Boost in Performance by Control of the Sintering Atmopshere.

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Abstract

Powder metallurgy is known to be a cost effective technology to manufacture components with narrow tolerances in combination with required mechanical properties. A key aspect is the sintering process. Through control and creation of internal stresses guided by the sinter hardening atmosphere give you properties that even outperform sintered and case hardened properties at considerable lower cost. Creation and control of such atmosphere is essential to increase the competiveness of the PM technology

In this paper concepts for carbon control and carbon gradient are presented and described in terms of how to create it through addition and measurements. Influences of created internal stresses by the atmosphere on PM applications are presented.

Introduction

Sintering in continuous mesh belt furnaces up to 1150 °C in nitrogen-hydrogen based atmospheres is a complex process. A lot of sintering parameters influence the final microstructure and the chemical properties and hence the mechanical properties such as hardness and strength. Base powder, alloying elements, alloying method, lubricant, graphite, time-temperature profile and atmosphere composition are maybe the most important.

The sintered steel starts out as a green porous brittle compact containing iron powder and alloying element, lubricant, along with (metallic) oxides and graphite. After delubrication and sintering the steel has gained mechanical properties. In both delubrication and sintering the porous compact reacts with the atmosphere. The atmosphere plays an important role in oxidising and transporting processes of the decomposed lubricant. If the atmosphere is reducing with respect to carbon in the delubrication zone the soot formed from the lubricant residuals dissolves in the steel and contributes to the carbon content. At the same time, it is important not to oxidise the base powder or the graphite in the mix. Failure in fulfilling these two conditions can cause either carburization or decarburization prior to sintering. Upon the subsequent heating, oxides on the powder particles are reduced with the admixed graphite and/or hydrogen in the atmosphere. The reduction of the oxides activates the surfaces enabling the graphite to dissolve in the matrix and the actual sintering process to start. Sintering is a diffusion process driven by minimisation of the surface energy. Sintering is followed by cooling and the cooling rate has a big impact on the final microstructure. Figure 1 shows schematically the interaction between the atmosphere and the sintered steel.

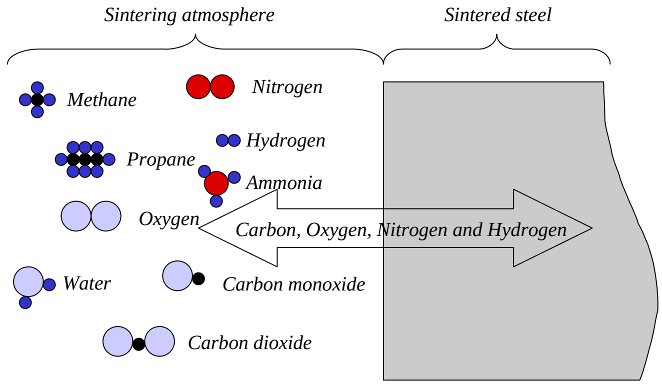


Figure 1: Species in the sintering atmosphere

Nitrogen-hydrogen based atmospheres contain a lot of gas species. The species originate either from the gas supply or are a product from reactions at high temperature. The supplied nitrogen and hydrogen contain some ppm of oxygen and water. The major part of the oxygen is leaked into the furnace from leaking muffle flanges or from the furnace exit. Oxygen originates also from oxides on the mesh belt, from parts and from the lubricant. Ammonia is present in the gas supply if the hydrogen source is dissociated ammonia while hydrocarbons are present if enrichment gas is added. At higher temperatures the oxygen reacts with hydrogen and graphite from the parts forming water, carbon monoxide and carbon dioxide. There is an exchange of carbon, oxygen, nitrogen and hydrogen between the steel and the atmosphere.

Control of the carbon activity in sintering atmospheres is of major importance for producing sintered components to high performance. One of the benefits of the Endo gas is the possibility to set the carbon potential through the ratio between carbon monoxide and carbon dioxide. By this a maintained or even carburization can be obtained at the surface of the PM component.

For the nitrogen /hydrogen atmosphere system carbon control by addition of CO content is possible. There are at least two alternatives to create a carbon controlled atmosphere. One alternative is to set a carbon potential at sintering temperature the other one is to create carburization during cooling down.

Experimental procedures

The chemical composition of the material are shown in table 1

Table 1. The chemical composition of the adopted powder mixes.

Mix code	Base powder	Ni (%)	Mo (%)	Cr (%)	Graphite (%)
Distaloy AQ	Distaloy AQ	0.5**	0.5**		0.2
As. CrA	Astaloy CrA	2*		1.8***	0.6
Ast. CrM	Astaloy CrM		0.5***	3***	0.4

* Admixed, ** Diffusion bonded, *** Pre-alloyed

All mixes contained added 0.8% Amide Wax as a lubricant and syntetic F10 graphite.

Compaction

Specimens according to the ISO standard for static and dynamic properties were compacted at 700 MPa using a 140-ton Result hydraulic press.

Sintering

Specimens were sintered at 1120°C for 30 minutes in a mesh belt furnace in 90%N_2 and 10%H_2 with 0.2% methane addition. Sintering atmosphere was controled by measuring the dewpoint, and partial pressure of oxygen. The dew point was < -28°C and the partial pressure of oxygen at < $5.5*10^{-18}$ atm.

Sinter hardening

Material was sinterhardened by using pure N_2 with addition of natural gas. This was done to create a carbon gradient in the specimens. The cooling rate was set to 3-5°C/s. All sinter hardened specimens were tempered at 200°C for 60 minutes in air.

Heat treatment

Through hardening was done on Distaloy AQ at 860°C for 20 minutes with a carbon potental of 0.6%, followed by tempering at 200°C in air for 60 minutes.
Case hardening was done on Distaloy AQ at 860°C for 20 minutes with a carbon potental of 0.8%, followed by tempering at 200°C in air for 60 minutes.

Mechanical properties

Mechanical properties were evaluated according to standards for GD ISO3927, tensile test bars for evaluation ISO 2740, method for testing according to ISO 6892-1, carbon ISO 7625 and hardness ISO 4498.

Fatigue investigation

Four-point bending fatigue tests were performed for as compacted, un-notched ISO 3928 test bars, modified with a chamfer. The following test parameters were used: load ratio R =-1; frequency: 25-29 Hz; broken specimens stopped after 2.5% increased compliance; run out at 2 million cycles; fatigue endurance [σA,50%] and standard deviation were determined by the staircase method according to MPIF Standard 56..

Results and Discussion

Carbon gradient through carburization during cooling.

To a nitrogen atmosphere hydrocarbon in the form of natural gas was added in order to investigate the carburization. Added amount was from 0.06 to 0.13% CO. Boundary for CO content was soot formation and reduction potential for the atmosphere. Tensile specimens were used in these trials. The addition was made to the incoming nitrogen gas. Normal decarburization for investigated material, Astaloy CrM is 0.05% due to reduction of internal oxides. Final sintered carbon content for that reason will be 0.35%.

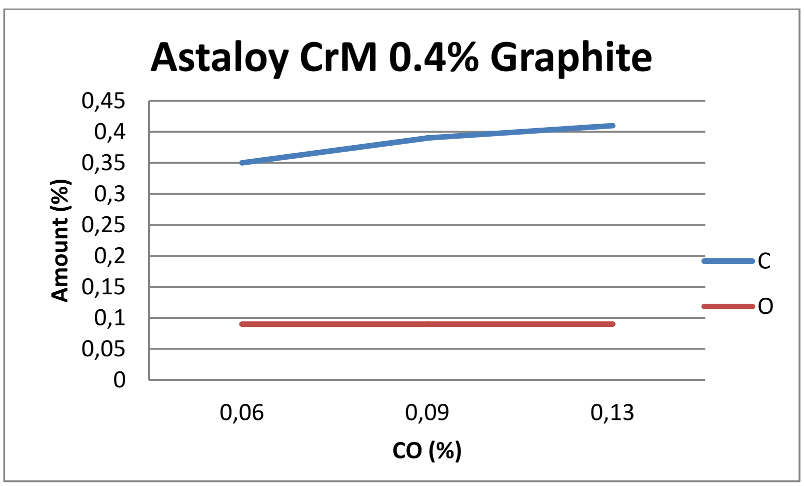
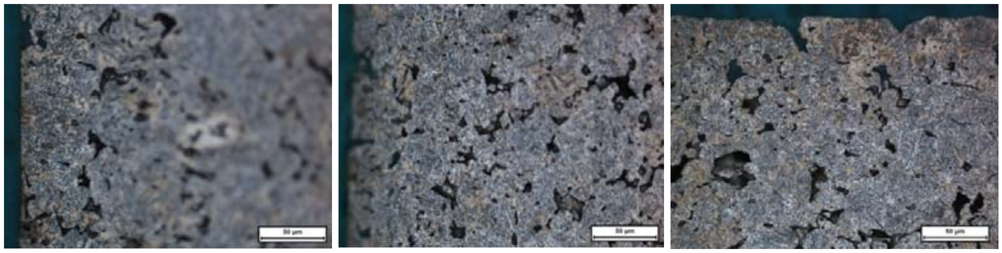


Figure 1 Carbon content vs CO

At low CO level a maintained bulk carbon content is achieved. The carbon analys is as expected 0,35%. The bulk carbon content increases at higher CO content. A carbon gradient is formed as can be seen in figure 2. The oxygen content of the sintered specimens is for all investigated CO content the same. The added amount of natrual gas also give a hydrogen amount that is high enough to secure, together with the CO level, that no surface oxidation occours during cooling down. Important when using natural gas addition is to secure that enough oxygen is availably to crack the natural gas to CO and hydrogen. If not, the amospher will be extremly dry and the cracking of naturalgas will go to methane. Uncontroled atmosphere is then obtained.



Surface, CO= 0.06% Surface, CO= 0.09% Surface, CO= 0.13%

Figure 2. Surface carburization at different CO content

At a CO amount of 0.06% the surface contains martensite and the overall carbon content is 0.35%.

At a CO amount of 0.09% the surface contains smaller amount of martensite and the overall carbon content is 0.39%.

Carburization is seen on the surface at CO amount of 0.13%, The carburization is high and the average carbon analyse is 0.41%. The martensite zone is deeper at the surface facing the gas stream. The atmosphere creates small amount of soot seen on the parts.

Mechanical properties

Mechanical properties for the investigated materials sintered under different condition either to maintain the carbon content at the surface (– Carbon control) or by creation of a gradient (– Carbon gradient) are shown in table 2. This also contains data for through and case hardened Distaloy AQ.

Table 2, Mechanical properties

	Mix code	GD	SD	TS	YS	HV10	Elong.	C
		g/cm^3	g/cm^3	MPa	MPa		%	%
Sintering	Distaloy AQ	7.14	7.15	456	333	146	1.7	0.58
	Distaloy AQ	7.19	7.24	357	190	105	8.7	0.17
	Ast. CrA	7.07	7.10	859	633	240	1.1	0.54
Sinter hardening carbon control	Ast. CrA		7.10	1162	868	369	0.88	0.56
Sinter hardening carbon gradient	Ast. CrA	7.07	7.14	1093	864	421	0.57	0,59
Through hardening	Dist. AQ		7.16	994	989	380	0.19	0.51
Case hardened	Dist. AQ		7.23	1034	942	441	0.34	0.38

Figure 3 show the change in properties obtained by different processes. The sinterhardening atmopsheres maintain the carbon content at the surface or creates a carbon gradient that regards to mechanical and dynamic properties are in the same level as for through and case hardened

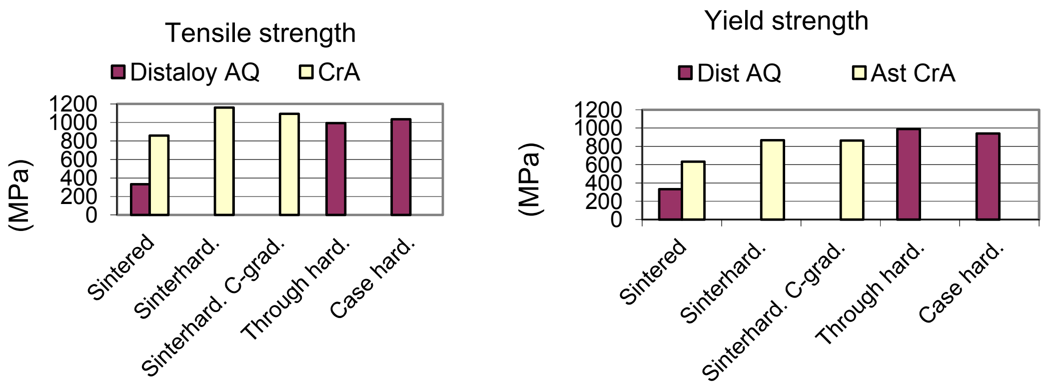


Figure 3, Mechanical properties vs processes.

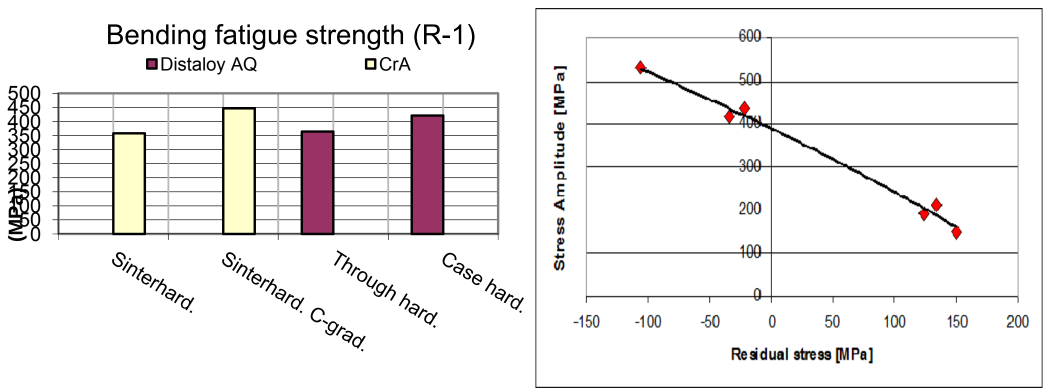


Figure 4, Residual stresses effect on fatigue properties

The effect of residual stresses on bending fatigue is shown in figure 4.
Compressive stresses at surface give raise to additional ~100MPa in bending fatigue. This is in In the same range as for the bending fatigue investigation for sinterhardening with maintained carbon at surface and the increase by the creation of a carbon gradient for the carburizing sinterhardening atmosphere.

The atmosphere used for the sinter hardening process was 90/10 N_2/H_2 with 0.2% methane addition for carbon control and nitrogen with natural gas addition to obtain 0.10% in CO content for carbon gradient. The atmosphere was controlled by measuring carbon CO, CO_2, dew point and O_2. Gases were added through mass flow meters and inserted from behind. No active steering of the gas additions was made. Active control of the gas additions is preferable to compensate for leakage or disturbance of the gas flow [1].
Overall gas consumption is 9 Nm^3/h. No soot formation was found in the sintering trials. Methane addition gives carbon control, but no carbon gradient at the surface. Static properties are in the same range for the two used atmospheres with slightly reduced elongation for the natural gas atmosphere, for which a gradient is obtained. This is shown in the fatigue performance of 447 MPa [2] for the nitrogen + natural gas atmosphere compared to 364 MPa for the 90/10 N_2/H_2. Through atmosphere control an increase in performance is possible [3].
This atmosphere composition also offers a cost advantage by a reduction of ~35% in gas cost.
Addition of small, controlled amount of oxygen is preferable since the system is easier to control by this addition. The need for pure nitrogen can for this reason be discussed. The natural gas will react with this oxygen and give carbon dioxide to a controlled level.
Overall it has been shown that sinter hardening compared to heat treatments, such as through hardening and case hardening, is an alternative when it comes to static and dynamic properties.

The investigation indicates a cost advantage for a process route with sinterhardening using an atmosphere that creates a carbon gradient or maintains the carbon content at the surface.

Conclusions

- Sinter hardening with sintering atmosphere control offers the same properties as through and case hardening.
- Sinter hardening using nitrogen with natural gas addition to a CO level of 0.1% creates a carbon gradient without the risk of soot formation.
- Carbon gradient improves the fatigue performance by 23%, reaching 447 MPa
- Compaction and sinter hardening can eliminate the through hardening and case hardening operation to secure a lower total cost.
- Highest cost performance ratio is obtained by selection of Astaloy CrA in a sinter hardening process.

References

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