

**EFFECTS OF NITROGEN UPTAKE DURING SINTERING ON  
THE PROPERTIES OF PM STEELS PREALLOYED WITH  
CHROMIUM**

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**Abstract:** Powders prealloyed with chromium have recently been introduced on the market for sintered steels. Due to chromium's high affinity for oxygen, sintering is performed in nitrogen/hydrogen-based atmospheres with low oxygen partial pressures. However, chromium also has a high nitrogen affinity, which will lead to nitrogen uptake by the steel during the sintering process. The effects of nitrogen uptake during sintering have been studied for a water atomised iron powder fully prealloyed with 3% chromium and 0.5% molybdenum. Test specimens with varying graphite additions and green densities were sintered for 30 minutes at 1120°C in a mixture of nitrogen and hydrogen (90%N<sub>2</sub>/10%H<sub>2</sub>). Different cooling rates after sintering were applied. Evaluation of the sintered specimens included metallography, phase analysis, chemical analysis, and mechanical testing. Based on the evaluation results, conclusions are drawn regarding how nitrogen uptake and nitride formation during sintering affect the material properties.

## INTRODUCTION

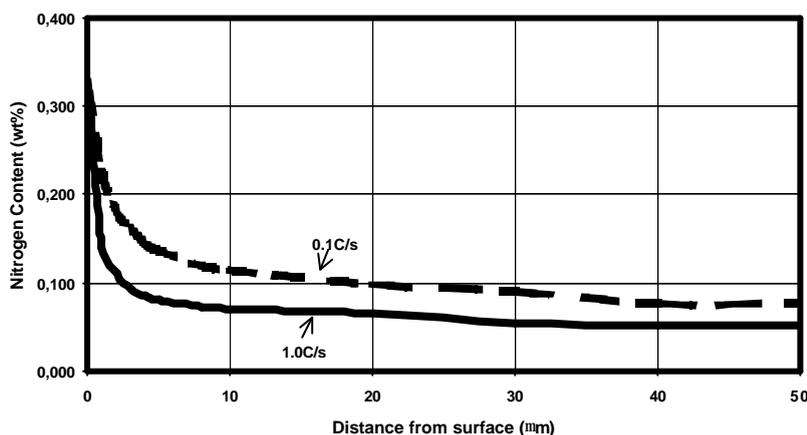
Chromium is an alloying element with a lot of advantages since it gives good hardenability, is relatively cheap, and is easy to recycle. However, the major drawback of alloying with chromium in PM grades is that chromium has a high affinity for oxygen, which may lead to problems with oxidation during the sintering process. A few years ago, Höganäs AB introduced the powder grade Astaloy CrM, which is a water atomised iron powder fully prealloyed with 3% chromium and 0.5% molybdenum. By prealloying the base powder with chromium the oxidation sensitivity of the material has been reduced, allowing the material to be sintered at 1120°C in conventional mesh belt furnaces. The protective atmosphere in the sintering furnace must have a low oxygen content in order to avoid oxidation during sintering. Consequently, a mixture of 90%N<sub>2</sub> and 10%H<sub>2</sub> with an oxygen partial pressure below  $5 \cdot 10^{-18}$  atm is recommended as protective atmosphere when sintering Astaloy CrM [1]. However, sintering in a nitrogen-based atmosphere will lead to nitrogen uptake by the material, due to chromium's high affinity for nitrogen. The effect of this nitrogen on the material properties depends on the amount of nitrogen taken up and if nitrides precipitate. It is well recognised that nitrides in steels may have a positive effect, as in the case of nitriding [2], but they may also lead to deterioration of mechanical properties if precipitation occurs at grain boundaries [3]. The purpose of this investigation was to study how nitrogen uptake during sintering of Astaloy CrM in N<sub>2</sub>/H<sub>2</sub> (90/10) affects the material properties of the sintered material.

## THEORY

### Simulations of nitrogen uptake

A computer model has been used to simulate the nitrogen uptake during sintering of Astaloy CrM. This model, termed Ndiff, is based on a numerical solution of the transient one-dimensional diffusion equation [4]. Transfer of nitrogen from gas to solid depends on a mass transfer coefficient, which is primarily dependent on atmosphere dew point, and the nitrogen activity difference between gas and specimen surface. The nitrogen activity of the gas atmosphere is given by the square root of the nitrogen partial pressure. The description of the nitrogen activity of the alloy takes into account the temperature and alloying elements (Cr, Mo, C) using the thermodynamic description by Jarl [5].

Simulations were made for a spherical particle ( $\phi = 100 \mu\text{m}$ ) with the composition Fe-3Cr-0.5Mo-0.3C, assuming that single powder particles of Astaloy CrM + 0.3% C are exposed to the sintering atmosphere in an open porosity. The partial pressure of nitrogen was set to  $p_{\text{N}_2} = 0.9 \text{ atm}$  and the atmosphere dew point to  $-50^\circ\text{C}$ . The temperature cycle used for the calculations consisted of heating from  $600^\circ\text{C}$  to  $1120^\circ\text{C}$  during 10 minutes, sintering for 30 minutes at  $1120^\circ\text{C}$ , and cooling from  $1120^\circ\text{C}$  to  $600^\circ\text{C}$  for 520 seconds ( $1.0^\circ\text{C/s}$ ) or 5200 seconds ( $0.1^\circ\text{C/s}$ ). The results from the simulations are presented in the form of nitrogen profiles for the specified geometry (see Figure 1).



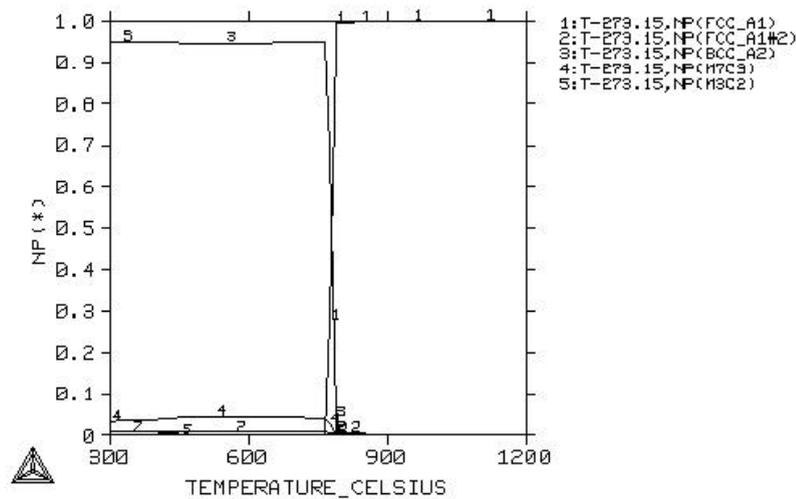
The nitrogen content in the material is considerably higher for the lower cooling rate, since more time has been allowed for nitrogen transfer and diffusion. Due to slow diffusion at low temperatures, the nitrogen content at the particle surface is much higher than in the rest of the particle for both cooling rates.

**Figure 1** Results from simulations of nitrogen uptake during sintering in a spherical particle of Fe-3Cr-0.5Mo-0.3C.

The simulation results indicate that the average nitrogen content in the powder particle is approximately 0.1 wt% after sintering and cooling with a rate of  $0.1^\circ\text{C/s}$ , and 0.065 wt% after sintering and cooling with a rate of  $1.0^\circ\text{C/s}$ . As comparison, the solubility of nitrogen in the  $\gamma$ -phase of a Fe-3%Cr alloy at  $900^\circ\text{C}$  and 1 atm  $\text{N}_2$  pressure is 0.08 wt% at thermodynamic equilibrium [6]. The effect of the other alloying elements on the nitrogen solubility is that molybdenum increases the solubility while carbon has a slightly negative impact on the solubility [5].

### Thermodynamic considerations

The computer model Thermo-Calc was used for calculations on the system Fe-3Cr-0.3C-0.08N. This system was intended to simulate the powder grade Astaloy CrM with carbon added and with nitrogen picked up during sintering. The absence of molybdenum in the simulated system is of marginal importance. These calculations are based on thermodynamic equilibrium conditions and the time aspect is not included. The time aspect is naturally of major importance since the nitrides need a certain time to precipitate.



In Figure 2, the calculation results are shown in terms of the different phases that are expected to form in the system at temperatures between 300°C and 1200°C. The results show that the nitride phase CrN will form in the material and that it starts to precipitate at a temperature of around 850°C. Furthermore, the carbide phase  $M_7C_3$  appears at temperatures below 800°C and at around 450°C some  $M_3C_2$  carbide may start to precipitate.

**Figure 2** Amount of phases as a function of temperature for the system Fe-3Cr-0.3C-0.08N at thermodynamic equilibrium (FCC\_A1#2 = CrN).

## EXPERIMENTAL PROCEDURE

### Test materials

A water atomised steel powder fully prealloyed with 3 wt% chromium and 0.5 wt% molybdenum was studied in this investigation. This material is designated Astaloy CrM and is produced by Höganäs AB. The amount of graphite (Kropfmühl UF4) admixed to the base powders before compaction varied from no addition to additions of 0.25 wt% and 0.45 wt%. Furthermore, 0.6% lubricant was added to all powder mixes before compaction. Test specimens were cold compacted at compacting pressures between 600 and 700 MPa to reach a green density of 7.0 g/cm<sup>3</sup>, or warm compacted at compacting pressures around 700 MPa to reach a green density of 7.2 g/cm<sup>3</sup> (see Table 1). Standard test bars for fatigue testing and impact energy testing were produced for all test materials.

Material	Composition	Green Density (g/cm <sup>3</sup> )
CrM0LD	Astaloy CrM (Fe-3Cr-0.5Mo)	7.0
CrM25LD	Astaloy CrM (Fe-3Cr-0.5Mo) + 0.25C	7.0
CrM25HD	Astaloy CrM (Fe-3Cr-0.5Mo) + 0.25C	7.2
CrM45LD	Astaloy CrM (Fe-3Cr-0.5Mo) + 0.45C	7.0

**Table 1** Compositions and green densities of the test materials.

### Sintering experiments

A laboratory tube furnace was used for the sintering experiments. Dewaxing was done at 600°C for approximately 25 minutes and sintering was performed at 1120°C for 30 minutes in all experiments. A mixture (90/10) of nitrogen and hydrogen was used as process atmosphere and the partial pressure of oxygen was kept below 10<sup>-18</sup> atm in order to avoid oxidation. Two different cooling rates were applied – “slow cooling” (SC, ~0.05°C/s) and “medium cooling” (MC, ~0.75°C/s).

## Testing and evaluation

Chemical analysis was made on specimens from each experiment to determine the contents of the elements carbon, oxygen and nitrogen (C, O, N) after sintering. Also, x-ray diffraction analysis was performed on phase-isolated materials from selected experiments. Sintered test bars from each experiment were sectioned and prepared for metallographic analysis in a light optical microscope (LOM). Etchant 3.3 (100 ml ethyl alcohol, 2 g Picric acid, 1 ml HCl) was used for etching. Furthermore, mechanical properties in terms of impact strength, fatigue strength, and hardness were evaluated for the sintered specimens. Impact energy tests were carried out in a Charpy tester. The fatigue strength was determined in axial mode at  $2 \cdot 10^6$  fully reversed ( $R = -1$ ) cycles. Hardness measurements were made on cross sections of sintered specimens.

## RESULTS AND DISCUSSION

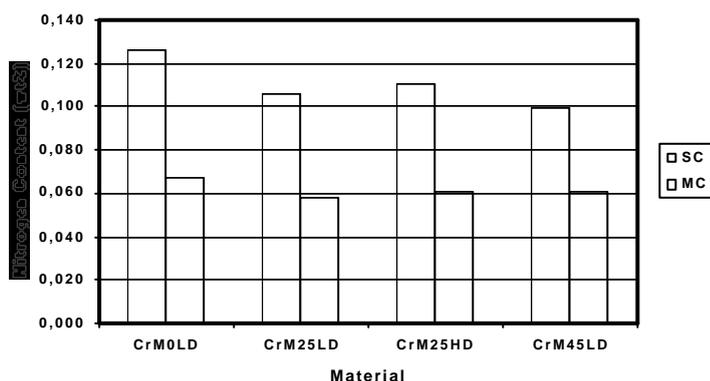
### Chemical analysis

The results from chemical analyses performed on the test materials after sintering and subsequent cooling are presented in Table 2.

Material	CrM0LD		CrM25LD		CrM25HD		CrM45LD	
Cooling Rate	SC	MC	SC	MC	SC	MC	SC	MC
Carbon Content (wt%)	0.02	0.01	0.21	0.20	0.23	0.24	0.39	0.38
Oxygen Content (wt%)	0.125	0.130	0.089	0.082	0.093	0.101	0.080	0.075
Nitrogen Content (wt%)	0.126	0.067	0.106	0.058	0.110	0.061	0.099	0.061

**Table 2** Results from chemical analyses performed on Astaloy CrM materials after sintering at 1120°C for 30 minutes in N<sub>2</sub>/H<sub>2</sub> (90/10) and subsequent cooling at different rates.

Nitrogen uptake during sintering was greatly influenced by the cooling rate, which is illustrated in Figure 3. After slow cooling (SC, ~0.05°C/s), the nitrogen contents of the sintered materials are almost twice as high as the levels after medium cooling (MC, ~0.75°C/s).



**Figure 3** Nitrogen levels in Astaloy CrM after sintering (1120°C, 30 min., 90/10) and subsequent cooling.

This is well in agreement with both the results from the simulations of nitrogen uptake during sintering (see Figure 1) and the findings of a previous study on the subject [7]. Hence, a major nitrogen uptake has occurred in the materials during cooling. Furthermore, the results show that neither carbon content nor porosity had any major influence on the nitrogen levels after sintering.

### Phase analysis

The x-ray diffraction analyses detected the phases CrN and M<sub>7</sub>C<sub>3</sub> in both CrM25LD and CrM45LD after sintering and subsequent slow cooling. These two phases are expected to form in the materials according to thermodynamic considerations (see Figure 2).

Consequently, the cooling rate has been sufficiently slow for the nitrides and carbides to precipitate. Also, the nitrogen content in these materials is above the solubility limit, which enhances the formation of nitrides during cooling. The fact that CrN, and not Cr<sub>2</sub>N (normally termed ε), is the stable chromium nitride phase in low-alloyed chromium steels has been confirmed by several experimental investigations [8], [9], [10]. No nitride or carbide phases were detected by the phase analysis performed on CrM25LD after sintering and subsequent medium cooling.

## Microstructures

The sintered microstructure of CrM0LD was mainly ferritic but it also contained some areas of bainite and pearlite for both cooling rates. Sintering followed by slow cooling (SC) of material CrM25LD resulted in a bainitic microstructure mixed with some ferrite, while sintering followed by medium cooling (MC) of the same material gave a fully bainitic structure. Similar microstructures were obtained for CrM25HD after sintering and subsequent cooling.

After sintering and slow cooling (SC) of material CrM45LD, the microstructure was composed of bainite, pearlite and relatively few areas of ferrite. A higher cooling rate (MC) after sintering of CrM45LD resulted in a bainitic microstructure with some pearlite present. Also, thin films of ferrite around the powder particles were observed throughout the structure. These films may be a consequence of oxidation during the sintering process, probably at the dewaxing stage, causing a carbon loss in the material.

For all materials that were cooled slowly after sintering, distinct and relatively large precipitates were observed along the grain boundaries in the ferritic areas of the microstructures. Only traces of such precipitates could be detected in ferritic areas of the materials that were cooled at a medium rate. These findings and the results from the phase analyses indicate that the grain boundary precipitates may consist of some chromium nitrides (CrN). This is also supported by results from other investigations that report of incoherent CrN particles forming at grain boundaries in ferritic areas of Fe-Cr alloys [8], [11], [12].

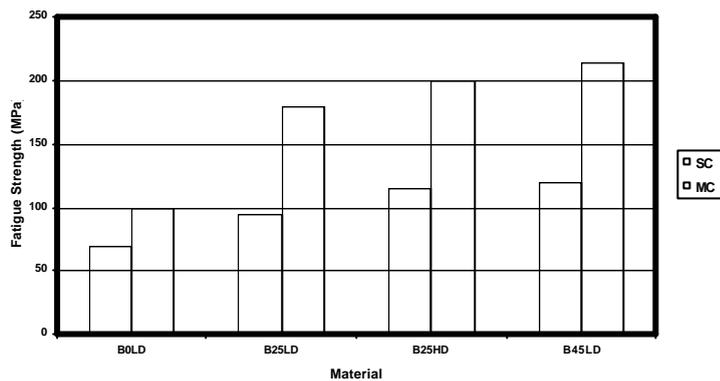
## Mechanical properties

The mechanical properties for the sintered test materials are presented in Table 3.

Material	CrM0LD		CrM25LD		CrM25HD		CrM45LD	
	SC	MC	SC	MC	SC	MC	SC	MC
Hardness (HV <sub>5</sub> )	74	78	107	192	107	203	145	237
Fatigue Strength (MPa)	70	100	95	180	115	200	120	215*
Impact Energy (J)	35.0	26.8	27.3	20.5	31.1	21.1	23.8	17.0

**Table 3** Mechanical properties for Astaloy CrM materials after sintering (1120°C, 30 minutes, 90N<sub>2</sub>/10H<sub>2</sub>) and subsequent cooling (SC, MC). \*) Value is taken from reference [13], since process irregularities led to inaccurate fatigue testing results for this material.

As expected, the apparent hardness is strongly dependent on the carbon content of the material and the cooling rate. Carbon content had also a clear effect on the impact strength, since the material is more ductile at lower carbon levels. Moreover, the influence of cooling rate on impact strength is obvious for all material types, with higher strength values after slow cooling. Also, higher density gave somewhat better impact strength. The effect of cooling rate on the fatigue limit of the sintered materials is illustrated in Figure 4. This effect is remarkably large for the carbon-containing materials.



**Figure 4** Fatigue strength for Astaloy CrM after sintering (1120°C, 30 min., 90/10) and subsequent cooling.

The major reason for the poor strength values after slow cooling is the fact that relatively large amounts of ferrite appear in the microstructure. However, a contributing factor may be the grain boundary precipitates that were observed in the microstructures. Furthermore, it is interesting to note that high nitrogen contents in the sintered materials coincide with low fatigue strength values.

## CONCLUSIONS

Based on the results of this investigation, the following conclusions are drawn regarding nitrogen uptake during sintering of Astaloy CrM in the atmosphere 90%N<sub>2</sub>/10%H<sub>2</sub>:

- The nitrogen uptake is strongly dependent on the cooling rate applied after sintering. However, neither carbon content of the material nor density of the PM part (in the region 7.0-7.2 g/cm<sup>3</sup>) has any significant influence on the nitrogen transfer from the sintering atmosphere.
- No negative effects of nitrogen uptake on material properties are observed when a cooling rate of 0.5-1.0°C/s is applied after sintering.
- At low cooling rates, not obtained at normal process conditions in continuous belt furnaces, chromium nitrides (CrN) may precipitate in the material as a consequence of the nitrogen uptake. Cooling rates as low as 0.05-0.1°C/s result in high nitrogen levels (>0.1%) and grain boundary precipitations of nitrides and/or carbides in ferritic areas of the microstructures. These precipitates are suspected to contribute to low fatigue strength values obtained after sintering.

## ACKNOWLEDGMENTS

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