found in Cr-alloyed steels. When mass-producing parts, RBO is often essential, which has the negative effect of heavily oxidising the metallic belt. Therefore, it is important to have good control in order to separate the atmospheres in the dewaxing zone and the sintering zone, which is done very well in this furnace.

4.2 Second production test – the positive influence when using high temperature sintering

The next test was performed in a pusher-type furnace operating at 1250°C/2280°F in a 90/10 N_2/H_2 atmosphere. The production rate was fairly low and conditions for sintering should therefore be excellent. Dewpoint of the inlet atmosphere was around -35°C/-31°F and the theoretical level for processing Fe-3%Cr-0.5%Mo is only approx. -12°C/10.4°F. Gas outlets mounted to the furnace body at the beginning of the high heat zone as well as by the end of this zone, were used for atmosphere sampling. Figure 6 below shows the analysed atmosphere.

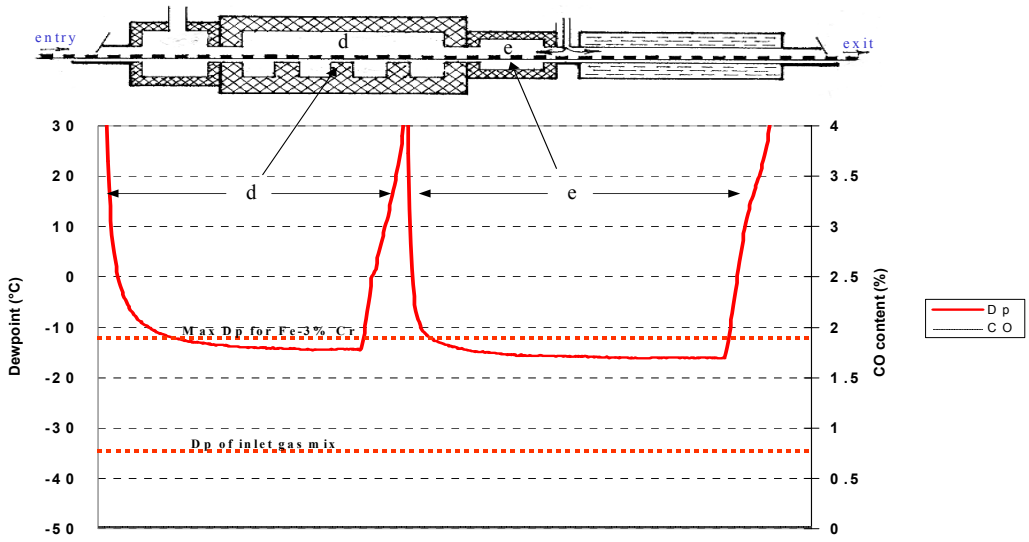


Figure 6: Dewpoint and CO measured in pusher furnace operating at 1250°C/2280°F in 90/10 N_2/H_2 atmosphere

No CO was detected, which is evidence that dewaxing gases do not disturb the atmosphere in the high heat zone. However, in this specified case there was a problem with water leakage from the cooling zone that deteriorated the conditions in the high heat zone Despite problems with the furnace there are still

margins to process Cr-alloyed PM steels. High temperature processing has now also improved the properties significantly after sintering and one important reason is the very low oxygen content in the sintered material (table IV).

Table IV: Chemical analysis and mechanical properties of test material

Chemical analysis		**Mechanical properties**				
C (%)	O (%)	Rm (MPa/ksi)	Rp02 (MPa/ksi)	HV10	A (%)	IE (J)
0.30	0.01	1010/146.5	610/88.5	250	1.5	28

Metallographic examination of the material shows more rounded porosity than in the first case, which is a result of the high-temperature sintering (figure 7)

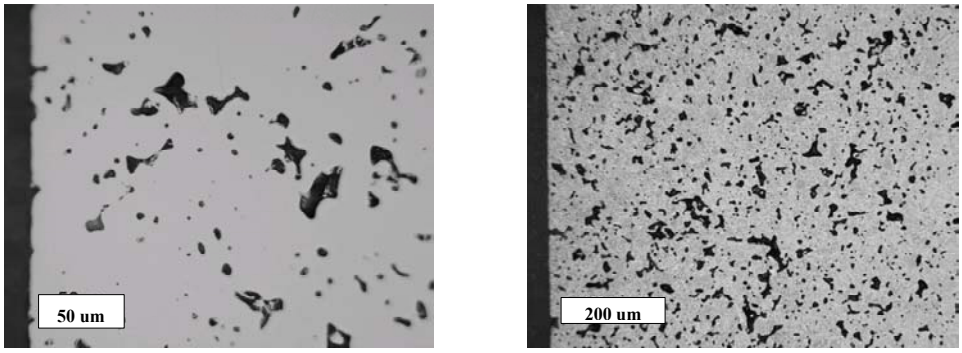


Figure 7: An unetched (left) and etched (right) section of the test material. Rounded porosity showing no traces of grain boundary oxides and an even carbon profile

4.3 Third production test – the negative influence of poor atmosphere control

By increasing the H_2 content in the atmosphere, the sintering conditions will improve (see figures 1 and 2) and this is illustrated in the next test. Theoretically, the dewpoint of the atmosphere only has to be lower than 0°C/32°F to be successful when sintering Fe-3%Cr-0.5%Mo. The measured dewpoint and CO-content in the furnace are showed in figure 8 below.

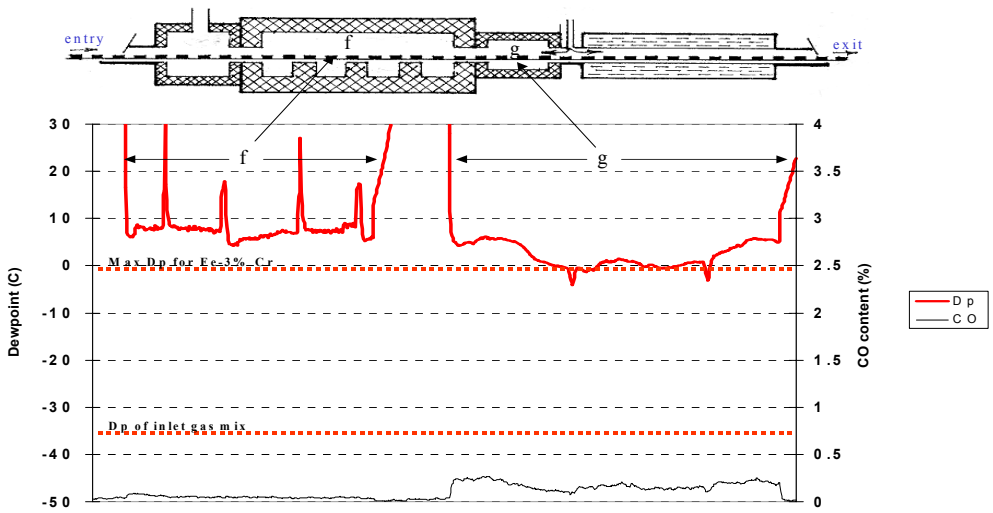


Figure 8: Dewpoint and CO measured in pusher furnace operating at 1120°C/2050°F in DA (25/75 N_2/H_2 atmosphere)

Two measurements were taken, one in the middle of the sintering zone (f) and one in the first cooling section (g) of the furnace as is indicated in the figure. Despite the powerful atmosphere for reduction (high relative H_2 content), the conditions in the sintering zone are not good. In the present case there were problems with both water leakage and air leakage and the conditions were not sufficient for sintering Fe-3%Cr-0.5%Mo. This can be seen from the variable figures and high level of dewpoint during measuring which occurred both in the high heat zone and in the cooling zone. A common occurrence, when there are no disturbances in atmosphere flow, can be seen in figure 6, where the conditions stabilise over time. A stabilisation time is necessary as the way from the furnace to the measuring device has to be cleaned from N_2 purged through the system in between the measurements.

In the present case the poor atmosphere is due to water leakage in the second cooling section and air entering the furnace during charging/discharging of material. The first measurement was done in the sintering zone where it is obvious when the entry doors as well as the exit doors are in operation. The entry door has more impact on the atmosphere quality than the exit door. This is seen by the two higher peaks (no 1 and 3), which show the interval of operating the entry door. Peaks no 2 and 4 originate from the operation of the exit door. In the cooling zone only the operation of the entry door is visible. It is interesting to note that the conditions are better in the cooling zone than in the high heat zone. This is probably because graphite carriers are partly oxidised (CO detected in the cooling zone) by the leakage of air. Furthermore, the presence of air is so low that insignificant CO is oxidised to CO_2 (sampling is in the first cooling zone, where the temperature still allows oxidation of the graphite carriers). No CO is, however, detected in the high heat zone, which reveals no problem with dewaxing.

Below in table V the chemical analysis and mechanical properties of the sintered test bars are presented.

Table V: Chemical analysis and mechanical properties of test material

Chemical analysis		**Mechanical properties**				
C (%)	O (%)	Rm (MPa/ksi)	Rp02 (MPa/ksi)	HV10	A (%)	IE (J)
0.26	0.20	700/101.5	490/71.1	200	1.4	14

The table indicates a small degree of decarburisation and shows a high oxygen content. This resulted in poor mechanical properties. A metallographic section shows some loss of carbon at the surface and also oxidation at the grain boundaries (figure 9).

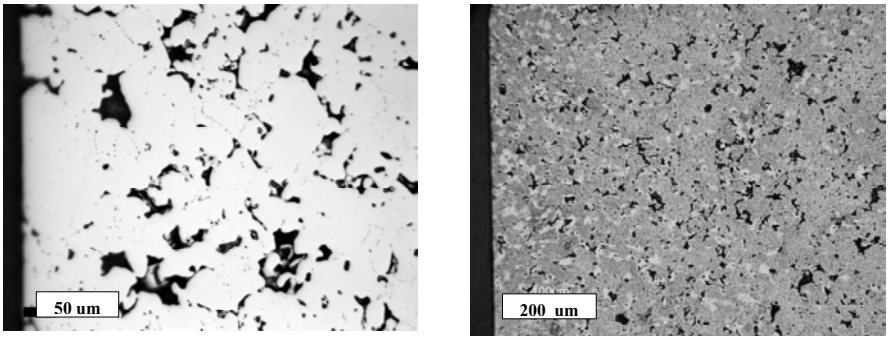


Figure 9: An unetched (left) and etched (right) section of the test material. Traces of grain boundary oxides and a small degree of decarburising

4.4 Fourth production test – the negative influence of too much oxygen added when using RBO

In the final study, a continuously loaded furnace operating at 1120°C/2050°F and using RBO, was tested. The furnace atmosphere was 90/10 N_2/H_2 and no hydrocarbon was used for carbon control. Sampling of atmosphere was made continuously from the entry side to the middle of the high heat zone. Figure 10 below shows the analysed atmosphere.

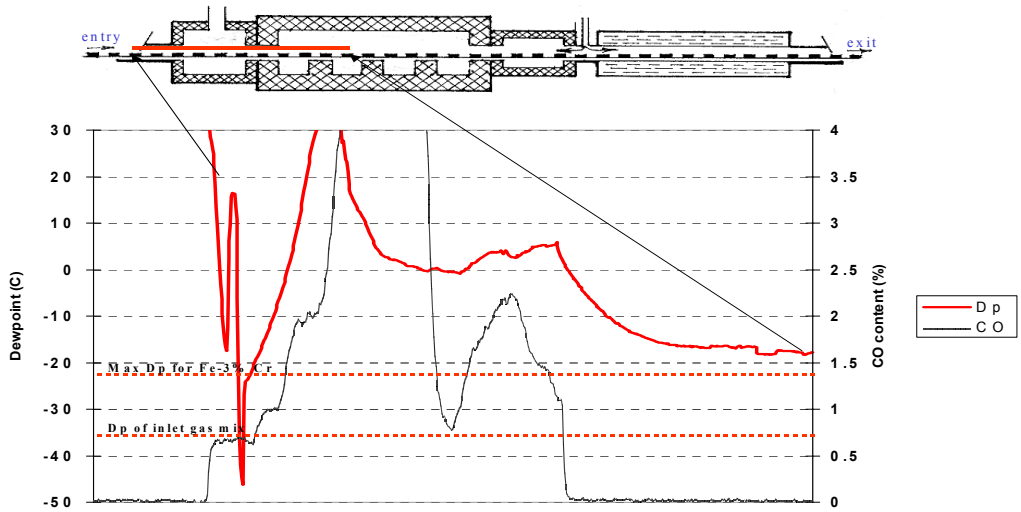


Figure 10: Dewpoint and CO measured in belt furnace operating at 1120°C/2050°F in 90/10 N_2/H_2 atmosphere (with RBO)

The detected CO varied very much in the dewaxing zone. Excessive addition of oxidation media is probably responsible for these variations. As a consequence, the metallic belt oxidises heavily and the following reduction of the belt in the high heat zone deteriorates atmosphere conditions, causing decarburisation (see table VI). It is interesting to note the absence of CO in the high heat zone, which suggests good separation of atmospheres in the dewaxing and sintering zones respectively. However, very poor conditions in the RBO zone effect the high heat zone and do not allow sintering of Fe-3%Cr-0.5%Mo. Evaluation of chemical analyses and mechanical properties showed the following (table VI):

Table VI: Chemical analysis and mechanical properties of test material

Chemical analysis		Mechanical properties				
C (%)	O (%)	Rm (MPa/ksi)	Rp02 (MPa/ksi)	HV10	A (%)	IE (J)
0.22	0.21	580/84.1	420/60.9	160	2.1	22

The chemical analysis reveals decarburisation, which also makes the material more susceptible to oxidation at the surface. This is also reflected in poor mechanical properties.

Figure 11 confirms decarburising at the surface where oxides are found in the grain boundaries.

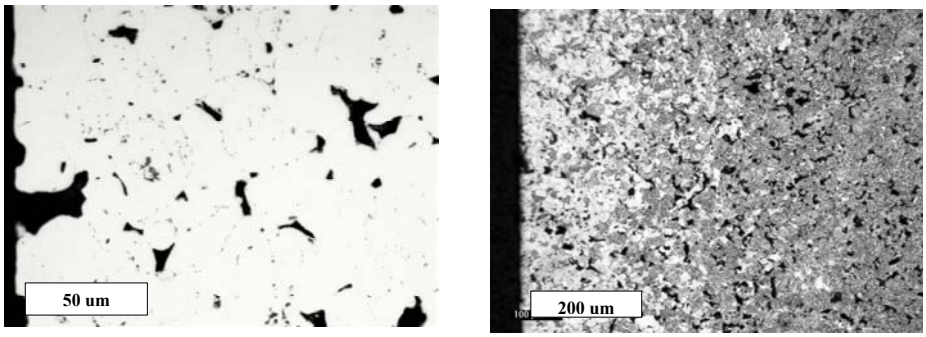


Figure 11: An unetched (left) and etched (right) section of the test material. Grain boundary oxides and decarburising

4.5 Concluding remarks of the furnace measurements

The different production tests have showed the relevance of measuring actual conditions in the high heat zone. Mechanical properties obtained for a Cr-alloyed PM steel are logical, when considering the analysed atmosphere profiles. Good process control at 1120°C/2048°F sintering results in an oxygen content of approx. 0.1% and mechanical properties in the high-performance range for a Fe-3%Cr-0.5%Mo PM steel. Increasing the process temperature to 1250°C/2282°F results in a significant improvement of the properties. This is due to low oxygen content (approx. 0.01%) and is easy to realise even with protective atmospheres of relatively poor quality.

5 Conclusions

The following conclusions can be drawn from the present tests:

1 PM steels containing Cr can be successfully processed in both belt furnaces and other commonly used sintering furnaces provided
- care is taken to avoid air/water leakage into the furnace
- excess addition of oxidation media is avoided during dewaxing
- proper control of sintering atmosphere flow is in place so atmospheres in the sintering- and dewaxing zones are kept separated

2 Increased sintering temperature reduces the requirement for atmosphere purity and has a major positive impact on mechanical performance for materials alloyed with Cr

3 On-line control of the sintering process is most relevant in the high heat zone and is very useful for assuring consistent production of any alloying system

4 Oxygen sensor technology has an important advantage compared to dewpoint measurement, namely fast response to actual processing conditions, though more development is needed to refine this technique for use at high temperature

6 References

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