Influence of sintering atmosphere on properties of sinterhardened steels

Ilaria. Forno, Marco. Actis Grande

***Abstract*—**The aim of this paper is to deepen the understanding of the influence of sintering atmosphere on the final properties of sinter-hardened steel components. A commercial Astaloy CrM powder has been uniaxially pressed in different shapes, identified in terms of area/mass index, with three different carbon additions (0.3 , 0.4 and 0.5 % w.) Sinter-hardening process has been conducted in a belt-furnace in order to re-enact industrial working conditions using six different protective / carburizing atmospheres. During the process, temperature profiles and atmospheres have been sampled and analyzed. Sintered samples have been analyzed in terms of oxygen contents, hardness and microstructure.

Particular attention has been paid to the decarburizing/carburizing effect of different atmospheres in terms of composition and the resulting mechanical properties.

***Keywords*—**powder metallurgy, steel, sinter-hardening, sintering atmosphere.

I. Introduction

Powder Metallurgy (PM) is widely used to produce highly resistant near net-shape components to be applied in a variety of industrial fields. In order to keep competitiveness when compared to wrought materials, continuous improvements in terms of mechanical properties are required to PM production.

Traditional treatments such as carburizing and steam oxidation are meant to improve surface properties whilst hardening could led to considerable achievements in terms of tensile strength, yield strength and hardness eventually affecting the whole part if the component is not oversized and therefore through-hardenable.

Due to the porosity of the PM parts, it is not possible to quench them in water; nor oil is a good solution since it has to be removed after the quenching to achieve good results in the following annealing processes. One applicable productive processing is therefore to include a gas quenching directly after the sintering step: this process is known as sinter-hardening [1], [2].

Many parameters influence the results of this process, among them powder composition, carbon content, sintering atmosphere and cooling rate [3]-[5]. Since the hardening capability of the powder is directly related to its carbon content, sintered properties are strongly dependent on the carbon activity in the sintering furnace. It is then extremely important to be able to maintain the desired carbon level at the surface or, more advantageous, get a carburization effect via use of proper atmospheres.

In order to keep the process competitive, great efforts are devoted to the use of effective elements with relatively low-cost such as Cr and Mn. When compared to commonly used alloying elements (Cu, Ni and Mo), these metals present a significant drawback: high sensitivity towards oxidation [6], [7], but are more and more applied due to their lower costs [8] - [10].

Chromium is among the most powerful elements with respects to hardenability, characteristic that permits to achieve high amounts of martensite with relatively low cooling rates [11]. Despite the clear advantages offered, the use of chromium in order to achieve the desired increment in mechanical properties is highly demanding in terms of control of the sintering atmosphere in terms of the oxygen partial pressure and carbon activity. Therefore sintering atmospheres must be tightly controlled in order to ensure the desired increment of properties [12].

Sintering atmosphere has mainly three functions when sintering compacts of metallic powders:

- Removal of the lubricant in the form of volatile products at the end of the entry part of the furnace
- Preventing oxidation of parts
- Reduction of surface oxide films on the surface and inside the powder particles.

The presence of oxygen in the sintering atmosphere is responsible not only of oxidation but also of decarburization.

The oxygen responsible for decarburization comes from the sintering atmosphere or from the material itself, as oxides, since carbon is able to reduce the metallic oxides giving carbon monoxide. In this way, if oxides are present in the powder, they will force a basic decarburization even in protective atmospheres. It is necessary to know the material decarburization in different atmospheres: thanks to this information, corrective gases addition to the sintering atmosphere – or extra graphite amounts in the base mix – may be planned, in order to restore the desired carbon level in the material [13], [14].

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In this experimental work one powder system showing good sintering hardening behavior, a sintering cycle and a set cooling rate have been selected and kept constant during the whole study whilst experimental efforts have been focused on the analysis of the effect of different sintering atmospheres on the final properties of the compact.

II. Material and experimental methods

Experimental set-up has been established in order to re-enact industrial practice. Considering the need of high hardenability, Astaloy CrM (Hoganas AB) powder has been used. Astaloy CrM is a fully pre-alloyed ferrous powder containing 3% w. Cr and 0.5% w. Mo as alloying elements.
Three different powder mixes were produced in order to receive different carbon contents. Three different mixes were set, adding to the base powder a constant amount of 0.6%w of lubricant (kenolube) and 0.3%w, 0.4%w, and 0.5%w of graphite for the three selected carbon levels

- Astaloy CrM + 0,3%C + 0,6% kenolube
- Astaloy CrM + 0,4%C+ 0,6% kenolube
- Astaloy CrM + 0,5%C+ 0,6% kenolube
- ASC 100.29+ 0,6% kenolube

ASC 100.29 was used as a reference material as it consists of pure iron.
Two types of samples were compacted at 600 MPa for all the mixes.

- IE bars -Impact energy test ISO 5754 (10 x 10 x 55)
- TS bars - Tensile-strength test ISO 2740 (shaft 6 x 6)

Sintering trials (1120°C per 30 minutes) were carried out using a sinter-hardening belt furnaces, connected with a rapid cooling unit (RCU) where a turbulent gas flow is generated by a gas tight fan to cool down sintered components with a cooling rate (evaluated between 800°C and 500°C) of roughly 1°C/s.

Considering the carbon control, different atmospheres were taken into account. Since chromium has a high affinity to oxygen, the oxygen level in the furnace must be kept under control and maintained low, thus atmosphere such as Endogas are not suitable limiting the possible compositions to N_2-H_2 blends, thanks to their low oxygen content.
In this experimental work different atmospheres have been investigated:

- 90:10 N_2-H_2
- 97:3 N_2-H_2
- 90:10 N_2-H_2+ 0,2% vol. CH_4
- 90:10 N_2-H_2+ 0,2% vol. CH_4 (1/3 moisturized with water at 30°C)
- 90:10 N_2-H_2+ 0,4% vol. CH_4
- 96:2 N_2-H_2 2% CO

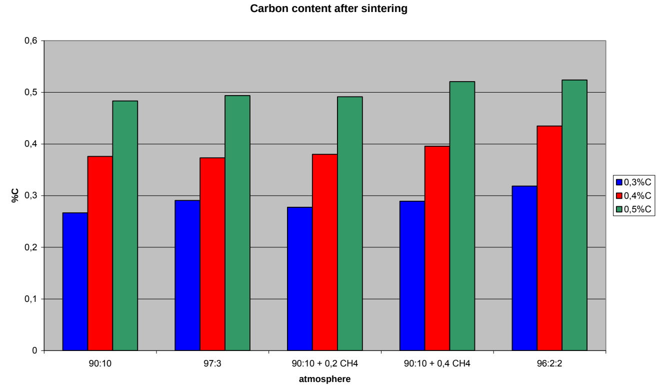
The total gas flow in the furnace was set to 10 nm^3/h in all cases.
During sintering the atmosphere was sampled using an oxygen and CO probe. To further deepen the understanding of what is happening during sintering, different mapping of the furnace were carried out, different atmosphere both with powder compact and not. Oxygen and carbon monoxide distribution through the sintering zone was investigated both parallel and perpendicular to the furnace.
On sintered samples microstructure analysis has been made in order to evaluate any variation of carbon content. Moreover hardness test and chemical analysis have been carried out.

III. Results and discussion

A. Chemical analysis

Bulk analysis of carbon and oxygen content were carried out on sintered samples both on IE and TS bars considering their different geometric index (area/mass). This kind of analysis gives overall information of the condition of the part. The higher the geometric index the more this analysis is giving information on the conditions at the surface. Thus analysis from IE bars (lower A/M index – massive component) give information of the bulk behavior, whilst TS bars are more relevant when considering the influence of the atmosphere on the surface.

As reported in Fig.1 the results from IE bars, sintered in different “non-carburizing” atmospheres, (without carbon carrier) show a constant loss in carbon content, even if those atmospheres are classified as “protective” when considering their partial pressure of oxygen. The reason for this constant loss of carbon can be understood taking into account the oxygen level in the material before and after sintering: the higher in the powder mix than in the material sintered in protective atmospheres. The raw powder, due to the atomizing process and to the following annealing treatment, shows a relative oxidation on the surface; carbon added to the mix as graphite takes care of these oxides during the heating, reducing them to form carbon monoxide. The higher the addition of graphite the lower this loss is. Sintering with 96:2 N2-H2+ 2% CO has the main carburizing effect even on IE bars. This influence is even highly noticeable on TS bars.



Fig, 1 Pure iron sintered in 90:10 atmosphere

B. Metallographic investigation

Metallographic investigation has been carried out on both pure iron and Astaloy CrM. Pure iron shows a highly ferritic microstructure. Fig. 2 shows the microstructure obtained sintering in 90:10 + 0.2% methane. At increasing magnifications (Fig. 3) it's possible to identify perlitic, Fe3C + α, areas. Such areas lie close to the surface and are smaller than 10μm^2. This carburizing effect is only slightly higher when considering addition of 0.4% vol. of methane. (Fig. 4).

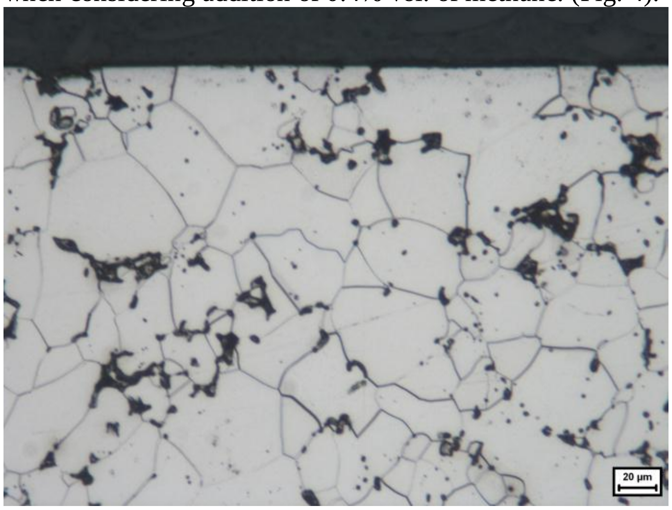


Fig. 2 Pure iron sintered in 90:10 atmosphere

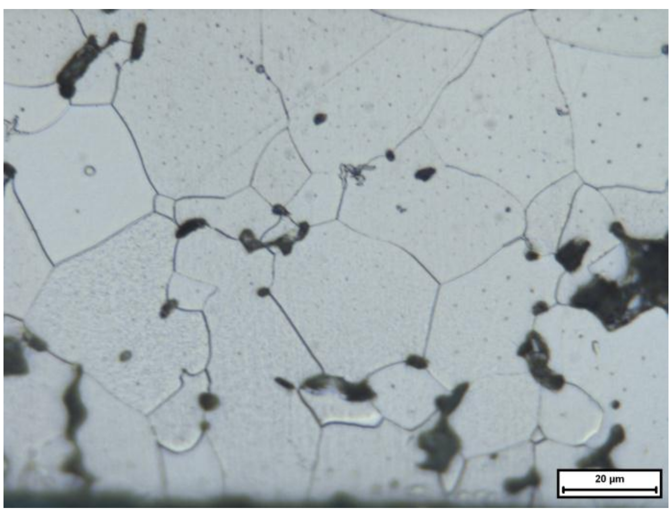


Fig. 3 Pure iron sintered in 90:10 + 0.2% vol. CH_4

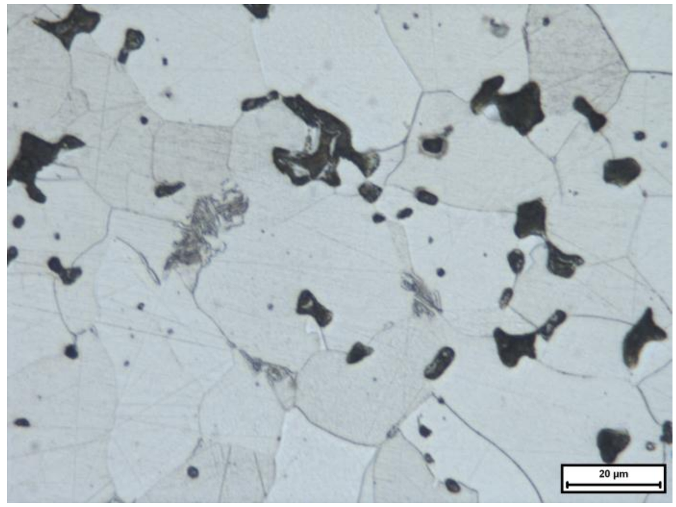


Fig. 4 Pure iron sintered in 90:10 + 0.4% vol. CH_4

Astaloy materials contain very homogeneous basic powder particles. This chemical uniformity also results in a very homogeneous microstructure, mainly consisting of bainite and martensite.

Comparing Fig. 5 and Fig. 6 it is possible to notice an increasing amount of martensite close to the surface, due to the carburizing effect provided by the addition of carbon monoxide to the atmosphere.

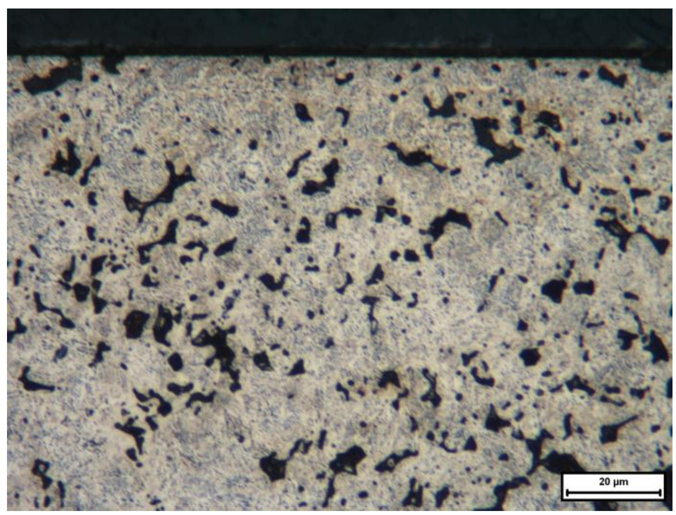


Fig. 5 Astaloy CrM + 0.3% C sintered in 90:10 atmosphere

Fig. 6 Astaloy CrM + 0.3% C sintered in 90:10 + 2% vol. CO atmosphere

An higher addition of graphite results in a higher final quality amount of martensite in the microstructure (Fig. 7). Moreover, sintering in a 90:10 atmosphere with an addition of methane does not result in any carburized profile.

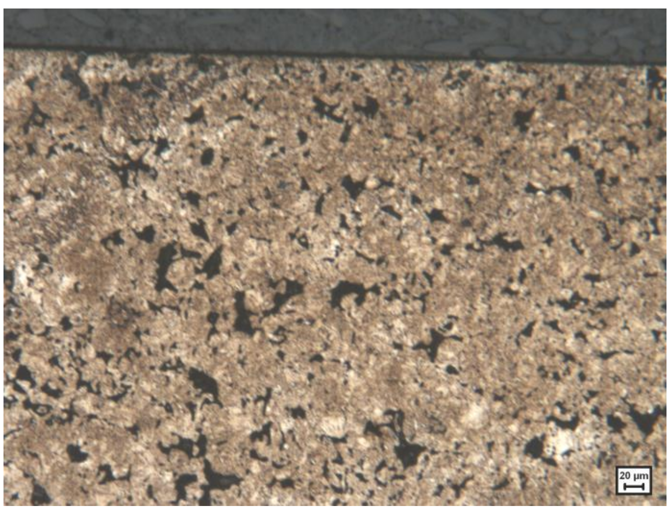


Fig. 7 Astaloy CrM + 0.5% C sintered in 90:10 + 0.2% vol. CH_4 atmosphere

Moisturizing the atmosphere with water determines an heavy decarburization of the surface. In Fig. 8 a decarburized profile is detectable; at the surface the microstructure is made of ferrite only, then a bainitic layer is noticeable, in the bulk the microstructure is again martensitic.

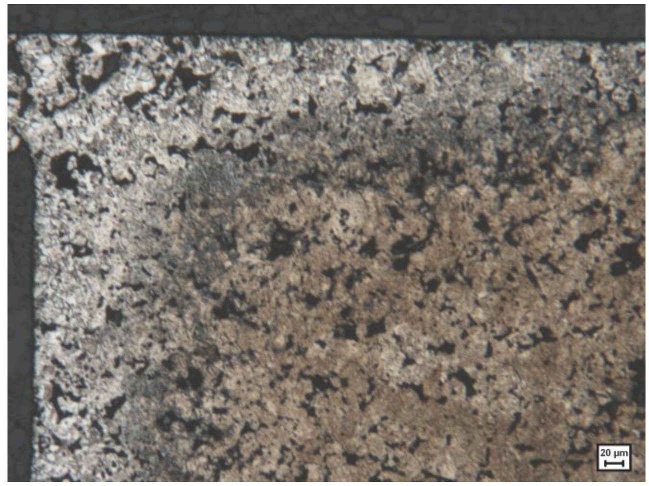


Fig. 8 Astaloy CrM + 0.5% C sintered in 90:10 + 0.2% vol. CH_4 atmosphere partially moisturized with water.

C. Hardness

HV10 was measured on both side of TS bars and IE bars sintered in different atmospheres. As shown in Fig 9. clearly visible effects on the apparent hardness are achieved using carburizing atmospheres.

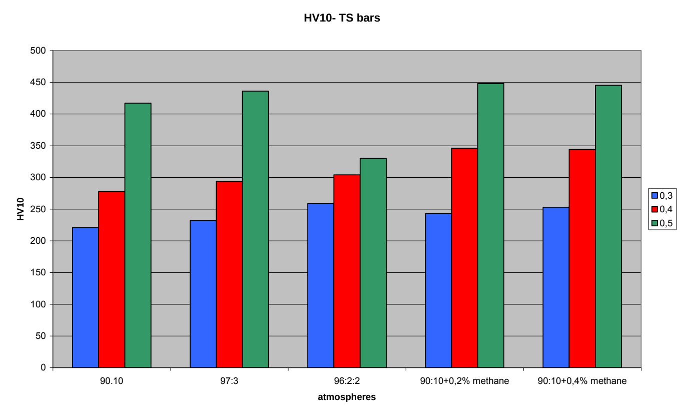
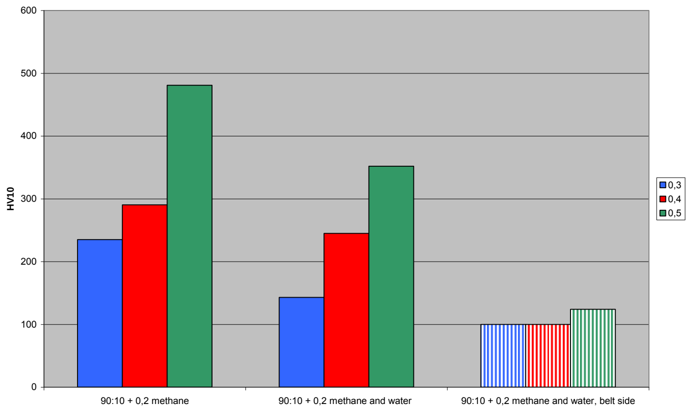


Fig. 9 Hardness Vickers 10, measured on TS for different sintering atmospheres.

This can be related to the improved hardening capability of parts with an increasing content of carbon on the surface. Using chromium containing powders, a heavily carburized layer on the surface leads to hardened condition even with a low cooling rate. This behaviour is mainly detectable when at least 0,4% of graphite is added to the base powder.

An addition of water, moisturizing on third of the atmosphere leads to a depletion of the properties achieved. Hardness is no more uniform on the top and on the bottom of samples, surfaces directly in contact with the atmosphere show the worst results (Fig. 10).



Fig, 10 Effect of water addition in a 90:10 + 0,2% methane atmosphere on hardness.

D. Furnace mapping

Different mappings of the furnace were carried out with different atmospheres either with load or not. Oxygen and carbon monoxide distribution through the sintering zone was investigated both parallel and perpendicular to the furnace. Before starting sampling of the furnace, the accuracy of probe was tested using gases of known composition, and the tube was cleaned with a flow of pure nitrogen.

Since several hours are needed to get rid of carbon monoxide, and to renew the atmosphere changing from endogas to N2/H2 the furnace was usually started some hours in advance to ensure the desired atmosphere.

Atmospheres were sampled both perpendicular and parallel to the furnace. The tube used for gas sampling was placed as follows:

- At the side of the furnace belt with the sampling tube laying on the belt
- At the side of the furnace belt with the sampling tube approximately 2 cm above the belt
- At the side of the furnace belt with the sampling tube approximately 12 cm above the belt

Then the tube used for the gas sampling was positioned on the side of the belt, wired on it, so that it can follow the sintering path.

This kind of investigation has been repeated placing the tip of the tube in different positions, as it can follow the sintering path, both before all trays containing samples and after trays.

In Fig. 11 and Fig. 12 atmosphere control was carried out in 90:10 and 90:10 + 0,2% of methane with tube positioned in the middle of the sintering load (9 trays before and 9 after) on the side of the belt, following the belt. The first peak represent, flames in the entrance of the furnace, the second peak corresponds to the dewaxing zone.

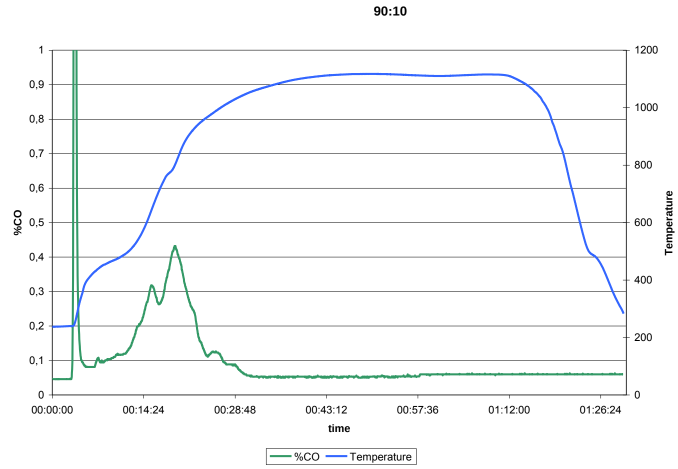


Fig. 11 Furnace temperature profile and atmosphere CO content during sintering in a 90:10 atmosphere

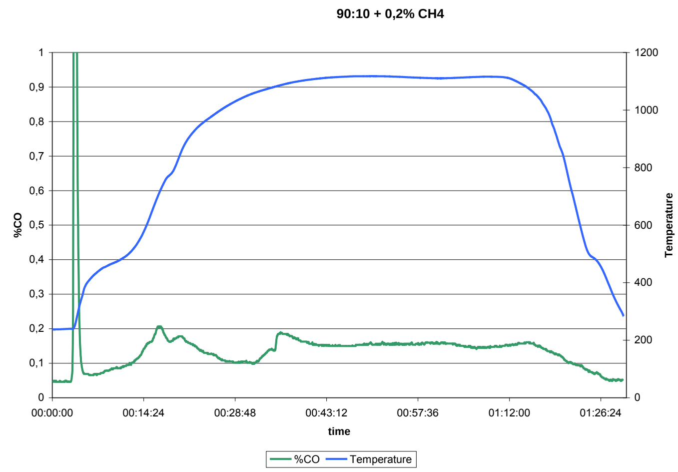


Fig. 12 Furnace temperature profile and atmosphere CO content during sintering in a 90:10 atmosphere with an addition of 0.2& CH_4

In all the trials, CO%, oxygen potential and dew point have been calculated, in order to further deepen the knowledge of the atmosphere in a real-like furnace.

IV. CONCLUSION

The aim of this investigation was to understand the behavior to oxidation and decarburization during sintering in different atmospheres. For this purpose a chromium containing material was used, mainly for its sensitivity to non protective atmospheres.

Decarburization occurs in atmospheres not containing any carbon carrier, and in the one with methane addition. In all atmospheres it is important to consider that a carbon depletion through the whole part can be present due to the reduction of the oxygen present in the powder. This results in a evidence of loss of carbon content in samples sintered in not carburizing atmospheres. This kind of loss can be compensate with planned increased initial graphite additions.

The usage of slightly carburizing atmospheres, as small additions of methane to hydrogen-nitrogen atmospheres, leads to hardened surface and to a slightly carburized structure.

The usage of methane addition is mainly recommended in order to get a protective atmosphere from decarburization rather than a carburizing atmosphere.

As a carburizing agent carbon monoxide, despite of the risk in its use, is the most effective carbon carrier.

Sampling and control of the atmosphere is really important to avoid oxidation and achieve better sintering conditions. Usage of both oxygen probe and carbon monoxide sensor can give precious information on the quality of the sintering.

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