CHORMIUM ALLOYED PM STEELS – A NEW POWDER GENERATION

Author: Björn Lindqvist, Höganäs AB

Abstract: The dominating part of mass produced PM- steels today are sintered in continuous furnaces operating at maximum 1150°C. The alloying elements Cu,Ni,Mo and C are normally used to obtain good material properties. However, environmental concerns and cost might restrict the use of especially Cu and Ni, as additives to PM-steels, in the future. Since many years, Cr-alloyed PM-steels are available as complement to the existing Cu/Ni-alloyed materials. This family of materials has many advantages and the most important are cost, the ability to be recycled and hardenability. However, still PM part production of Cr-steels is mainly limited to top performance applications sintered at high temperature. In the present paper focus is put on processing Cr-alloyed PM-steels in furnaces operating at maximum 1150°C. It shows necessary precautions to be taken for the successful sintering of PM-steels alloyed with Cr.

1 Introduction

Cr-alloyed materials have been available on the market for many years ever since the middle of the 80-ies. In e g (1) and (2) processing and properties of low alloyed Cr-steels, atomised during reduced conditions, are discussed and in (3) similar grades which are water atomised are presented. However, by that time the market was not prepared to meet this new material category and those were mainly used for specific top performance applications which also is the case of today. One important reason to the restrictive use of Cr-steels is sensitivity to oxidation, a fact which has formed unjustified opinions claiming that the maximum allowed sintering temperature used in conventional belt furnaces are not sufficient for the sintering of Cr-alloyed steels.

In 1998 a Cr/Mo alloyed material, Astaloy CrM, was presented (4) to be used as complement to the existing Cu/Ni/Mo alloyed materials for mass production of high performance components no matter if sintering is performed at high temperature or in conventional belt furnaces. Since the introduction, some production has started of Astaloy CrM and this grade has also been used extensively in many sintering experiments. This has gained lots of sintering experience of Cr-alloyed PM-steels.

Astaloy CrM with an addition of 0.3% C was often compared to Distaloy AE + 0.5% C which is well known since the middle of the 70-ies. The tensile strength of Astaloy CrM + 0.3% C and Distaloy AE + 0.5% C is quite similar when properly processed at 1120°C. However, increasing the sintering temperature to 1250°C, the merit of Astaloy CrM compared to Distaloy AE, is obvious. For high temperature sintering, a higher carbon content is preferably used in Astaloy CrM to improve performance. A comparison of typical properties received during sintering at 1120°C and 1250°C respectively is found in figure 1.

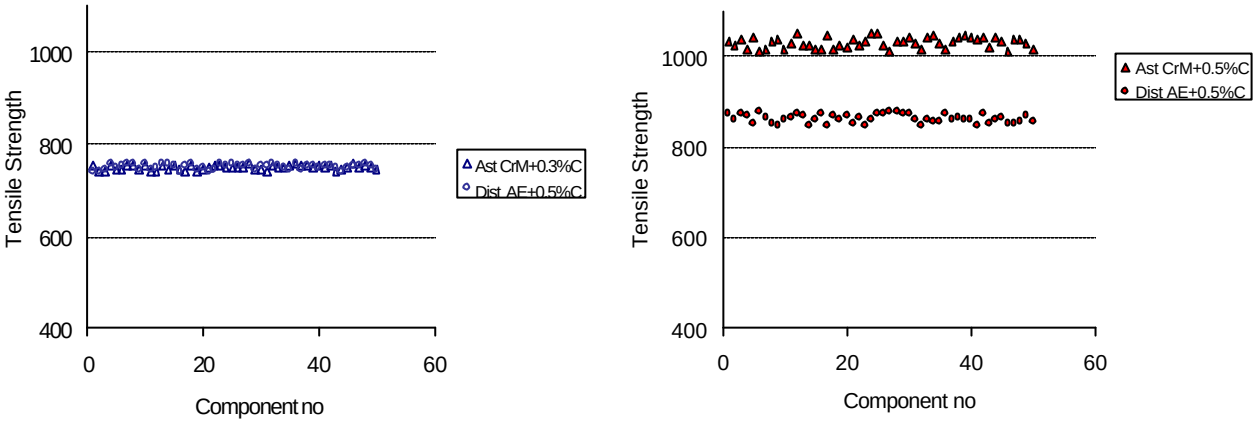


Figure 1: Tensile strength and scatter for Astaloy CrM and Distaloy AE processed at 1120°C (left) and 1250°C (right) respectively

However, considering sintering tests performed at 1120°C, all of them were not successful. In such cases, the following difference in tensile strength was typically found (figure 2).

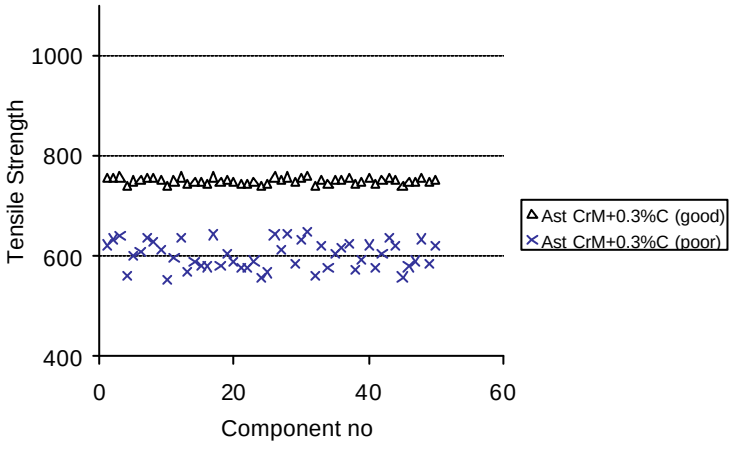


Figure 2: Tensile strength and scatter for Astaloy CrM sintered at 1120°C during good conditions and poor conditions

The relatively low strength and large scatter received for Astaloy CrM was normally due to poor control of directing sintering atmosphere and/or the use of excessive oxidation media

during dewaxing. This was typically found as a high analysed oxygen content of the sintered parts and was also revealed as an oxide network in the grain boundaries (see below chapter 3).

In conjunction to the 1998 Cr-material introduction, an equipment for the evaluation of oxygen partial pressure (PO_2) in sintering furnaces, was developed. The aim of that development was to offer service of measuring atmosphere conditions in intended processing equipment for those being interested in producing Cr-alloyed PM steels. By knowing oxygen partial pressure of the atmosphere it is possible to judge whether proper sintering can be performed or not, no matter the atmosphere composition (5). This is not possible by only knowing dewpoint of the atmosphere. In the case of Astaloy CrM oxygen partial pressure should not exceed $5x10^{-18}$ atm or log PO_2 = -17.3 atm.

In the following paper, atmosphere conditions of some tested production furnaces operating at maximum 1150°C, are analysed and discussed. It shows necessary precautions to be taken for the successful sintering of PM-steels alloyed with Cr.

2 Experimental

In all experiments, Astaloy CrM with addition of 0.3% graphite, was used. Astaloy CrM has the following chemical composition (table 1).

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

Table 1: Chemical composition of Astaloy CrM

Specimens for impact energy testing according to ISO 5754-1978 was used for the determination of hardness, impact energy and chemical analysis. Sections were also prepared for metallographic studies revealing eventual carburisation/decarburisation and/or oxidation.

The specimens were compacted at 700 MPa and sintered in furnaces operating at maximum 1150°C. During sintering the atmosphere was sampled at different locations and a profile of oxygen partial pressure (PO_2) as well as a CO profile of the furnace was monitored. The sampling was primarily made from the sintering zone and optionally from the dewaxing zone as well as from the cooling zone. A schematic test set-up is showed in the following figure 3.

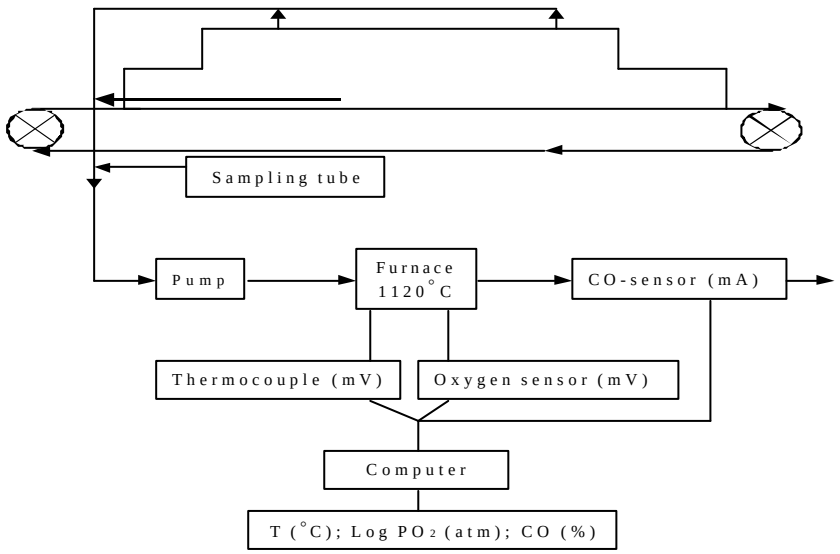


Figure 3: Test set-up for measuring oxygen partial pressure (PO_2) and CO content in sintering furnaces

The furnace atmosphere was sampled either via a stainless steel (SS) tube, put through the entry side of the furnace, or via gas outlets mounted on the furnace body and transported to the measuring equipment. The measuring unit consists of an encapsulated furnace pre-set at 1120°C and equipped with an oxygen sensor and a thermocouple. The sampled gas is heated to 1120°C when passing this furnace and is further transported to a carbon monoxide sensor monitoring the CO-content. The electrical signals received from oxygen sensor, thermocouple and carbon monoxide sensor respectively are transmitted to a data logger and then further transferred to a computer where the data are processed.

A pre-set temperature of 1120°C was selected for the encapsulated furnace due to that actual sintering conditions (or close to actual conditions) of the tested furnace were to be characterised. However, the oxygen sensor operates properly provided that only ionic conduction occurs in the oxygen sensor electrolyte. At 1120°C, some electronic conduction will occur and result in a signal output deviating somewhat from actual conditions. The presence of electronic conduction is due to the combined effect of oxygen partial pressure difference in the reference (air) and in the measured atmosphere plus the effect of measuring at elevated temperature. Consequently, the oxygen profile achieved is somewhat conservative i e the actual conditions in the furnace is better than measured. In figure 4, theoretical figures and experimental figures is showed for pure hydrogen with a defined dewpoint of 0°C.

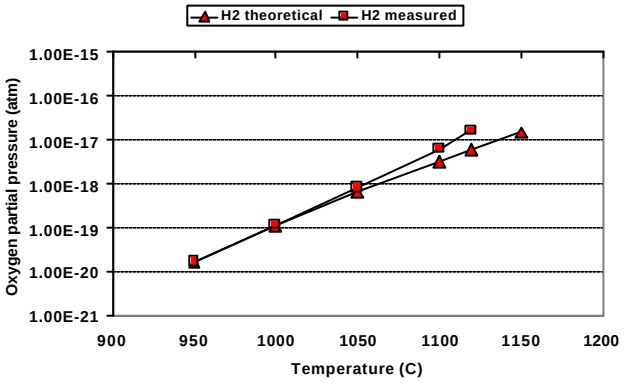


Figure 4: Theoretically calculated – and corresponding measured oxygen partial pressure for hydrogen with a dewpoint of 0°C

In the figure, theoretical figures and experimental data are showed for hydrogen with a dew point of 0°C (H_2 bubbled through ice water). From this figure it is obvious that electronic conduction occurs at temperatures exceeding approx 1000°C.

Due to the conservative oxygen figures measured, sintered specimens of Astaloy CrM were carefully investigated to judge the processing possibilities offered by the tested furnaces. Mechanical properties were evaluated and metallographic sections showed the carbon profile and eventual unintentional oxidation. The CO-sensor was used in conjunction to the oxygen sensor, basically to establish the carbon activity, according to the reaction $C + ½ O_2 = CO$, in the furnace but more work has to be done in that area. In the tests so far, the CO-sensor has showed to be an excellent indicator of atmosphere flow stability.

This paper presents testing of three different furnaces, one pusher furnace and two conveyor belt furnaces. In the belt furnaces, sampling of the atmosphere was made by introducing a SS-

tube from the furnace entry by loosely mounting the tube by the side of the belt. Atmospheres from different furnace sections were sampled and analysed

- from the sintering zone to the entry side by pulling the SS-tube backwards, awaiting stabilised conditions at selected locations (second test) and
- from the dewaxing zone to the sintering zone by keeping the tube at selected locations, awaiting stabilised conditions (third test)

However, when testing the pusher furnace (first test), gas outlets mounted on the furnace body were used to extract the atmosphere. In this case, the cooling section could also be analysed.

3 Result and discussion

In the first test a pusher furnace operating at 1130°C was tested. The atmosphere is DA and no addition of hydrocarbon was made for carbon control. No rapid burn-off (RBO) of lubricant was installed in the furnace. Both at the entry side as well at the exit side there were doors opened at specified intervals for loading and discharge. In figure 5 below the measured oxygen partial pressure (PO_2) and the CO-content in the furnace is showed.

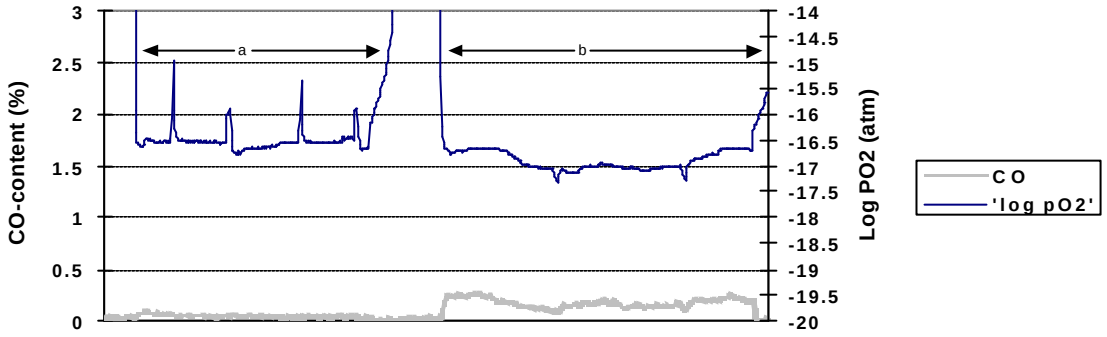


Figure 5: Measured oxygen partial pressure (PO_2) and CO content in pusher furnace operating in DA

The furnace is equipped with gas outlets on top of the furnace body. Sampling was done in the high heat zone (a) as well as in the beginning of the gradually cooling zone (b). The atmosphere conditions were significantly worse to what was expected in a DA atmosphere (log PO_2 is normally in the order of –18.5 atm in an unaffected DA gas mix analysed at 1120°C). Although reaction products will have some minor effect of atmosphere quality in a continuously loaded furnace but the conditions should not be affected that much, as was the case here.

The frequency in the peaks of log PO_2 revealed that disturbances in atmosphere stability occurred when the entry – and exit doors were in operation. This is clear when analysing the conditions in the high heat zone where the regularity of the log PO_2 peaks corresponds well to loading and discharge. The atmosphere never recovered to the expected figures of log PO_2. CO was detected in the gradually cooling zone revealing air leakage whereas no hydrocarbon was added to the atmosphere. Graphite trays were used and probably somewhat oxidised due to the relatively high temperature when the load entered the gradually cooling zone. Therefore, correct operation of the entry/exit doors is of large significance.

Below in table 2 the mechanical properties and chemical analyses of the sintered test bars are presented.

Chemical analysis		Mechanical properties	
C (%)	**O (%)**	**HV10**	**IE (J)**
0.26	0.20	200	14

Table 2: Chemical analysis and mechanical properties of test samples

The table suggests somewhat decarburizing and shows high analysed oxygen content (proper sintering results in an oxygen content in the order of 0.1% for this material). This resulted in poor mechanical properties. A metallographic section confirms loss of carbon at the surface and some obvious oxidation at the grain boundaries (figure 6).

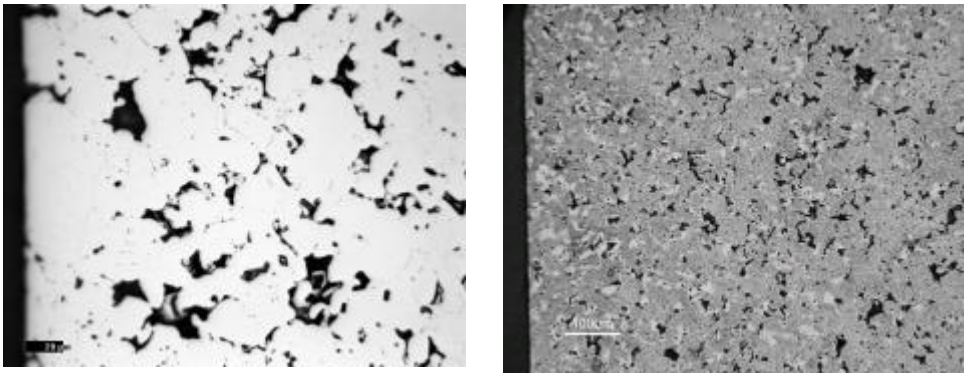


Figure 6: An unetched (left) and etched (right) section of the test sample. Oxides at the grain boundaries (left) and somewhat decarburised (right)

In the following test, an example is given of very high production rate in a belt furnace and the consequences it had on part performance. The furnace was operated at 1120°C in a 97/3 N_2/H_2 atmosphere with addition of CH_4 to control carbon. RBO was used and the furnace is open at both ends. In figure 7 below the measured oxygen partial pressure (PO_2) and the CO-content in the furnace is showed.

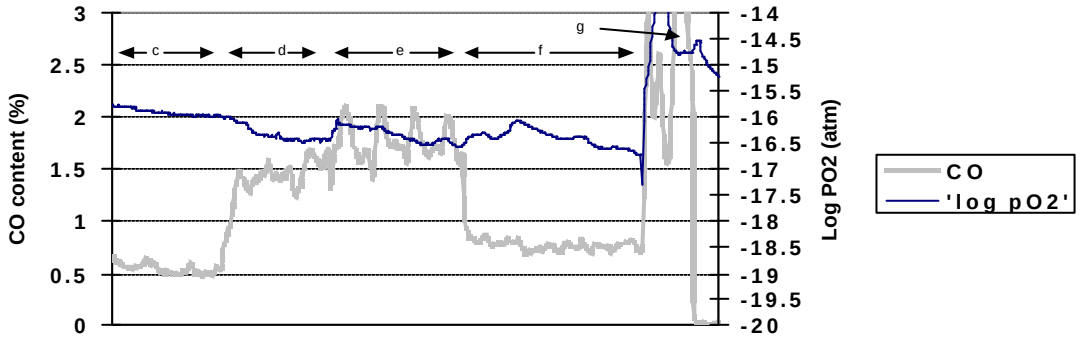


Figure 7: Measured oxygen partial pressure (PO_2) and CO content in a belt furnace operating in 97/3 N_2/H_2 atmosphere and using RBO

At first, no sampling was made during feeding of the tube from the entry side of the furnace to the end of the high heat zone. Then, sampling started and when the conditions stabilised, the SS-tube was pulled out in steps of 1 m each (5 measuring points labelled c, d, e, f and g respectively). Actually, the atmosphere conditions were found to be the worst at the end of the sintering zone (c) where normally the best conditions are found. The reason was the heavy dewaxing which oxidised the belt and most of the belt reduction did not occur until the end of the sintering zone.

Due to the delayed belt reduction, the atmosphere conditions improved when analysing the conditions versus the beginning of the high heat zone. Apart from the delayed belt reduction, CO produced during dewaxing obviously had some positive influence on atmosphere quality, despite the fact that dewaxing vapours contains lot of CO_2. This is obvious when the dewaxing zone (g) finally was sampled and analysed (high oxygen content in the atmosphere). In this furnace it is important to make an accurate control of atmosphere flow stability and also check whether there is too much excess of oxidising media during RBO of lubricant. Evaluation of chemical analysis and mechanical properties of the tested parts showed the following (table 3).

Chemical analysis		**Mechanical properties**	
C (%)	**O (%)**	**HV10**	**IE (J)**
0.30	0.23	200	8

Table 3: Chemical analysis and mechanical properties of test samples

The table shows high analysed oxygen content and poor mechanical properties. Metallographic examination reveals heavy decarburising which was partly compensated for by the addition of CH_4. However, an even carbon profile was not possible to achieve mainly due to the depth of decarburised layer. An oxide network is also found at the grain boundaries (figure 8)

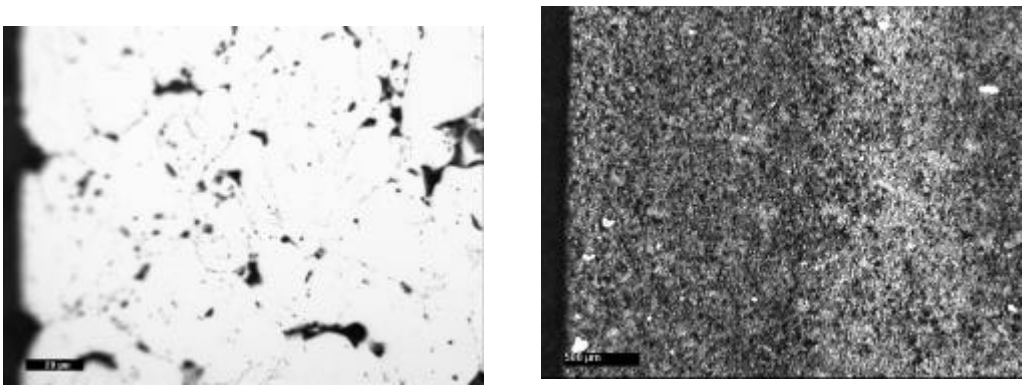


Figure 8. An unetched (left) and etched (right) section of the test sample. Oxides at the grain boundaries (left) and heavy decarburising followed by carburising from the methane addition (right).

In the final test a belt furnace operating at 1120°C was tested. The furnace atmosphere was 85/15 N_2/H_2 and RBO was used. No hydrocarbon was added for carbon control. The furnace is open in both ends. Sampling of atmosphere started in the end of the RBO zone and the feeding of the tube was temporarily stopped in order to make the conditions stabilise. The same procedure was repeated in the beginning of the high heat zone and in the end of the high heat zone. In figure 9 below the measured oxygen partial pressure and the CO-content in the furnace is showed.

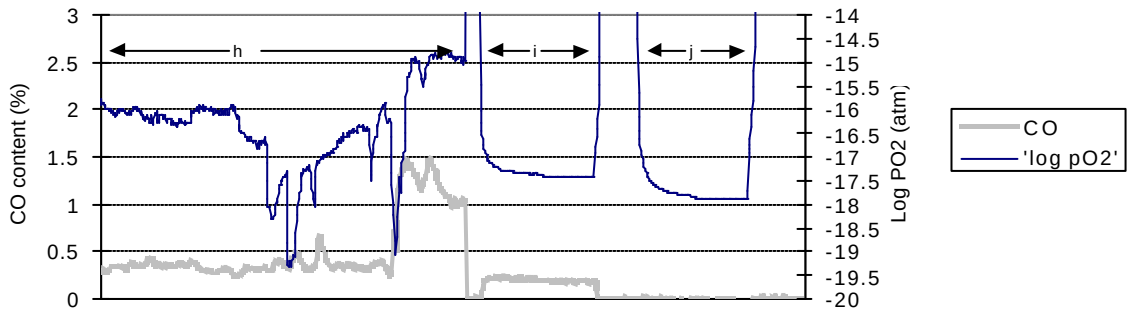


Figure 9: Measured oxygen partial pressure (PO_2) and CO content in a belt furnace operating in 85/15 N_2/H_2 atmosphere and using RBO

This shows an example of proper conditions for the mass production of components. There is a stable flow versus the entry side of the furnace and very little of the contaminated atmosphere from the dewaxing is affecting the conditions in the high heat zone. Little CO is detected in the beginning of the high heat zone (i) revealing some of the vapours originating from the dewaxing (h). In the end of the high heat zone (j) no CO is detected and the atmosphere conditions have also improved. Evaluation of the test bars showed desired chemical analysis and material performance (table 4).

Chemical analysis		**Mechanical properties**	
C (%)	**O (%)**	**HV10**	**IE (J)**
0.32	0.12	240	19

Table 4: Chemical analysis and mechanical properties of test samples

A metallographic section confirmed a proper carbon profile even though the sample is somewhat carburised (figure 10).

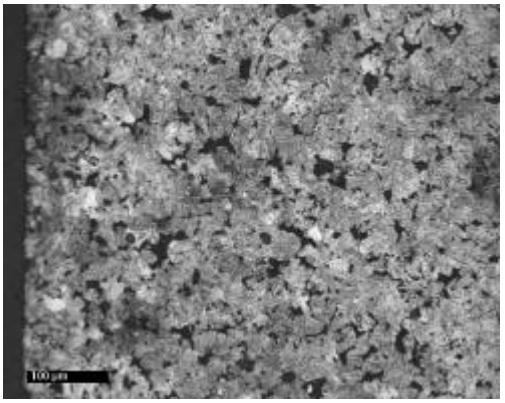


Figure 10: An etched section of the test sample. An even carbon profile with some minor carburising

4 Conclusions

Cr-alloyed PM-steels is a new family of materials being a complement to the existing Cu/Ni/Mo-alloyed materials for the production of PM components. Most Cr-alloyed materials are presently produced in high temperature sintering to assure good properties after sintering. One reason might be atmosphere flow and quality which is no actual concern at high temperature sintering.

For mass production of components, sintering at maximum temperature of 1150°C is the most common practice today. For Cr-alloyed PM-steels the sintering step is also a critical step in the process chain from powder to component. The sintering is successful provided that

- the atmosphere flow is well controlled especially when production rate is high
- only sufficient excess of oxidation media is used in RBO

If sintering is a problem, it is recommended to analyse partial pressure of oxygen, preferably in the sintering zone.

5 References

1 M Ichidate et al. “Sintering of Oil Atomized Low Alloy Steel Powder”; Horizons of Powder Metallurgy, Part 1, pp. 57 – 60, 1986

2 I Karasuno et al. “Some Properties of Oil Atomized Low Alloy Steel Powders Containing Chromium”; Horizons of Powder Metallurgy, Part 1, pp. 53 – 56, 1986

3 K Ogura et al. “Cr and Mn Containing, Low Oxygen Steel Powder Produced by Water-atomisation and Vacuum-Annealing”; Metal Powder Report, Vol 42, no 4, 1987

4 O Eriksson et al. Binder of new prealloyed Cr/Mo-steel powder released by Höganäs AB during 1998 Powder Metallurgy World Congress

5 J Arvidsson et al. ”On-Line Measurement of Sintering Atmospheres”; Proceedings 1998 Powder Metallurgy World Congress, Vol 2, pp. 253 - 260