

## LEAN SINTERED STEELS OBTAINED THROUGH THE MASTER ALLOY ROUTE: MECHANICAL PROPERTIES

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### **Abstract**

*Fe-Mn-Si master alloys, specifically designed to create a liquid phase below the conventional sintering temperatures, have been used as a vehicle for introducing oxidation sensitive alloying elements into low alloy steels. By combining plain water atomized iron base powder, with 0.6 wt. % graphite and small additions ( $\leq 4$  wt. %) of different master alloys based on the Fe-Mn-Si system, sintered steels with less than 3 wt. % of alloying elements were prepared. After pressing at 600 MPa, green compacts were sintered at 1120°C or 1250°C for 1 hour in  $N_2-10H_2$  atmosphere. Final oxygen contents were below 0.1 wt. % for sintering schedules at 1120°C and 0.02 wt. % for sintering at 1250°C. The best combination of properties is achieved by the use of small master alloy particles ( $< 10 \mu m$ ) and high sintering temperatures, which provide UTS values of 600 MPa combined with 3 % elongation and impact energy of 30 J.*

**Keywords:** *Fe-Mn-Si master alloys, mechanical properties, oxidation sensitive elements*

### **INTRODUCTION**

Lean steels can be defined as low alloy steels with a minimized content of alloying elements, which maintain or even improve the level of properties in conventional sintered steels. Improvement of properties at a lower alloying cost can be achieved by introducing elements such as Cr, Mn or Si, which have been used for many years in conventional wrought steels, but have limited applications in powder metallurgy due to their high affinity for oxygen. Oxidation can be minimized or even avoided if these elements are combined (alloyed) with other elements with lower affinity for oxygen, due to the reduction of their chemical activity. With the “master alloy” route the alloying elements are combined in a master alloy powder (containing for instance iron or high carbon levels to prevent oxidation) which is designed to be mixed with a base iron powder so that the final composition of the steel is achieved during sintering [1-5]. Besides, the composition of the master alloy powder can be specifically designed to create a liquid phase below the common sintering temperatures, giving the possibility of enhancing sintering and promoting homogeneous distribution of alloying elements.

The first approach to the master alloy concept for introducing elements with high oxygen affinity, was made in the 70's by manufacturing master alloys based on complex carbides named MCM (Fe-Mn-Cr-Mo-C) and MVM (Fe-Mn-V-Mo-C) [6-10]. The high thermal stability of carbides proved to be efficient for protecting the elements against oxidation during the heating stage. However, dissolution of these carbides usually required

very high sintering temperatures, and therefore homogenization of alloying elements was somehow limited [11, 12].

Master alloys based on complex carbides were effectively used in the seventies in high loaded PM parts production and they were eventually abandoned by the nineties due to the excessive tool wear caused by the hard carbide particles. The Mn and Si addition in low alloy sintered steels was not efficiently achieved until the ternary Fe-Mn-Si master alloy appeared in the 80's [10, 13]. These master alloys provided surprisingly good mechanical properties that belonged to the best data available at that time on comparable materials, with a simple sintering process and without any additional treatment. Moreover, the combination of Mn and Si in the appropriate ratio proved to provide good dimensional control of the sintered part [14-16]. The best combination of properties was obtained for steels containing a master alloy Fe-41Mn-19Si mixed with an iron base powder and graphite to a final composition of Fe-3.2Mn-1.4Si-0.4C (wt.%). Sintering this composition at 1250°C in hydrogen, and without any additional thermal treatment, provided UTS values around 1000 MPa with 3% deformation and dimensional changes of only 0.06%. However, in spite of the extremely good properties reported for sintered steels containing Fe-Mn-Si master alloys, only a few more publications reported the use of this system [17-20] and, so far, Mn-Si sintered steels have never been able to reach the market.

In this work, sintered steels have been manufactured from mixes containing plain iron powder, graphite and master alloy powders with different compositions (all of them containing Fe-Mn-Si). Master alloys have been designed to have liquidus temperatures below 1250°C and solidus temperatures below 1120°C, in order to promote the distribution of the alloying elements by the formation of a liquid phase. The amount of master alloy added is 4 wt.%, which gives a total amount of alloying elements below 3 wt.%. The objective is to evaluate the level of properties that can be achieved by using only small additions of an Fe-Mn-Si master alloys, when no specific requirements are applied to the atmosphere (sintering is carried out in conditions close to industrial).

## MATERIALS AND EXPERIMENTAL PROCEDURE

Sintered steels modified with master alloy additions were obtained from mixes containing plain iron powder (grade ASC 100.29 from Höganäs AB), natural graphite (Kropmulf UF4), lubricant (Amide wax) and "home made" master alloys atomized in N<sub>2</sub>. In order to improve the distribution of the different additives within the mix, graphite, lubricant and master alloy powders were bonded to the surface of the plain iron base powder. The bonding process was carried out by the company Höganäs AB, combining the additives in the proportion: Fe + 4 wt.% MA + 0.6 wt.% C + 0.8 wt.% lubricant.

Six different master alloy powders were considered (from MA1 to MA6) and classified taking into account the particle size distribution (Group A and B), Table 1. By means of a "Jet Milling" process, the particle size distribution of Group A master alloy powders was modified from the distribution obtained after atomization ( $d_{50} \sim 30 \mu\text{m}$  and  $d_{90} \sim 80 \mu\text{m}$ ) to a distribution characterized by  $d_{90} \sim 10 \mu\text{m}$ . After the jet milling process the oxygen content was increased from 0.04 wt.% to 0.1 wt.%.

Standard impact energy and tensile strength bars were produced by pressing bonded mixes at 600 MPa in a double effect press. Delubrication of the green compacts was done in a tubular lab furnace at 600°C for 10 minutes in N<sub>2</sub> atmosphere (heating rate 10°C/min). Sintering was carried out in a lab scale furnace AHT Silitstabofen under N<sub>2</sub>-10H<sub>2</sub>-0.1CH<sub>4</sub>. Sintering temperature was either 1120 or 1250°C for 60 min and then samples were cooled at approximately 0.75°C/s.

Tab.1. Studied steel groups. Name and composition of each steel and total percentage of alloying elements without including carbon (% AE).

	Master alloy		Steel		
	Particle size	name	Composition [wt. %]	name	% AE
Group A	$d_{90} \sim 10 \mu\text{m}$	MA1	Fe-1.6Mn-0.7Si-0.60C	A-MA1	2.3
		MA3	Fe-1.5Mn-0.4Si-0.65C	A-MA3	1.9
		MA5	Fe-1.6Mn-0.6Si-0.4Ni-0.64C	A-MA5	2.6
Group B	$d_{50} \sim 17 \mu\text{m}$	MA2	Fe-1.6Mn-0.6Si-0.64C	B-MA2	2.2
	$d_{90} \sim 43 \mu\text{m}$	MA4	Fe-1.6Mn-0.4Si-0.6Cr-0.62C	B-MA4	2.6
		MA6	Fe-1.6Mn-0.6Si-0.4Ni-0.2Cr-0.64C	B-MA6	2.8

Chemical analyses were carried out to obtain the level of oxygen and carbon in the sintered samples by using LECO-TC500 and LECO-CS200 analyzers respectively. To complete the microstructural characterization, sintered steels were prepared following the conventional metallographic process using a mix (1:1) Nital 2% - Picral 4% as etching agent. Sintered properties, such as density, hardness, tensile strength and impact energy, were evaluated following conventional standards [13, 14, 15, 16].

## RESULTS AND DISCUSSION

### Microstructure

Figure 1 presents the microstructures of steels belonging to Group A (with the master alloys with the lowest particle size  $< 10 \mu\text{m}$ ) sintered at 1120°C and 1250°C. For steels sintered at the low temperature, fine and coarse pearlites, and even some ferrite grains, are observed in the core of the original iron particles, depending on the diffusion distance reached by the alloying elements. Mixtures of bainite and martensite are present, depending on the local concentration of alloying elements. Surrounding the locations of the original master alloy particles, the hardenability is increased and therefore martensite formation is enhanced.

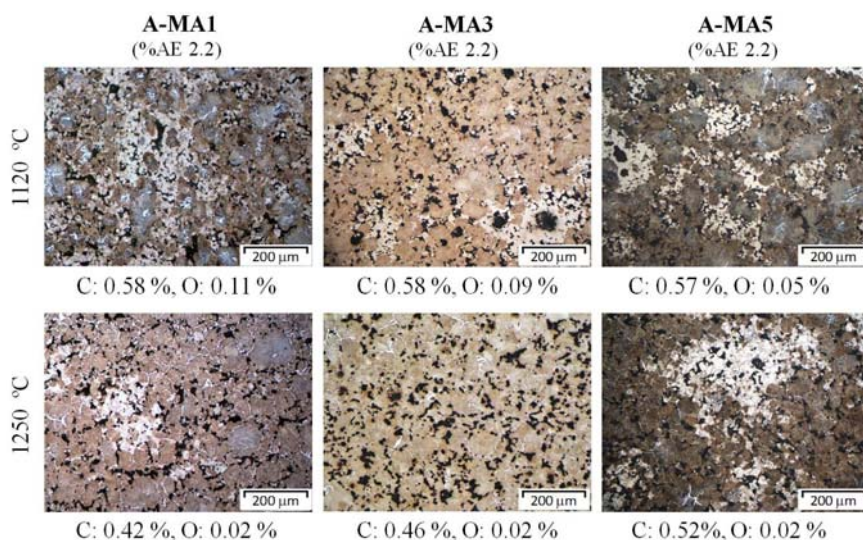


Fig.1. Microstructures, carbon and oxygen content of steels A-MA1, A-MA3, A-MA5 sintered in N<sub>2</sub>-10H<sub>2</sub> for 1h at 1120°C or 1250°C.

By increasing the sintering temperature to 1250°C, more homogeneous microstructures are achieved. Once more, the microstructures are mainly pearlitic with a few isolated areas containing bainite and martensite. The rising of thermal activation has led to a better homogenization of the alloying elements.

Thanks to the master alloy particle size, sintered samples present a small and rounded porosity. However, relatively coarse secondary pores can be found. This might be a consequence of the agglomeration of finer particles, and also of the dissolution of the base powder in contact with the liquid master alloy.

Microstructures of Group B steels are gathered in Fig.2. The particle size of the master alloys determines the coarser secondary pores. Furthermore, there is a higher amount of residues of undissolved particles, especially for the lower sintering temperatures. An increase in the sintering temperature does not provide such homogeneous microstructures as those observed in Group A, since the coarser size of the master alloy particles used in Group B steels leads to a higher local concentration of alloying elements.

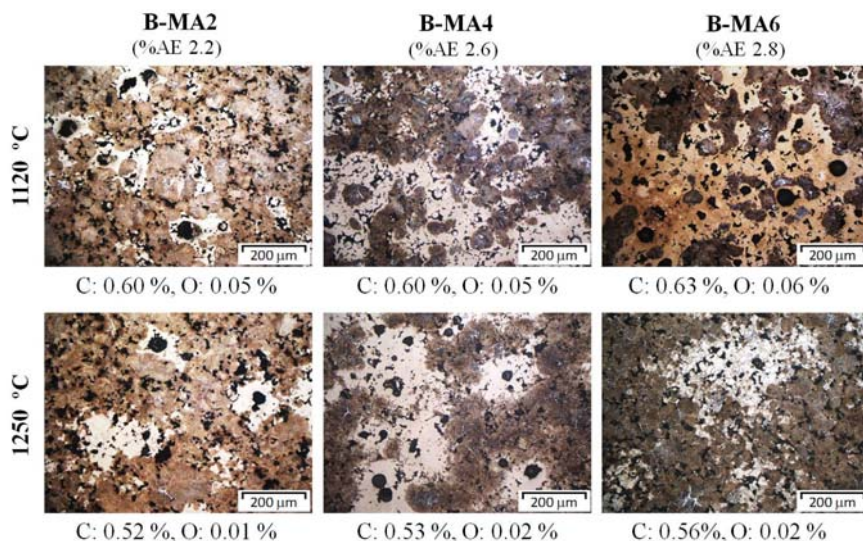


Fig.2. Microstructure of steels S-MA2, S-MA4, S-MA6 sintered in N<sub>2</sub>-10H<sub>2</sub> for 1 h at 1120°C or 1250°C.

Upon liquid phase formation, the distribution of the liquid through the pore network is hindered by the dissolution of the iron base powder in the liquid master alloy [21, 22]. Therefore, the alloying elements remain concentrated around the location of the original master alloy particles, where large high alloyed areas containing bainitic and martensitic phases are usually found. Retained austenite is observed in B-MA6 due to the presence of Ni in the master alloy composition. The microstructure at the core of the original iron particles contains mainly fine pearlite with few ferrite grains in the steels sintered at lower temperatures. An increase in the sintering temperature in Group B steels allows the complete dissolution of the master alloy particles and provides a more rounded porosity, but does not seem to improve homogenization of the microstructure.

In Figure 3 the final oxygen contents are represented against the carbon losses. In spite of the presence of high oxygen affinity elements, the oxygen content is considerably low (below 0.12 wt.%). An increase in sintering temperature gives rise to a more effective



reduction of oxides due to the enhanced carbothermal reduction, which is accompanied by more important carbon losses.

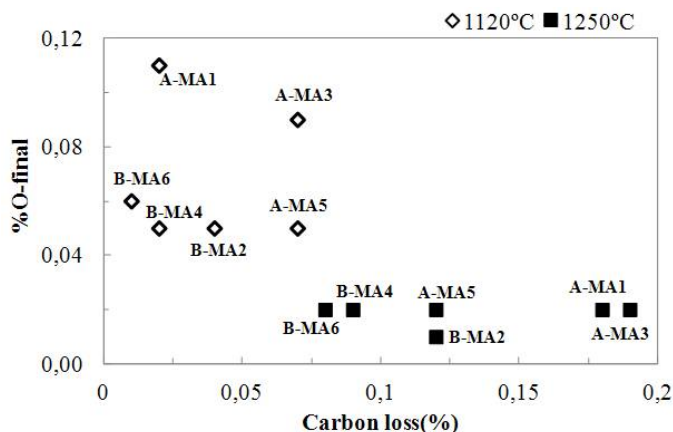


Fig.3. Final oxygen content against carbon losses for all steels studied.

Oxygen level of Group A depends on the jet milling process and particle size, and it is clear when sintering is performed at low temperature. The lower particle size in Group A leaves more surfaces available for oxidation. However, the Ni content in A-MA5 has provided further protection against oxidation.

In the case of sintering at 1250°C, the oxygen content is similar for all steels and is around 0.02 wt.%, indicating an effective reduction of the oxides. The highest oxygen content, observed in A-MA1 and A-MA3 at 1120°C, is accompanied by a higher carbon loss when sintering at 1250°C, and is due to the more important carbon consumption in the reduction of the higher amount of oxides present in these steels.

### Mechanical Properties

Study of mechanical properties revealed two main influencing parameters: density and total amount of alloying elements. The degree of densification directly affects elongation and impact energy values (see Fig.4), while the amount of alloying elements influences especially tensile strength and apparent hardness (Fig.5).

Steels with the highest relative densities in Fig.4 correspond mainly to steels from Group A (except for B-MA2 sintered at 1250°C). Lower master alloy particle sizes reduce swelling upon liquid phase formation and enhance densification during isothermal sintering. Therefore the highest values of elongation and impact energy are found in Group A steels.

Sintering temperature strongly affects densification and therefore mechanical properties. Enhanced densification at the higher sintering temperature is followed by an increase in both impact energy and elongation values, and is found to follow a similar tendency for both properties. The effect of sintering temperature seems to be much more beneficial for Group A steels, in which the lower master alloy particle size leaves smaller secondary porosity.

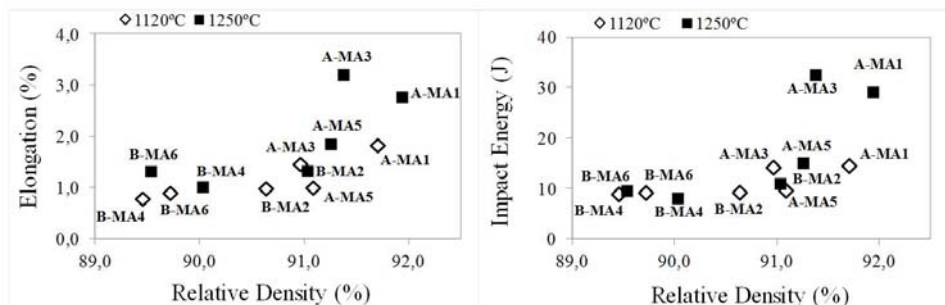


Fig.4. Elongation (left) or impact energy (right) vs. relative density [%].

Tensile strength and apparent hardness are not significantly affected by density, but instead are found to depend mainly on the total amount of alloying elements. Figure 5 represents tensile strength and apparent hardness against the total alloying content (without including carbon).

Tensile strength increases linearly with the amount of alloying elements at the high sintering temperature. At the low temperature the tendency is less clear due to the presence of undissolved master alloy particles, especially the coarser particles (Group B).

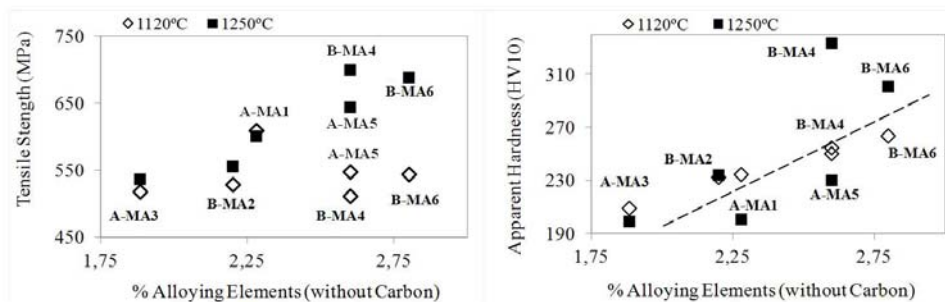


Fig.1. Tensile strength (left) or apparent hardness (right) vs. % alloying elements (without C).

The highest tensile strength values for the low sintering temperature are found in steels containing MA1, which presents the highest Si content (0.7 wt.%). High sintering temperature promotes melting and leads to a significant increase in the properties of steels containing master alloy MA4. MA4 steels provide the highest tensile strength values at the higher temperature, probably due to the combined effect of Cr and Mn.

Hardness values are presented on the right side of Fig.5. In Group A steels, hardness decreases with increasing sintering temperature. This peculiar effect can be a consequence of higher carbon losses in steels sintered at the higher temperature. Besides, as shown by the microstructure of these steels, a better distribution of alloying elements at the higher temperature leads to homogeneous microstructures, with very few high alloyed areas where hard phases can be formed at the cooling rates applied. Therefore, the overall apparent hardness of these steels is lowered.

In Group B steels, an increase in the sintering temperature promotes complete melting of the master alloy particles, and provides higher amounts of alloying elements

available. Hence, sintering at high temperatures increases the size of the highly alloyed areas where harder non-equilibrium phases can be formed during cooling. This increase in hardness is particularly important in MA4 steels, for which higher sintering temperatures are critical for achieving complete melting of the master alloy particles.

Both hardness and tensile strength values of steels containing MA4 are remarkable at the high sintering temperature, when the particles dissolve completely. Using similar Mn contents (around 1.6 wt.% for all steels studied), the additional 0.6 wt.% Cr added to MA4 steels seems to provide a significant increase in properties.

For the low sintering temperature (1120°C), the best combination of properties is provided by A-MA1 steels which present ultimate tensile strength values of 600 MPa and hardness ~230 HV10, combined with deformations around 2% and impact energies around 15 J.

At the high sintering temperature, B-MA4 steels show the highest tensile strength (700 MPa) and hardness values (~ 330 HV10). These steels, however, present low elongations (~ 1%) and impact energy values (~ 8 J). Steels containing MA1 (with the highest Si content) sintered at the high temperature provide lower strength values (600 MPa) but considerably higher elongations (~ 3%) and impact energies (30 J).

The upper graph of Fig.6 represents the ultimate tensile strength of commercially available steels, against the percentage of alloying elements introduced. Reference data [23] correspond to steels with a density close to  $7 \text{ g}\cdot\text{cm}^{-3}$ , sintered at different temperatures and without any additional thermal treatment. Steels presented in this study show competitive strength values with less than 3 wt.% of alloying elements. Better combinations are only achieved by the use of fully prealloyed powders.

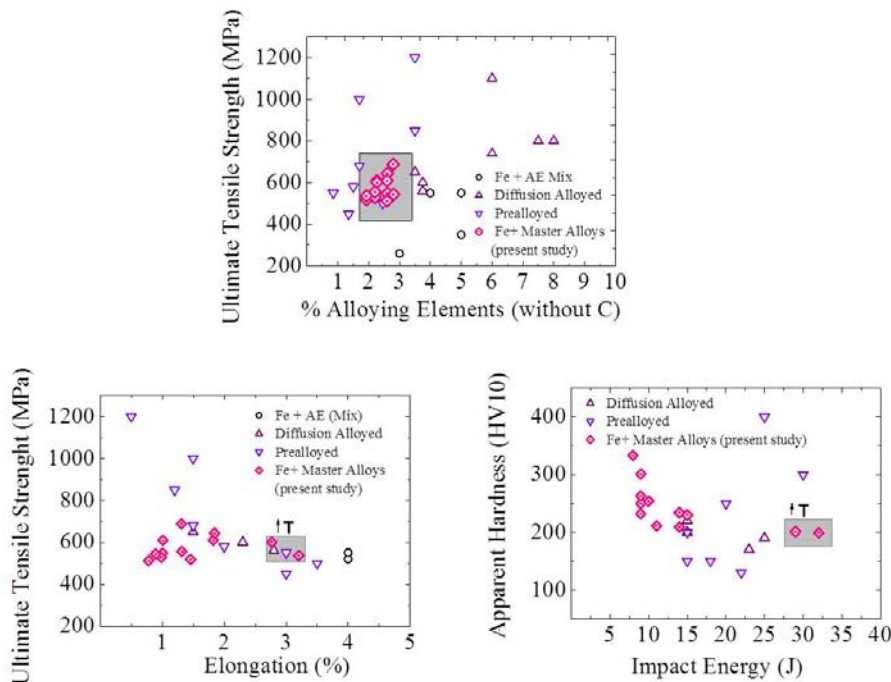


Fig.6. Mechanical properties of commercial sintered steels compared with the properties obtained in this study [23].

With the master alloys proposed in this study, combinations strength/deformation comparable to that of steels obtained from commercially available powders are achieved by using alloying elements with lower cost, and without applying any specific sintering requirements.

## CONCLUSIONS

Lean sintered steels with an alloying content lower than 3 wt.% have been obtained using the “master alloy route”. The sintered properties are comparable and competitive to that of sintered steels commercially available, but with low cost alloying elements. Based on the results, it can be concluded that:

- Particle size of the master alloy powder has a critical influence on the final properties of the steel. Lower particle sizes improve densification and reduce the diffusion distances necessary to homogenize the alloying elements.
- Using low master alloy particle sizes, higher densities are achieved, improving properties such as impact energy and elongation. Density does not have a significant effect on tensile strength (mostly influenced by the amount of alloying elements).
- Enhanced diffusion of alloying elements at higher temperatures gives place to a higher increase in tensile strength. The effect of sintering temperature on apparent hardness depends on the diffusion distance of alloying elements and therefore on the master alloy particle size. When high sintering temperatures and small master alloy particle sizes are used, a decrease in hardness is detected, due to the high homogenization of alloying elements which leaves fewer areas with an alloying content high enough to provide hard non-equilibrium microstructures.
- In spite of the presence of elements with a high affinity for oxygen, the final oxygen content in the sintered steels is lower than 0.12 wt.% for samples sintered at 1120°C and 0.02 wt.% for those sintered at 1250°C. A better carbothermal reduction of the oxides at higher sintering temperatures leads to lower oxygen contents and higher carbon losses.
- Under standard sintering conditions, the addition of only 4 wt.% of Fe-Mn-Si based master alloy powders (less than 3 wt.% of alloying elements) provide competitive mechanical properties comparable to those of commercially available steels. UTS around 600-700 MPa combined with deformations of 1-3%, apparent hardness around 200-350 HV10 and impact energies between 10 and 35 J are obtained in the as-sintered condition. Sintering at high temperatures allows combining the best strength properties with the highest deformation values.

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