



NEW CHANCES FOR THE MASTERALLOY APPROACH

Raquel de Oro Calderon, Maryam Jaliliziyaeian, John Dunkley, Christian Gierl-Mayer, Herbert Danninger

Abstract

The Masteralloy (MA) alloying route has a great potential for reducing the alloying costs in sintered steels, while allowing the introduction of innovative alloying systems. However, in order to achieve an efficient use of the alloying elements, the particle sizes needed are often below 25 μm , which means that for standard gas atomization a significant fraction of the batch has to be discarded or at least recycled. This work evaluates the performance of steels containing MA powders obtained with a novel atomization technique (Ultra-High-Pressure Water atomization) that allows the production of low-cost powders with low oxygen contents, rounded morphologies and mean particle sizes as low as 6 microns. Mechanical properties, dimensional variations and interstitial contents were measured in steels containing different MA compositions sintered at either 1120 °C or 1250 °C in $\text{N}_2\text{-}5\text{H}_2$ atmospheres. Already with less than 3 wt.% of alloying elements these steels present excellent combinations of properties, reaching strength levels of 560-915 MPa and hardness 220-260 HV10, combined with elongations of 1.3-3.2% and impact energies around 20-30 J/cm².

Keywords: *Lean low alloy steels, Alloying design, Masteralloys, Mechanical properties*

INTRODUCTION

The Masteralloy (MA) route applied to sintered steels consists on mixing Fe base powder with an MA powder that contains all alloying elements in a combined form. It allows the introduction of oxygen sensitive elements such as Si, Mn and Cr [1-3], which can significantly improve the properties of low alloy steels. The composition of the MA can be designed to promote the formation of a transient liquid phase that enhances sintering [4-11]. Other advantages of the MA route are the flexibility in the selection of the final composition and the possibility to retain the compressibility of the Fe base powder. The development of master alloys for PM steels has been a topic of research since the early 70's. At that time, some very interesting master alloys named MCM (Mn-Cr-Mo), MVM (Mn-V-Mo) and MM (Mn-Mo) were thoroughly studied for almost two decades, with the aim of using them in the production of highly loaded PM parts [1-3], but were eventually abandoned in the 90's due to the excessive tool wear caused by the very hard and angular MA powder particles (at that time produced by casting and then milling the ingots).

In the last two decades the use of gas atomization techniques has boosted the research in MA's because it allows obtaining powder particles with adequate morphology and low oxygen contents.

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However, the process often yields particle size distributions centred at ~ 50 - $100\ \mu\text{m}$ while for many applications the particle size needed to ensure a proper distribution of alloying elements during sintering is below $\sim 25\ \mu\text{m}$. Therefore a significant fraction of the gas atomized batch has to be discarded or at least recycled.

This work reports the properties of steels containing MA powders produced using a newly developed atomization technique “Ultra High Pressure Water Atomization (UHPWA)” that allows obtaining MA powders with rounded morphologies, low oxygen contents ($\sim 1\%$), small particle sizes and at relatively low production costs.

MATERIALS AND METHODS

The materials used in this study were produced from mixes containing Fe-0,5%C-4%MA pressed at 600 MPa in a double action press using die wall lubrication. Water atomized iron (grade ASC 100.29, Höganäs AB Sweden - O < 0.1wt.%; C < 0.01wt. %) was used as base powder, and carbon was introduced as natural graphite (grade UF4, Kropfmühl). The characteristics of the master alloy powders used are presented in Table 1. Melting ranges of the master alloys were obtained through Differential Thermal Analysis (DTA) studies in Ar, carried out with a high-performance modular Simultaneous Thermal Analyzer Netzsch STA 449 C.

The MA powders were produced by Ultra High Pressure Water Atomization (UHPWA). This utilizes water pressures of 60-200 MPa and operates with induction melted batches of molten alloy, atomization being followed by dewatering and vacuum drying. As can be observed in Table 1, the oxygen values obtained are fairly low, and the MA powder particles present rather small particle size distributions and rounded morphologies (Fig. 1).

Tab.1 Characteristics of the master alloy powders used in this study.

Name	Nominal Composition	d10	d50	d90	O (%)	C (%)	Melting range
H45	Fe-32Cr-8Si-4C	3.21	7.84	18.4	0.14	4.01	1150-1220 °C
H46	Fe-42Mn-6Si-0.4C	2.33	6.7	16.1	1.60	0.54	1120-1200 °C
H47	Fe-28Mn-27Cr-6Si-3.7C	2.92	8.09	22.6	0.20	3.61	1095-1310 °C

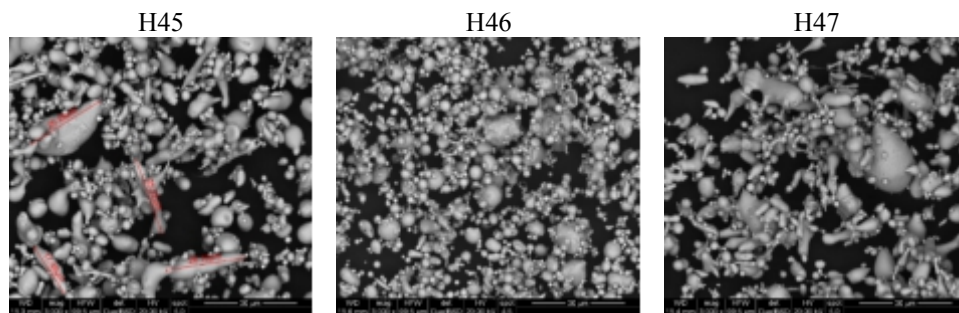


Fig. 1. SEM images of the master alloy powder particles.

Standard tensile test (ISO 2740) and impact test bars (ISO 5754) were produced for this study. Sintering was carried out in a lab scale furnace AHT Silitstabofen with gas-tight superalloy retort, at 1120 °C and 1250 °C under N_2 -5 H_2 atmosphere. The gas flow was introduced from the furnace outlet, and the samples were progressively pushed to the maximum temperature zone where they were kept for 30 min. The heating rate obtained using this procedure is estimated at around 30 K/min ($\sim 0.5\ ^\circ\text{s}$). After the holding period at

temperature, the samples were cooled in a water-jacketed exit zone under the same protective atmosphere used for sintering. The linearized cooling rate obtained using this procedure is about 45 K/min (~ 0.75 K/s).

RESULTS AND DISCUSSION

Microstructures

The Figure 2 shows the microstructures of steels containing masteralloys sintered at 1120°C and 1250°C.

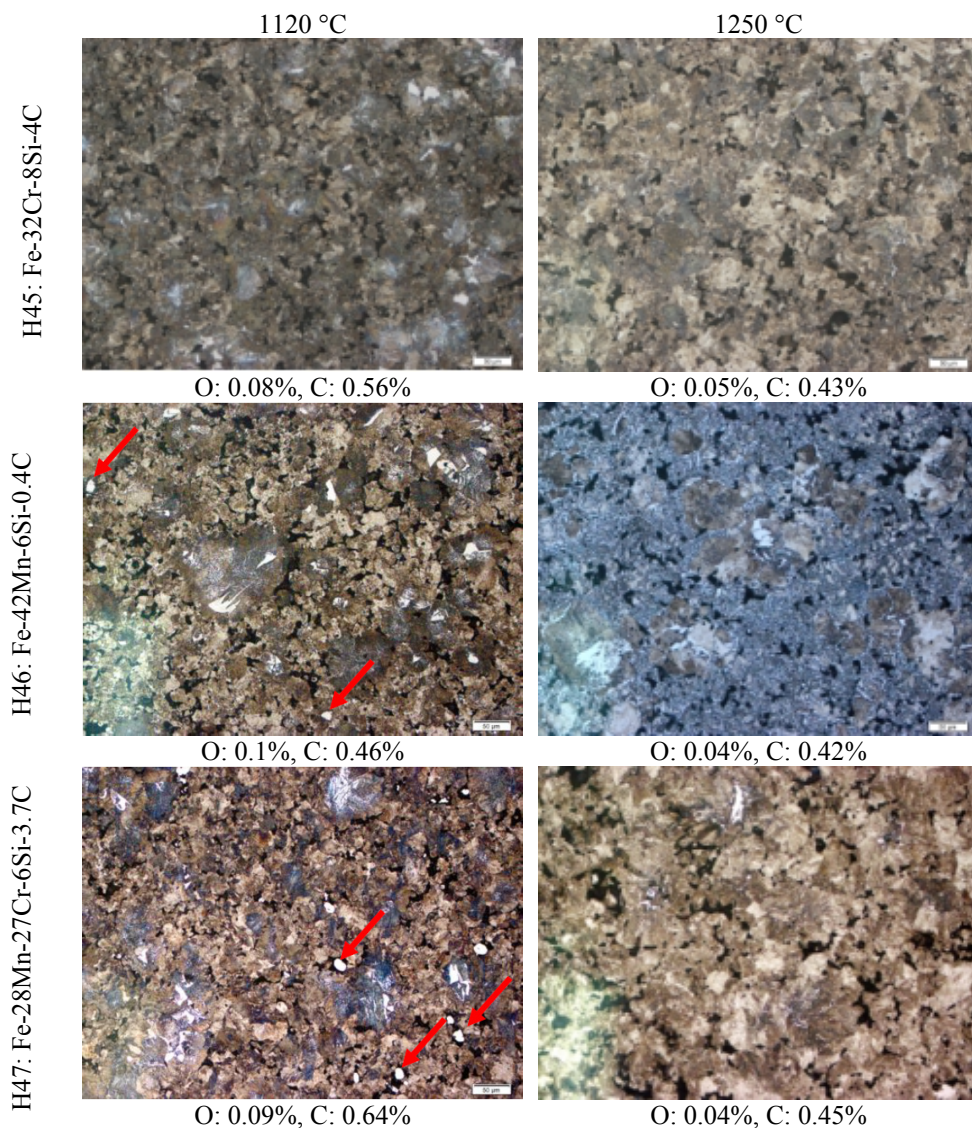


Fig.2. Microstructures and interstitial contents in steels containing masteralloys (Fe-0.5C-4MA) sintered at 1120 °C and 1250 °C for 30 min in N_2-5H_2 .

The typical microstructure consists of fine perlitic phases in the cores of the Fe base powder particles, surrounded by areas with a higher amount of alloying elements in which harder microstructures are developed. The homogeneous distribution of these phases within the sample suggests a fairly good distribution of the alloying particles in the mix. At high sintering temperatures the porosity is more rounded, and the diffusion of alloying elements is improved, which is evidenced by the decrease in the amount of ferritic/perlitic areas. Undissolved masteralloy particles are clearly discernible in steels containing masteralloys H46 and H47 sintered at 1120 °C, some of them have been marked with arrows in Fig. 2. This suggests that the sintering temperature/time has been insufficient to efficiently distribute the alloying elements present in the masteralloy.

Dimensional Changes and Density

Density and dimensional changes are represented in Fig. 3. In general, steels containing Fe-based masteralloys can give rise to swelling or shrinkage phenomena, depending on whether the swelling effect produced during the diffusion of alloying elements - or the melting of the masteralloy particles – can be or cannot be compensated by the shrinkage that takes place in the isothermal region. As the sintering phenomena are more activated at high temperatures, higher shrinkage effects (or lower swelling) are observed when increasing the sintering temperature. Dimensional changes -measured on the length of impact test bars - in steels containing H45 and H46 are around 0,1% or below. With these two masteralloys swelling is observed when sintering at 1120°C, while shrinkage takes place when sintering at 1250°C. Consequently, density increases with the sintering temperature, because the sintering phenomena are activated by the higher temperatures. The densities of steels containing H45 and H46 are in the range of 7.02-7.07 g/cm³.

Swelling is observed in samples containing masteralloy H47 both at 1120 and - to a lower extent- at 1250°C. As a consequence, the sintered density is lower than the green density, and the densities achieved are below 7 g/cm³.

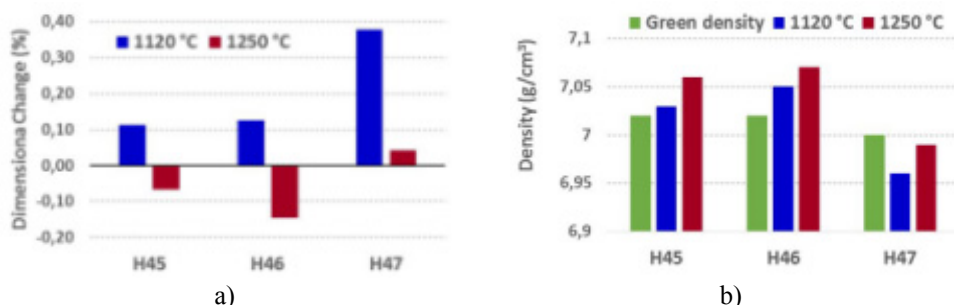


Fig.3. Dimensional changes (a) and density (b) in steels containing masteralloys (Fe-0.5C-4MA) sintered at 1120 °C and 1250 °C for 30 min in N₂-5H₂.

Mechanical Properties

Mechanical properties (represented in Fig.4) are strongly influenced by the sintering temperature. On one hand this is because of the enhanced distribution of alloying elements at higher sintering temperatures, and on the other hand due to the higher densities and more rounded porosity.

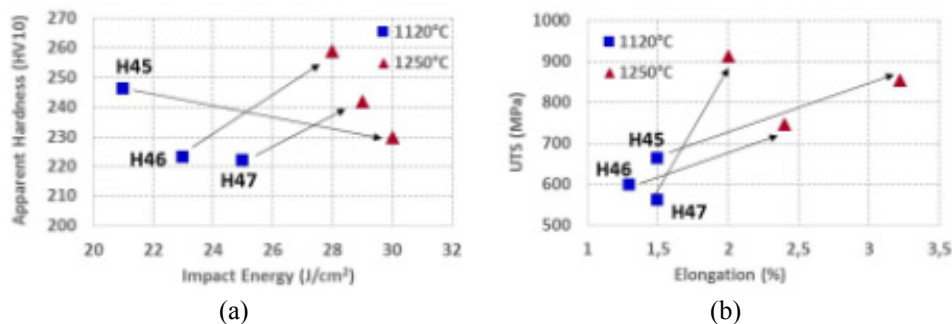


Fig.4. Apparent Hardness vs. Impact Energy (a), and Ultimate Tensile Strength (UTS) vs. Elongation (b) in steels containing masteralloys (Fe-0.5C-4MA) sintered at 1120 °C and 1250 °C for 30 min in N_2-5H_2 .

The as-sintered hardness values obtained (see Fig. 4a) are in the range of 220-260 HV10 which is in good agreement with the microstructures observed for these steels (see Fig.2). With masteralloy H45 the hardness decreases when increasing the sintering temperature. Apart from the decrease in the carbon content at 1250 °C (due to the enhanced reduction of oxides at high temperatures) also the differences in the distribution of alloying elements play a role on this effect. At higher sintering temperatures, the alloying elements are more homogeneously distributed in the sample, and therefore the amount of highly alloyed (solution hardened) areas decreases, and so does the apparent hardness. Also local sinter hardening might play a role.

A different effect is observed in steels containing H46 and H47, for which the increase in the sintering temperature causes an increase in the hardness values. In this cases, as suggested by the microstructures from Fig.2, some masteralloy particles are still not dissolved in the Fe base powder, and therefore the alloying elements are not fully utilized. An increase in the sintering temperature promotes the homogenization of the alloying elements, resulting in a significant increase in the apparent hardness values. The highest hardness is observed in steels containing H46, in which bainitic microstructures are developed in the highly alloyed areas (see Fig.2).

The impact energy values obtained are reasonably high - 20-26 J/cm²- already at 1120 °C (see Fig.4a). The higher sintered densities, more rounded porosity and lower carbon contents obtained when sintering at 1250 °C contribute to increased impact energy, that reaches values around 28-30 J/cm².

The Ultimate Tensile Strength (UTS) of steels sintered at 1120 °C is around 550-700 MPa and is combined with elongations around 1.5%. By increasing the sintering temperature both the UTS and elongation values are increased, reaching UTS of 747-913 MPa combined with elongations above 2 %.

Comparison with commercial sintered steels

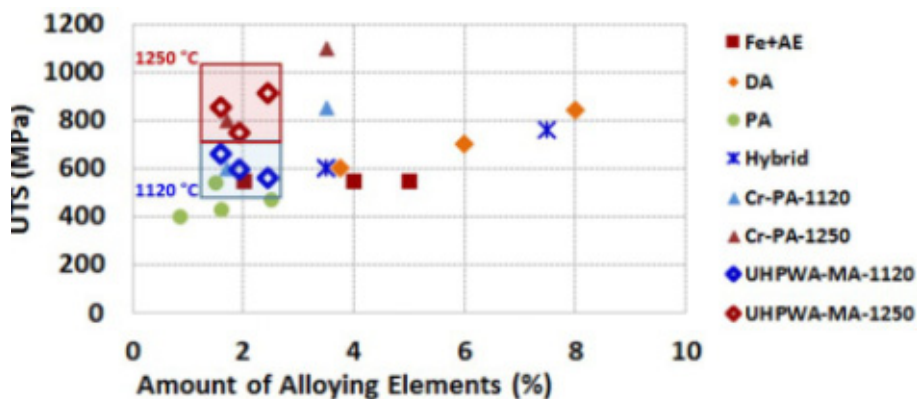
The Figure 5 shows a depiction of properties in which the steels produced in this study are compared with steels produced using commercial powders (data obtained from [12, 13]). As can be observed in Fig.5a, steels obtained using UHPWA-masteralloys (from this study) present very competitive UTS values with a very low content (below 3 wt.%) of inexpensive alloying elements (Cr, Mn, Si). In the graph from Fig.5a, the positioning of steels containing UHPWA masteralloys is similar to those obtained with Cr-prealloyed

powders with a similar amount of alloying elements (both for 1120°C and 1250°C sintering temperature).

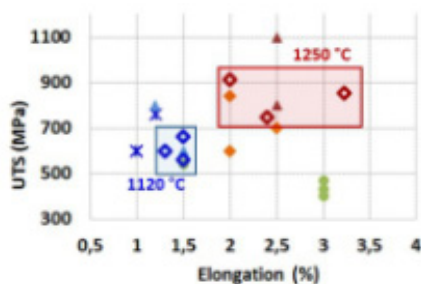
A similar comparison is presented in Figs.5b and c, but in these latter cases UTS is represented against elongation (Fig.5b) and apparent hardness is plotted against impact energy (Fig.5c).

Excellent combinations of properties are observed in steels containing UHPWA master alloys, even when sintering at 1120°C, very competitive with those obtained with commercial powders and again comparable with Cr-prealloyed grades. At high sintering temperature (1250°C) the properties of steels containing masteralloys are boosted, presenting very interesting combinations of strength and ductility.

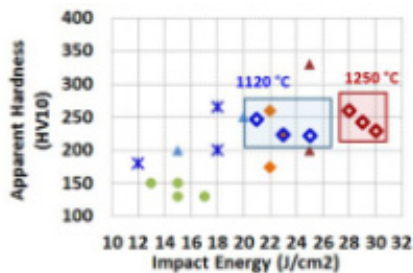
The fact that some of the masteralloy particles (H46 and H47) did not dissolve completely in the steel at 1120°C leaves some room for improvement. Working on the design of the masteralloy composition, it might be possible to obtain a better distribution of alloying elements at low sintering temperatures, thus positioning even better on the property map the steels obtained following the masteralloy route.



(a) UTS vs % Alloying Elements



(b) UTS vs Elongation (%)



(c) Apparent Hardness vs Impact Energy

Fig.5. Comparison of properties of the steels obtained in this study with steels produced under similar conditions using commercial powder grades.

*Fe+AE: Fe with alloying elements Mo, Ni, Cu, DA: diffusion alloyed, PA: conventional prealloyed grades, Cr-PA Cr prealloyed powders sintered either at 1120 °C or at 1250 °C, UHPWA-MA: steels from this study sintered either at 1120 °C or at 1250 °C.

CONCLUSION

A newly developed atomizing technique named Ultra High Pressure Water Atomization (UHPWA), which allows economic production of masteralloy powders with mean particle sizes as low as 6 µm, has been applied to produce the masteralloy powders used in this study. After sintering at 1120°C and 1250°C for 30 min in N₂-5H₂, the sintered steels prepared using these masteralloys show excellent combinations of properties: UTS~560-915 MPa, hardness ~220-260 HV10, elongation ~1.3-3.2% and impact energy ~20-30 (J/cm²). With less than 3 wt.% of inexpensive alloying elements these steels present combinations of properties that reach or even surpass the properties of steels obtained with commercial powders. In some of the steels produced, the masteralloy particles were not completely dissolved when sintering at 1120°C, which indicates that a re-design of the alloying composition to promote the diffusion of alloying elements at lower temperatures (by e.g. the formation of a liquid phase) could result in an even better combination of properties for low temperature sintering cycles.

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