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New masteralloys for sintered high strength steels – the attractive route between mixing and prealloying

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Institute of Chemical Technologies and Analytics, Technische Universität Wien (TU Wien), Austria

Atomising Systems Limited, England

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The combination of alloying elements in the form of a masteralloy (MA) powder gives the possibility to protect oxygen-sensitive elements against oxidation and to promote the formation of a liquid phase that enhances the sintering mechanisms. As compared to the prealloying approach, the MA route has lower impact on compressibility and provides more flexibility in the selection of the final composition. Knowledge of the chemical aspects of sintering combined with the possibility to tailor the properties of sintered steels through the use of specific MA compositions and with the development of novel atomizing methods to produce MA powders may, in the near future, position the MA approach as a very interesting alternative to conventional alloying methods. In this work, sintered steels containing cost-effective Fe–Mn–Si masteralloys are processed at increasing temperatures in the range between 1120 and 1300 °C. The combination with different base powders provides a good overview of the properties that can be obtained with this alloying approach. Besides, the evaluation of microstructure and mechanical properties as a function of temperature allow understanding the real benefits of increasing the sintering temperature, in order to find an appropriate balance between the economic requirements and the material performance.

Keywords: low alloy steels, masteralloys, liquid phase sintering, oxygen-sensitive alloying elements, sintering temperature, mechanical performance, alloying routes.

De Oro Calderon Raquel – PhD, Senior postdoc researcher at Institute of Chemical Technologies and Analytics, Technische Universität Wien (TU Wien) (Getreidemarkt 9, A-1060 Wien/Vienna, Austria). E-mail: Raquel.oro.calderon@tuwien.ac.at.

Jaliliziyaeian Maryam – Dr. techn., Postdoc researcher at Institute of Chemical Technologies and Analytics, TU Wien (Position from Oct. 1st, 2018: Voestalpine Stahl GmbH, A-4020 Linz, Austria). E-mail: maryam.jaliliziyaeian@voestalpine.com.

Dunkley John J. – PhD, Chairman, Atomising Systems Ltd. (371 Coleford Road, Sheffield S9 5NF, UK). E-mail: jjd@atomising.co.uk.

Gierl-Mayer Christian – Dipl.-Ing. Dr. techn., Assistant Professor at Institute of Chemical Technologies and Analytics, TU Wien. E-mail: Christian.gierl@tuwien.ac.at.

Danninger Herbert – Dipl.-Ing. Dr. techn., Dr.h.c.mult., Full Professor at Institute of Chemical Technologies and Analytics and Dean, Faculty of Technical Chemistry, TU Wien. E-mail: herbert.danninger@tuwien.ac.at.

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Introduction

Powder metallurgy (PM) steels are typically produced by mixing a plain iron (or prealloyed iron base) powder with graphite, further alloying elements being introduced by admixing or bonding elemental alloying particles (typically Cu, Ni and Mo) or — more rarely — masteralloys (MA), i.e. a powder that contains all of the alloying elements combined (Fig. 1). While the use of prealloyed powders provides homogeneous microstructures, the admixed approaches (i.e. powder mixes, diffusion bonded and masteralloys in Fig. 1) give the possibility of obtaining microstructures with defined heterogeneity that may offer combinations of mechanical properties not attainable by any other production route.

Growing usage of PM steels in the automotive sector has nowadays caused increasingly demanding requirements to provide 1) high cost effectiveness compared to competing technologies, 2) high level of material performance and 3) very close dimensional tolerances. The advances needed to simultaneously achieve these three

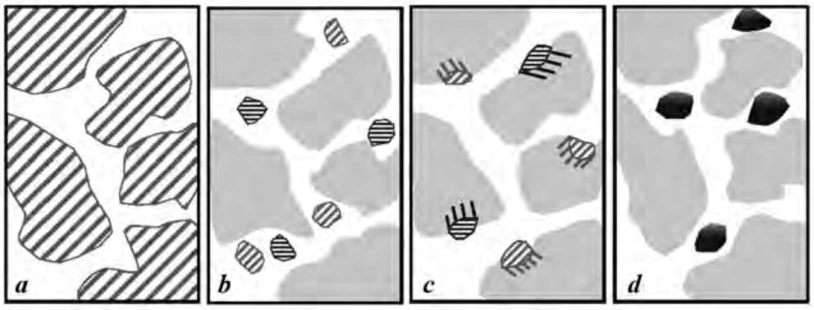


Fig. 1. Alloy variants for sintered steels
a – prealloyed; ***b*** – powder mixture; ***c*** – diffusion bonded; ***d*** – masteralloy

requirements can be made by finding alloying alternatives that combine lower production costs with a higher level of properties. Moreover, the search for alloying alternatives is also motivated by the high price volatility of the traditional alloying elements (Cu, Ni and Mo), the recycling problems resulting from the use of Cu and the fact that fine Ni powders have recently been classified as carcinogenic.

The investigation of new alloying alternatives not only concerns the use of new alloying elements, but also the more efficient usage of alloying elements oriented to obtain the so called «lean steels» (steels with a minimized content of alloying elements that maintains or even improves the properties of conventional sintered steels).

The use of cheaper and more efficient alloying elements such as Cr, Mn and Si (which are widely used in the production of wrought steel parts) is limited by their high affinity for oxygen (higher than that of the traditional Cu, Ni and Mo). The way to minimize oxidation during sintering is to introduce such oxygen-sensitive elements combined (i.e. alloyed) with other elements with a lower affinity for oxygen (for instance Fe). In such way, the oxygen affinity of the powder particles can be significantly lowered [1, 2]. There are two main routes to achieve this: by using prealloyed iron powders or by admixing masteralloy particles (instead of elemental Cr, Mn or Si powders) to the iron base powder.

Compared to prealloying, the master alloy route presents clear advantages such as the possibility to maintain the compressibility of the base powder, more flexibility in the selection of the final composition of the steel and the potential reduction of the overall cost (prealloyed powders are among the most expensive grades in the market). But maybe the most interesting advantage of using masteralloys is the possibility to specifically tailor the composition of the masteralloy to promote the formation of a liquid phase that enhances the sintering process. This latter characteristic is an important advantage as compared with the addition of alloying elements by admixing elemental powder particles (e.g. mixes with Ni or Mo powders), because the liquid phase not only accelerates the diffusion of the elements, thus improving the alloying efficiency, but also strengthens the sintering contacts, both effects strongly improving the properties.

The development of masteralloys for PM steels has been a topic of research since the early 70's. At that time, some very interesting masteralloys 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 [2—4]. However, the idea was eventually abandoned in the 90's for two reasons: 1) the need of high sintering temperatures (around 1280 °C) to dissolve the carbide phases present in the masteralloy particles, and 2) 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). Since then, different masteralloy compositions have been developed pursuing the introduction of oxygen-sensitive elements [2—6], or the formation of a liquid phase [7—10], or both aspects at the same time [11—22] (see schematic in Fig. 2). But the main boost of this research area did not occur until the end of the 90's, when two main parallel developments were available: On one hand, the use of inert gas atomization as a production method that allowed obtaining increasingly fine MA powder particles with rounded morphologies that minimize the damage to the compacting tool. And on the other hand, the use of computational tools to systematically search compositions with adequate melting points below the usual sintering temperatures [23, 24].

During the last few years, important advances in the MA field have provided relevant knowledge that may contribute to position the use of masteralloys as a versatile tool for producing cost-effective PM materials with improved performance:

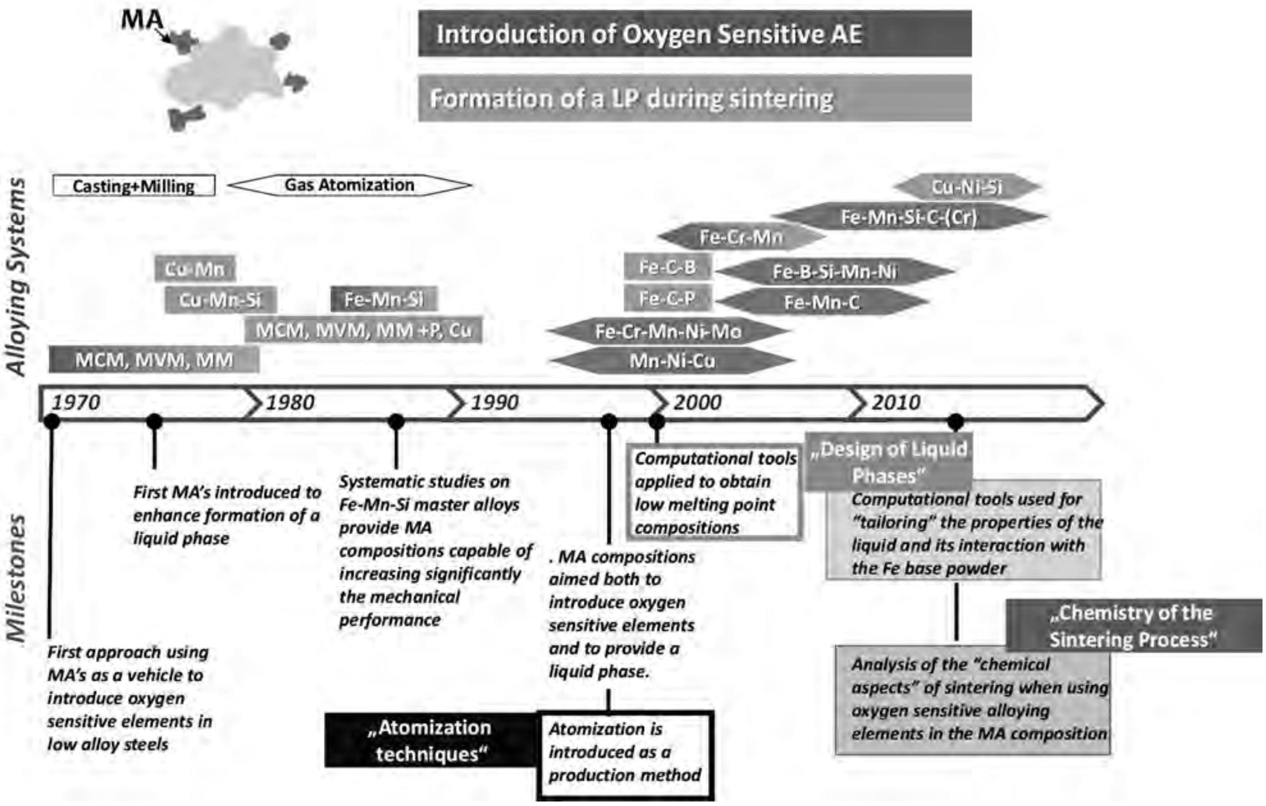


Fig. 2. Outstanding developments in the field of MA. Solid boxes represent compositions exclusively developed for introducing oxidation sensitive elements, dotted boxes to compositions aimed to form a liquid phase, and dashed boxes to both of them

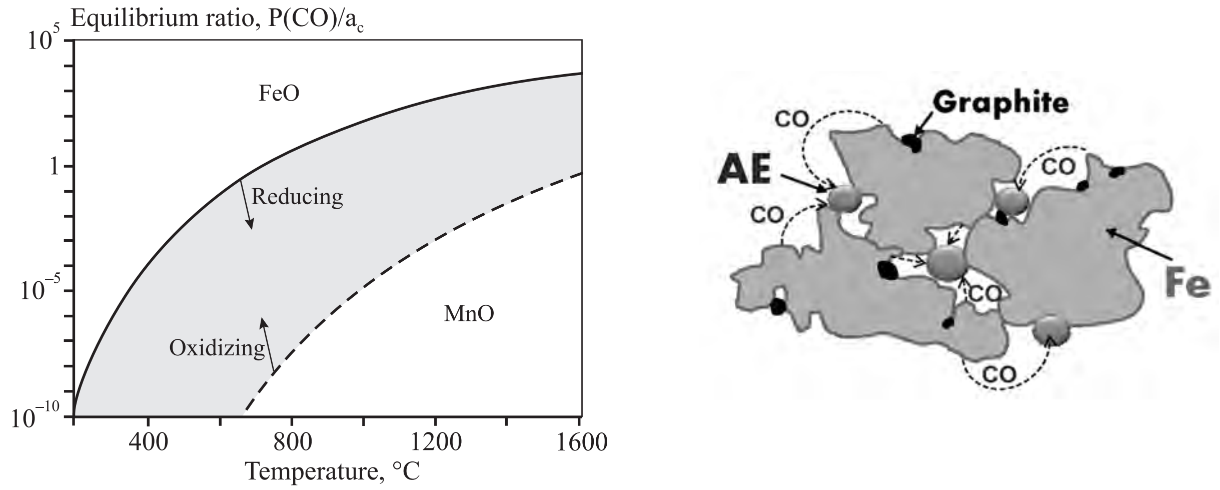
— The detailed study of the chemical processes that take place when sintering steels containing masteralloys [25—27].

— The implementation of a scientific methodology that allows designing liquid phases with special features [28—30].

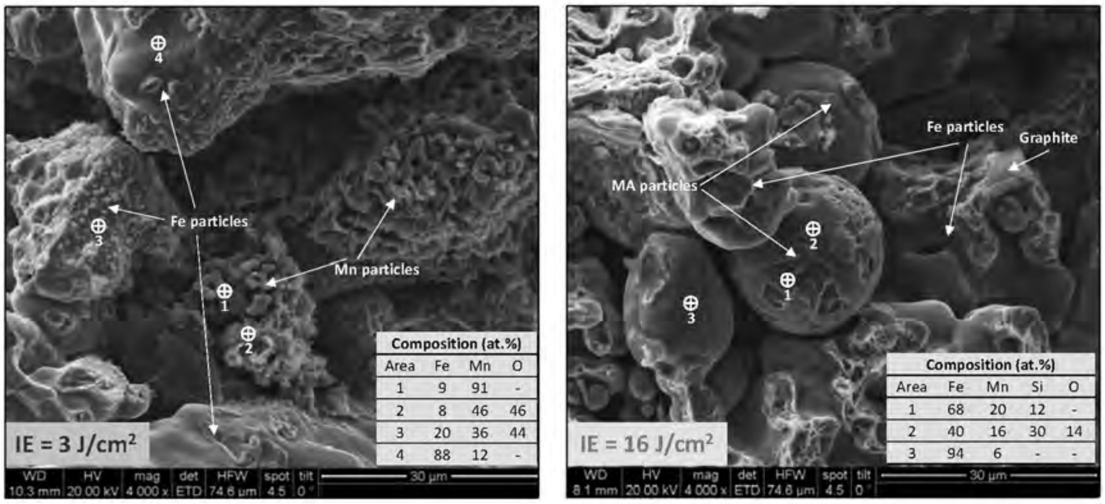
— The development of a new atomization technique — «Ultra High Pressure Water Atomization (UHPWA)» that allows obtaining MA powders with rounded morphologies, low oxygen contents (<1 %) and small particle sizes ($d_{50} < 8$ mm), at rather low production costs [31].

The study of the chemical processes taking place during sintering has shown that even in highly pure atmospheres, oxidation of the oxygen-sensitive elements may occur, the main source of oxygen being the Fe powder particles themselves and not the atmosphere [25—27]. The mechanism by which such oxidation processes take place is an oxygen transference («internal gettering»), that can take place within an individual powder particle (as is the case of prealloyed powders), or between the iron base powder and the alloying elements (in case of powder mixes). In case of powder mixes, the reduction products from the carbothermal reduction of the less stable Fe oxides (CO and/or CO_2) immediately react with the oxygen-sensitive alloying elements nearby, and the oxygen is simply transferred to the oxygen-sensitive powder particles (Fig. 3, *a*). The use of masteralloys considerably lowers the risk of oxidation as compared to elemental powders The benefits of using a masteralloy powder instead of elemental alloying powders are clearly observed when sintering at intermediate temperatures of the heating stage (temperatures within the «critical range» for oxygen-transference). As an example, Fig. 3 shows the fracture surface of steels with elemental additions of Mn (Fe + 0.5C + 4Mn in Fig. 3, *b*) versus additions of masteralloy (Fe + 0.5C + 4MA: Fe—40Mn—17Si in Fig. 3, *c*). Mn evaporation and subsequent oxidation on the surface of the contiguous Fe base particles contributes to the formation of an oxide network that reduces the (unnotched) Charpy impact energy to 3 J/cm^2 as compared to that of steels containing masteralloy (16 J/cm^2) in which the oxygen transference is minimized.

Furthermore, probably one of the most interesting benefits of using masteralloys is the fact that their composition can be specifically designed to promote the



(***a***) Schema of the internal getter mechanism (AE stands for Alloy Element)



Composition (at.%)			
Area	Fe	Mn	O
1	9	91	-
2	8	46	46
3	20	36	44
4	88	12	-

Composition (at.%)				
Area	Fe	Mn	Si	O
1	68	20	12	-
2	40	16	30	14
3	94	6	-	-

(***b***) Fe–0.5C–4Mn (***c***) Fe–0.5C–4MA (Fe–40Mn–17Si)

Fig. 3. «Internal getter» effect in compacts prepared from mixed powders – oxygen transfer through the gas phase
a – Schema of the process
Fracture surfaces of steels sintered at 900 °C in Ar with compositions: Fe + 0.5C + 4Mn (***b***)
and Fe + 0.5C + 4MA (MA: Fe–40Mn–17Si) (***c***), sintered 30 min at 900 °C in Ar 99.999 %

formation of a liquid phase that enhances the distribution of alloying elements and accelerates the sintering processes [20, 28—30, 32—34]. Here, the use of masteralloys offers a singular chance, as their compositions can also be specifically tailored to form a liquid phase with defined characteristics (Fig. 4). For instance, masteralloys forming liquids with low infiltration capacity (so called non-infiltrating) give rise to heterogeneous microstructures comparable to those obtained with diffusion bonded powders, with the peculiarity of presenting — in a single powder particle — a combination of different alloying elements. On the other hand, homogeneous microstructures can be obtained when using infiltrating liquids (Cu-like). If compared with prealloyed powders (which also provide homogeneous microstructures) infiltrating masteralloys offer the advantage of preserving the compressibility of the base powder and giving more flexibility in the selection of the final steel composition. But most importantly, a masteralloy forming an infiltrating liquid can be used to homogeneously distribute alloying elements that otherwise would require unrealistic sintering times/temperatures. As an example, a Cu-based masteralloy can be used to take advantage from the ability of Cu to penetrate inter-particle contacts and grain boundaries. Thus, Cu acts as a vehicle to distribute other alloying elements with a low diffusion rate in Fe (e.g. Ni) within the grain boundaries of the base iron powder, where the diffusion dis-

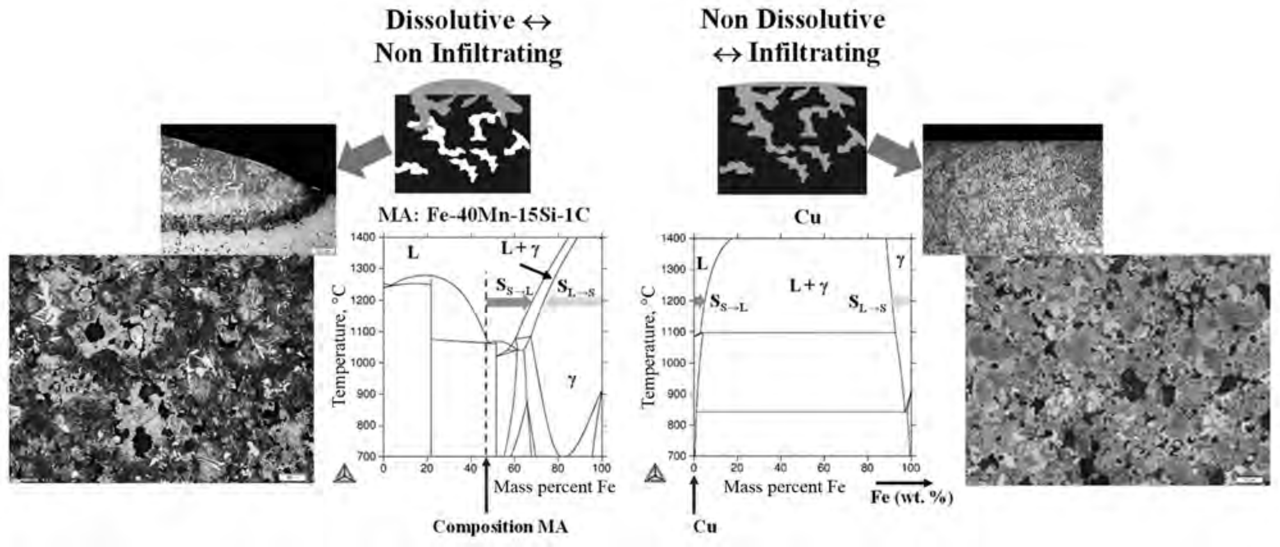


Fig. 4. Combination of thermodynamic calculations and macroscopic experiments to determine relevant characteristics of the liquid-solid interaction that affect the behavior during sintering

tances needed to achieve microstructural homogeneity are smaller. Either with infiltrating or non-infiltrating liquids, the masteralloy approach always offers the possibility to introduce several alloying elements simultaneously and thus take advantage of the synergistic effects of combining alloying elements instead of introducing them individually.

Achieving sufficient homogenization in the distribution of alloying elements when using non-infiltrating master alloys can be a complicated issue, particularly if low sintering temperatures are used (which are industrially more attractive). Here the use of masteralloy with small particle sizes is very helpful. However, the standard gas atomization process often yields particle size distributions centered at ~50÷100 μm while for many applications the particle size needed to ensure a proper distribution of alloying elements during sintering is below ~25 μm. In the last years, a newly developed atomization technique — «Ultra High Pressure Water Atomization» (UHPWA) — has allowed obtaining MA powders with rounded morphologies, low oxygen contents (< 0.1 %) and small particle sizes (d_{50} < 8 μm), at rather low production costs [31]. Such small particle sizes might be able to provide a sufficient enhancement of the diffusion of alloying elements even at low sintering temperatures.

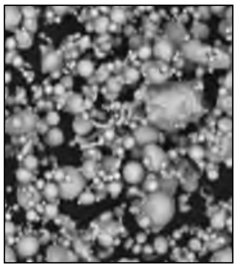
This work presents an overview on the properties that can be achieved when using these newly developed UHPWA masteralloys, considering their combination with different base powders, and analyzing the effect of the sintering temperature on the evolution of their microstructure and properties.

Experimental procedure

Sintered steels were produced from mixes containing Base Powder + 4 wt.% MA + 0.5 wt.% C using the starting materials described in Table 1. Masteralloy (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 narrow particle size distributions and rounded morphologies. Melting range of the masteralloy was determined through Differential Thermal Analysis (DTA) studies in Ar, carried out with a high-performance modular Simultaneous Thermal Analyzer Netzsch STA 449 C.

Mixes were pressed at 600 MPa in a double action press using die wall lubrication. Standard tensile test (ISO 2740) and impact test bars (ISO 5754) were produced for this study. Green parts were sintered in a lab scale SiC rod heated furnace with gas-tight superalloy retort. Sintering was carried out in N_2—$5H_2$ atmosphere for 30 min at varying temperatures (1120 °C, 1180 °C, 1220 °C, 1250 °C and 1300 °C). The gas flow was introduced from the furnace outlet and the samples were progressively pushed to the maximum temperature zone. After sintering, the samples were pushed into a water-jacketed exit zone and cooled under the same protective atmosphere. This procedure is used to simulate the process in an industrial belt furnace. The heating

Table 1. **Summary of the materials used in this study**

Base powders	Water atomized plain Fe powder (grade ASC 100.29, Höganäs AB Sweden) O < 0.08 wt.%, C < 0.01 wt.%
	Water atomized Fe–0.85Mo prealloyed powder (grade Ast85Mo, Höganäs AB Sweden), O < 0.07 wt.%, C < 0.01 wt.%
	Water atomized Fe–1.8Cr prealloyed powder (grade AstCrA, Höganäs AB Sweden), O < 0.15 wt.%, C < 0.01 wt.%
	Water atomized Fe–3Cr–0.5Mo prealloyed powder (grade AstCrM, Höganäs AB Sweden), O < 0.15 wt.%, C < 0.01 wt.%
Graphite	Natural graphite (grade UF4, Kropfmühl)
MA	 Ultra High Pressure Water Atomized (UHPWA) Nominal composition: Fe–42Mn–6Si–0.4C (in wt.%) d_{10} ~ 2.3 μm, d_{50} ~ 6.7 μm, d_{90} ~ 16 μm (Sieved below 16 μm), O ~ 0.1 wt.%, C ~ 4 wt.% Melting range (DTA): 1120–1200 °C

rate obtained using this procedure is estimated at around 30 K/min (0.5 °/s). The linearized cooling rate is about 45 K/min (~0.75 K/s). Oxygen and carbon contents were analysed using LECO-TC400 and LECO-CS230. Impact energy, apparent hardness and tensile properties were measured following standard procedures defined in ISO 5754:2017, ISO 4498:2010 and ISO 6892-1:2016, respectively.

Effect of masteralloys on compressibility

One of the potential advantages of using masteralloys is the possibility to preserve the compressibility of the base powder. The effect of masteralloy addition to different base powders can be observed in Fig. 5-left, where the green densities of different powder mixes are summarized (all mixes contain $0.5\%C_{\text{nominal}}$). The compressibility of the base powders decreases as the amount of alloying elements prealloyed increases (Fe > Fe—0.85Mo > Fe—1.8Cr > Fe—3Cr—0.5Mo), and for a certain base powder the green density decreases when increasing the masteralloy content. In order to evaluate the differences between different alloying approaches the green densities are represented in Fig. 5-right as a function of the amount of alloying elements introduced in the steel. For a similar total amount of alloying elements, the masteralloy approach or the «hybrid» (combination of prealloyed powder and masteralloy) provide in all cases green densities significantly higher than those achievable through the fully prealloyed route.

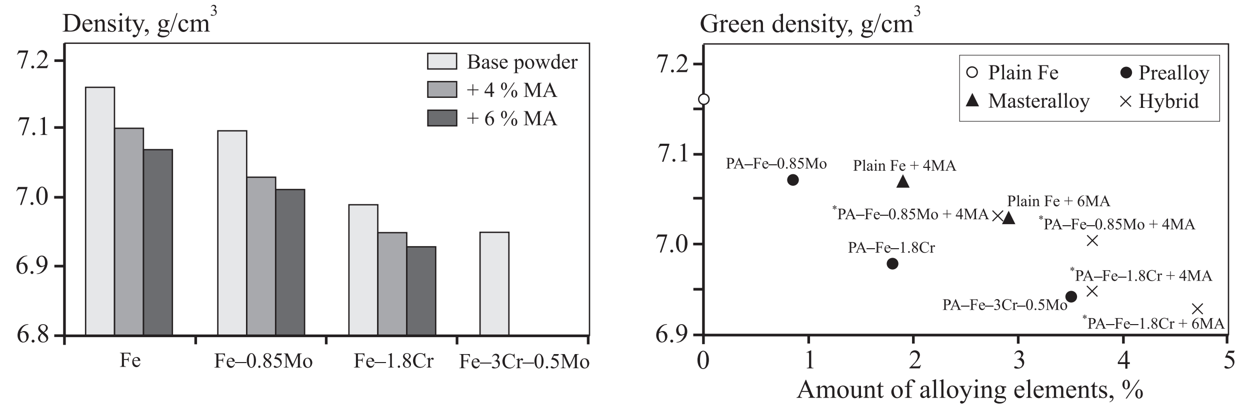
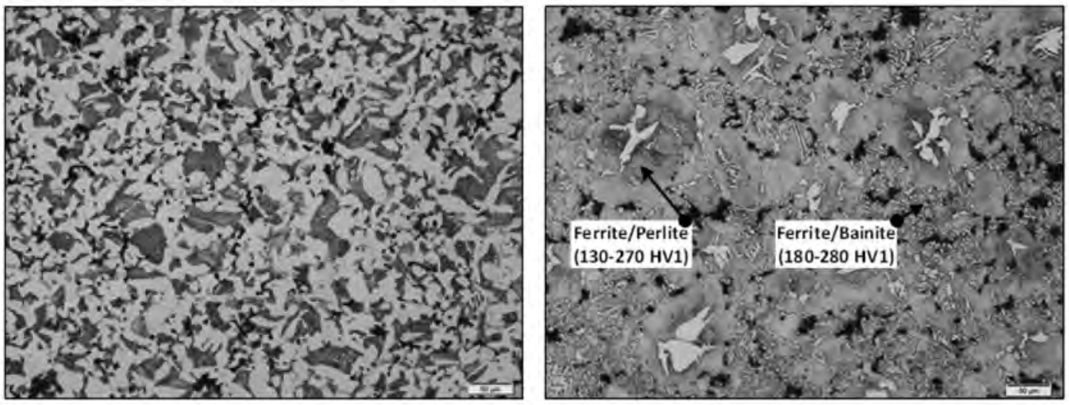


Fig. 5. Green density of steel compacts containing different combinations of base powders and masteralloy additions

Effect of masteralloys on steel hardenability

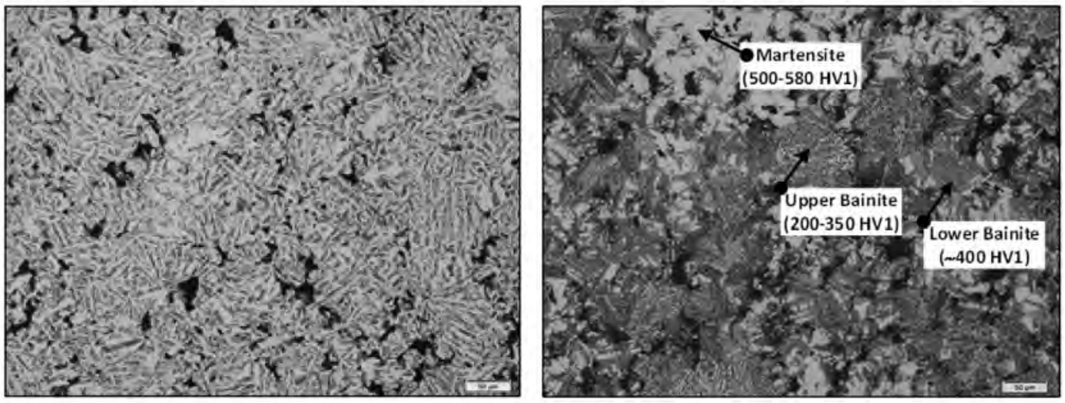
The microstructure of the base powders sintered at 1250 °C — without masteralloy addition — are presented in Fig. 6-left. Microstructures consisting of ferrite/pearlite are obtained both with Fe and Fe—1.8Cr base powders. The amount of pearlite in the latter is higher due to the shifting of the eutectoid to lower carbon contents with the addition of prealloyed Cr. The base powder

(*a*) Fe–0.5C (*b*) Fe–0.5C–4MA



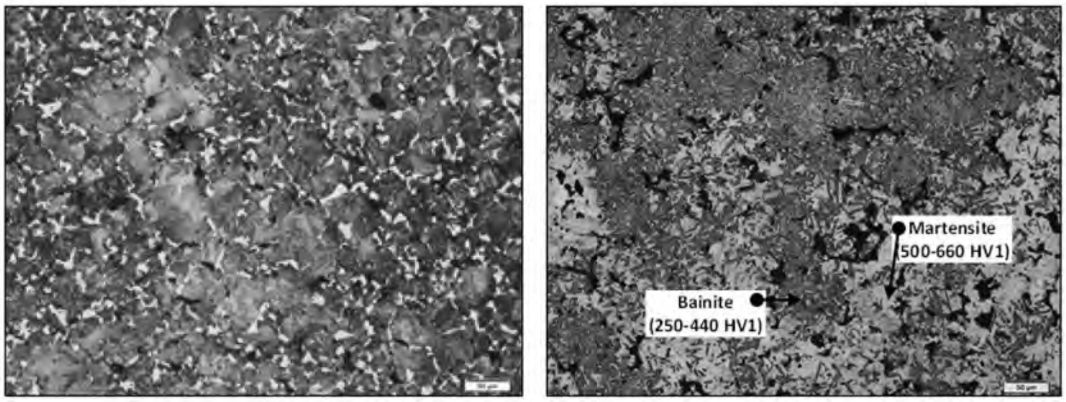
O: 0.01 %, C: 0.32 %, HV10: 128 O: 0.03 %, C: 0.33 %, HV10: 173, **AE: 1,9 %**

(*c*) Fe–0.85 Mo–0.5C (*d*) Fe–0.85Mo–0.5C–4MA



O: 0.01 %, C: 0.35 %, HV10: 156 O: 0.02 %, C: 0.32 %, HV10: 250, **AE: 2,8 %**

(*e*) Fe–1.8Cr–0.5C (*f*) Fe–1.8Cr–0.5C–4MA



O: 0.02 %, C: 0.30 %, HV10: 141 O: 0.03 %, C: 0.33 %, HV10: 310, **AE: 3,7 %**

Fig. 6. Microstructure, oxygen/carbon contents and apparent hardness of steels sintered at 1250 °C, with and without MA additions (cooling rate ~0.75 °C/s)

prealloyed with 0.85 Mo presents bainitic microstructures. None of the prealloyed powder grades presented in Fig. 6-left have sufficient hardenability to form martensite at the cooling rates applied here.

The microstructures of steels containing 4 wt.% additions of MA are presented in Fig. 6-right. Small additions (4 wt.%) of MA to a plain Fe base powder provides bainitic areas surrounding the pearlitic/ferritic microstructures present in the core of the iron base powders. In case of Fe—0.85 prealloyed powders, very significant effects are observed with the addition of 4 % MA, which provides microstructures consisting of small upper bainite cores surrounded by areas of lower bainite and martensite with considerably higher microhardness. Thus, the addition of MA provides an increase of the apparent hardness to 250 HV10 (from 156 HV10 in the Fe—0.85Mo base powder), for similar final (combined) carbon contents (~0.35 % C). But the most significant increase in apparent hardness is observed when using Fe—1.8Cr prealloyed powder. With 4 wt.% additions of MA the microstructure changes from pearlite/ferrite to lower bainite cores surrounded by broad martensitic areas, which give an apparent hardness of ~310 HV10 in the as sintered condition.

Fig. 7 shows a summary of the properties (HV10 vs Impact energy) of different materials processed at 1120 °C and 1250 °C in the as sintered condition. The materials can be divided in two groups depending on the total amount of alloying elements added to the steel (without considering carbon). The group with the lower total amount of alloying elements (<2 wt.%) contains the prealloyed grades Fe—0.85Mo and Fe—1.8Cr, as well as the steels produced by combining plain Fe base powder with 4 wt.% MA. The data highlighted in the box (HST) correspond to the samples sintered at 1250 °C, while the rest of the data corresponds to the sintering runs at 1120 °C. For the group with the lower total amount of alloying elements (<2 wt.%), the masteralloy approach seems to provide better (or at least similar) combinations of properties (HV10 vs Impact energy) than the prealloyed approaches. This holds both for the sintering runs at 1120 °C and at 1250 °C.

The group with the higher total amount of alloying elements (~3÷4 wt.%) shows considerably higher apparent hardness values. This group contains the prealloyed grade Fe—3Cr—0.5Mo, as well as the «hybrid» combinations which consist of prealloyed powders with small contents of alloying elements (Fe—0.85Mo and Fe—1.8Cr) mixed with small additions of masteralloy (4 wt.%). For a similar total amount of alloying elements, the «hybrid» approaches seem to provide the most advantageous combinations of properties at both sintering temperatures. Using the hybrid combinations, apparent hardness values around 250—350 HV10 are obtained in

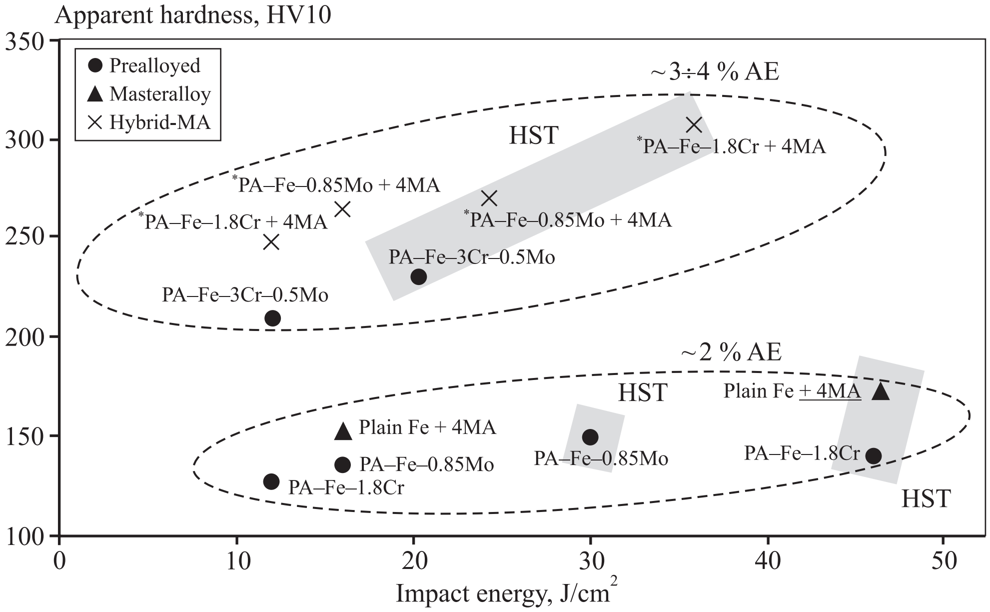


Fig. 7. Apparent hardness vs. Impact energy of steels alloyed through different routes

Plain MA approach: Fe + 4MA, Prealloyed approach: PA–Fe–1,8Cr or PA–Fe–3Cr–0,5Mo, Hybrid approach: PA–Fe–1,8Cr + 4MA and PA–Fe–0,5Mo + 4MA. Samples highlighted in a box and marked as HST were sintered at 1250 °C, the rest of the data correspond to the samples sintered at 1120 °C the as sintered condition for steels with final carbon contents around 0.30—0.35 %.

Effect of sintering temperature on microstructure and properties of steels containing masteralloys

It is well known that high sintering temperatures provide a significant increase in the mechanical performance of low alloy sintered steels, particularly for those containing elements such as Cr, Mn and Si, with a high affinity for oxygen (both in prealloyed and masteralloy approaches). However, such high temperatures are often less attractive for industrial production. In the particular case of masteralloys, the differences in properties can be attributed to various phenomena: enhanced reduction of oxides at high temperature, changes in the morphology of the pores, improved dissolution of masteralloy particles and thus better distribution of alloying elements, etc. In order to study the effect of the sintering temperature on the microstructure and properties of the steel, samples containing Fe—1.8Cr + 0.5C + 4MA were sintered at increasing temperatures in the range between 1120 and 1300 °C. Fig. 8 shows the evolution of the microstructure with temperature. The low magnification images (left column) give an idea of the distribution of the different phases, and the higher magnification images (on the right) show in more detail the phases present. After sintering at 1120 °C the core of the base powder particles present pearlitic microstructures, while the more highly alloyed areas exhibit mainly martensitic (and also some bainitic) areas. A significant amount of less alloyed pearlite areas (darker) are observed when sintering at 1120 °C. By increasing the sintering temperature to 1180 °C, the better distribution of the alloying elements is evidenced by the bainitic cores (instead of pearlitic), and especially by the considerably broader martensitic areas. As the sintering temperature increases, the size and amount of the bainitic areas decreases (due to the enhanced diffusion of alloying elements), and the porosity becomes smaller and more rounded.

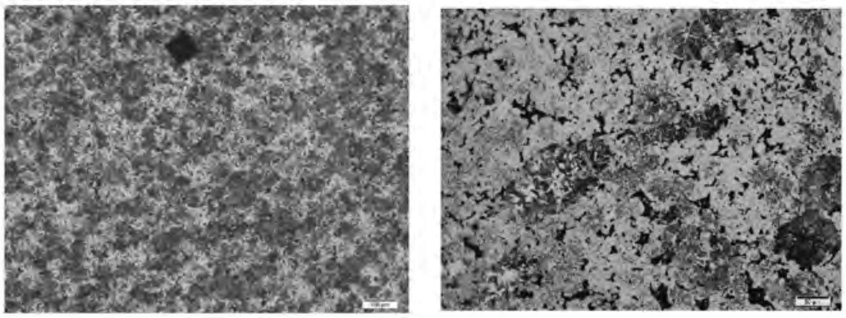
The amount of oxygen after sintering at 1120 °C and 1180 °C is approximately that of the starting powder mix, which suggests that hardly any removal of oxygen from the sample has taken place. Most likely only a transformation of the oxides carried on the starting powders (mainly Fe oxides) into more stable ones (Cr, Mn, Si containing oxides) occurred, as described in [26, 27]. A marked decrease of the oxygen content is observed after sintering at 1220 °C (~0.03 % O at 1220 °C. vs ~0.16 % O at 1120 °C), which indicates that at this temperature a significant reduction of the oxides is achievable under the sintering conditions used. The carbon content decreases at temperatures above 1220 °C, which corresponds to the consumption of carbon required for the reduction of the oxides. However, a significant decarburization is observed when sintering at 1300 °C that cannot be attributed exclusively to the reduction of oxides, but is most likely related to the conditions in the furnace during these runs, decarburization through reaction of C with H_2O to form CO + H_2 generally being promoted by higher temperatures.

Fig. 9 shows a summary of the mechanical properties obtained with steels sintered at different temperatures. Considering the relatively low amount of alloying elements used (~3.7 wt.%), these steels present excellent mechanical properties even at the lowest sintering temperature. For sintering at 1120 °C apparent hardness ~292 HV10 and UTS ~ 896 MPa are combined with an impact energy ~13 J/cm^2 and elongation ~1 %, for steels in the as-sintered condition. These properties are equivalent or even superior to those obtained under similar processing conditions using commercial alternatives based of diffusion alloyed grades which contain almost double the amount of more expensive alloying elements (Cu, Ni, Mo).

By increasing the sintering temperature to 1180 °C a significant improvement in apparent hardness and UTS values is observed, which is in agreement with the harder and more homogeneous microstructures observed in these steels. The better distribution of the alloying elements observed at this temperature is most likely caused by the formation of significant amounts of liquid phase by melting of the MA particles (with a melting range ~1120÷1200 °C). This suggests that a redesign of the MA composition to form a liquid phase at lower temperatures might help to obtain even better properties in sintering runs at 1120 °C. Such improvement in properties is actually observed in apparent hardness and UTS, while elongation and impact energies are very similar at 1120 °C and 1180 °C.

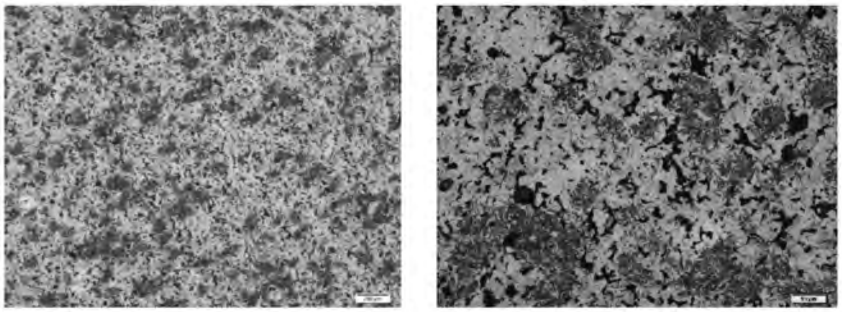
When increasing the sintering temperature to (and above) 1220 °C, UTS and apparent hardness show a slight increase, but the most significant effect on properties is observed in the elongation and impact energy values. Apart from the positive effect of the porosity rounding at high temperatures, the improvement in ductile properties observed when sintering at 1220 °C (and above) is most likely related with the more effective removal of oxides observed at these temperatures.

The very competitive properties observed at low sintering temperatures (1120 °C) are mainly a consequence



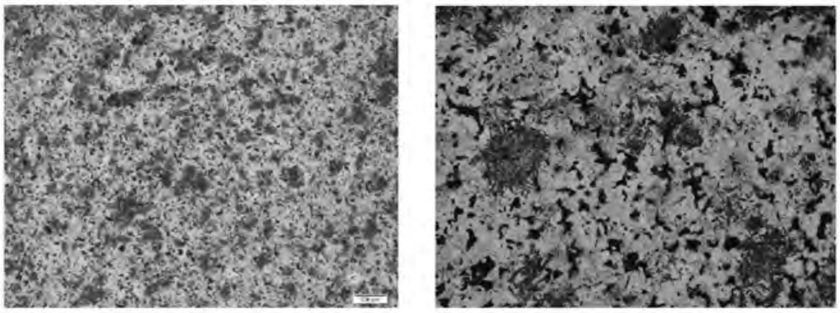
1120 °C

O: 0.161 %, C: 0.497 %, N: 0.05 %, HV10: 292



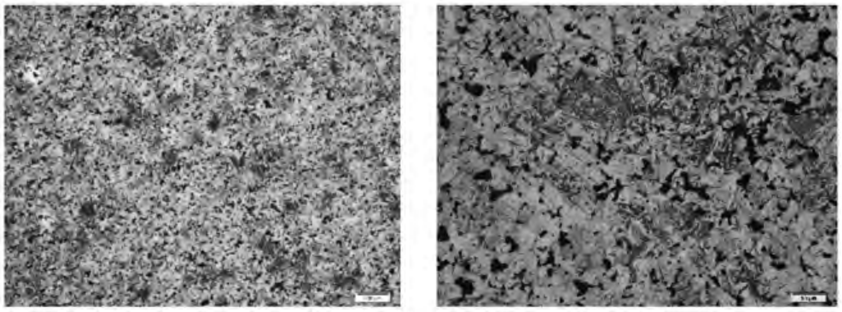
1180 °C

O: 0.153 %, C: 0.492 %, N: 0.05 %, HV10: 338



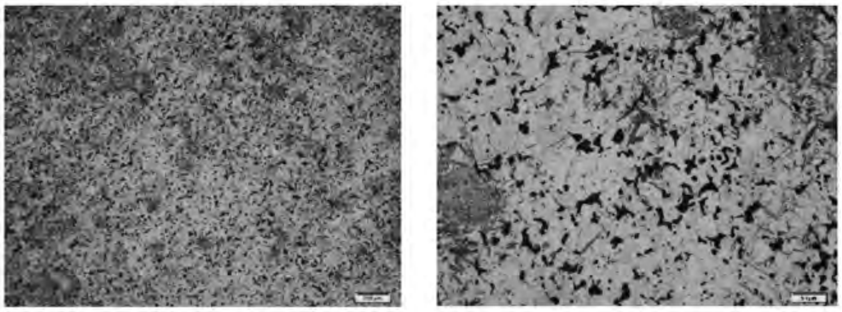
1220 °C

O: 0.033 %, C: 0.43 %, N: 0.05 %, HV10: 351



1250 °C

O: 0.021 %, C: 0.426 %, N: 0.05 %, HV10: 362



1300 °C

O: 0.020 %, C: 0.36 %, N: 0.05 %, HV10: 363

Fig. 8. Microstructure of steels Fe-1.8Cr+0.5C+4MA pressed at 600 MPa and sintered for 30 min in N_2–$5H_2$ at different temperatures (cooling rate ~0.75 °C/s)

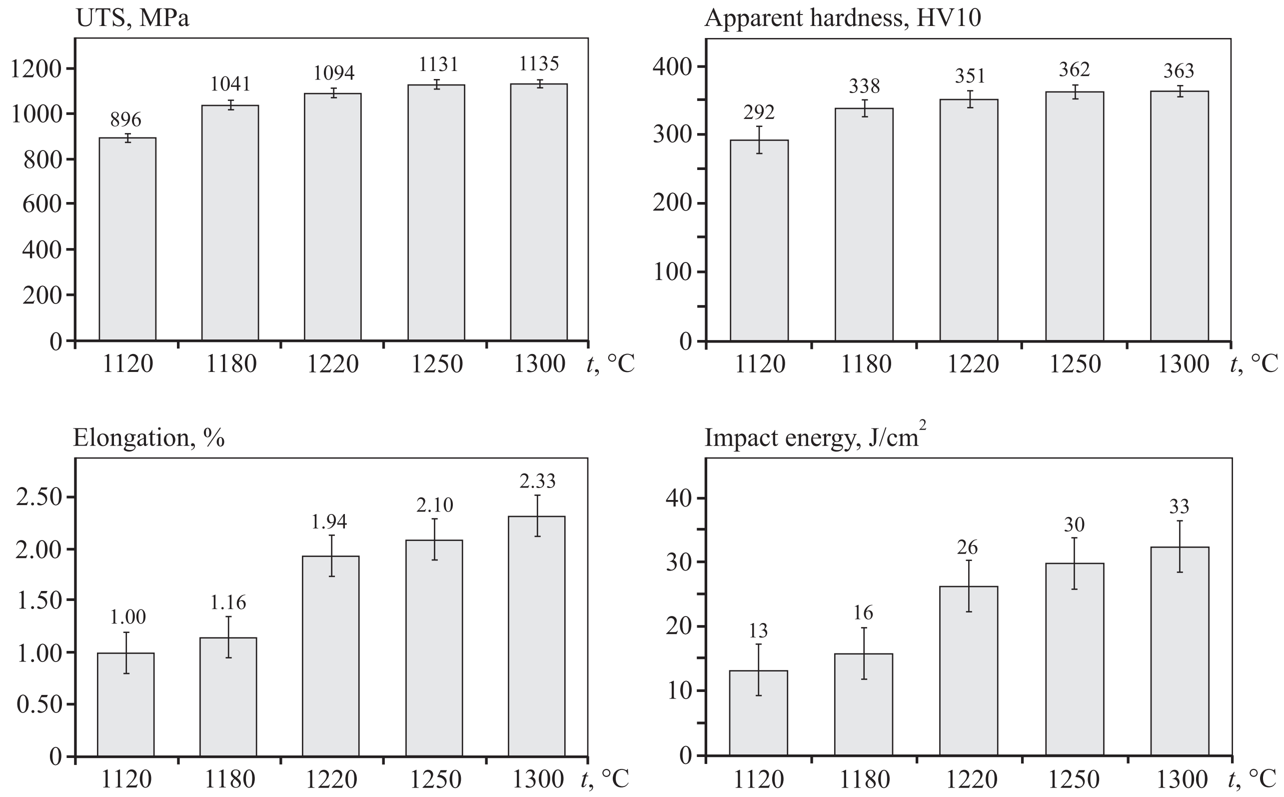


Fig. 9. Mechanical properties at different sintering temperatures

of the very positive effect of the alloying elements used on the hardenability of the material, which allows obtaining high values of hardness and tensile strength. Very reasonable elongations and impact energies are also observed at this temperature regardless of the high oxygen content. This is most likely due to the fact that the oxides still present are not anymore found as an homogeneous layer that covers the base powder particles, but as particulate oxides on the sintering contacts [35—37]. This means that, even if the oxygen content is not reduced when sintering at 1120 °C, the oxides do not inhibit diffusion, allowing the formation of sintering contacts between particles. By increasing the sintering temperature above 1220 °C it is possible to promote the reduction of these more stable oxides, which plays a very important role in improving the quality of the sintering contacts. Thus, both the impact energy and the elongation are significantly improved at this temperature, which shows that the full potential of these materials is only obtained at the high sintering temperatures required for the reduction of the oxides.

Summary and conclusions

The new developments in the study of liquid phase designs and chemical reactions, together with the advances made in atomization processes, open a completely new frame of possibilities for the commercial application of masteralloys.

Particularly the use of Ultra High Pressure Water Atomized (UHPWA) masteralloy powders provides the possibility of significantly increasing the hardenability of commercial steel powders at very low alloying cost and with more flexibility to select the final composition of the steel (as compared with the fully prealloyed approach).

The «hybrid alloying approach» presented in this paper (combination of an Fe—1.8Cr prealloyed base powder with 4 wt.% of an Fe—42Mn—6Si—0.4C masteralloy) can be used to obtain materials with excellent mechanical properties in the as-sintered condition, even when using low sintering temperatures. As-sintered samples processed at 1120 °C achieved apparent hardness ~292 HV10 and UTS ~ 896 MPa combined with impact energies ~13 J/cm^2 and ~1 % elongation.

Increasing the sintering temperature provides better homogenization of the alloying elements. Already sintering at 1180 °C gives microstructures consisting of bainitic cores surrounded by broad martensitic areas. The better homogenization of the alloying elements obtained using only a slightly higher sintering temperature (1180 °C) improves the apparent hardness and UTS values (~338 HV10 and ~1041 MPa respectively), for similar impact energies and elongations: (~16 J/cm^2 and ~1.2 %). Sintering at 1220 °C provides also a significant improvement in elongation and impact energy most likely due to the enhanced reduction of the oxygen content (~0.03 % O at 1220 °C, vs ~0.16 % O at 1120 °C). The oxygen-sensitive alloying elements present both in the base powder (Cr) and in the master alloy (Mn and Si) form stable oxides that require high sintering temperatures to be reduced. For the specific combination of base powder and masteralloy used in this study, the sintering conditions 1220 °C and N_2—$5H_2$ atmosphere seem to be sufficient to ensure a significant reduction of the oxides. This enhances the quality of the sintering contacts, thus providing better impact energy and elongation values (~26 J/cm^2 and 1.94 %) but only slightly higher apparent hardness and UTS (~351 HV10 and ~1094 MPa).

A proper design of the masteralloy composition and its interaction with the base powder could help to obtain materials with high hardness and UTS values even when sintering at 1120 °C (by providing a sufficiently good homogenization of the alloying elements at low temperature). However, the formation of strong sintering contacts requires a proper removal of oxides that, in systems containing elements such as Cr, Mn and Si, can only be achieved at higher temperatures. In this sense, thermoanalytical techniques are a good tool to identify the exact temperature ranges needed for obtaining a significant reduction of oxides for a certain combination of base powder and masteralloy. The full potential of these materials can only be achieved by sintering at a temperature sufficiently high to promote reduction also of the more stable oxides.

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