Paper

Liquid Phases Tailored for Introducing Oxidation-Sensitive Elements through the Master Alloy Route

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ABSTRACT

Introducing alloying elements through Master Alloy (MA) additions provides the unique opportunity of designing their composition to enhance sintering by forming a liquid phase. However, working with liquid phases poses important challenges like maintaining a proper dimensional control and minimizing the effect of secondary porosity on the final performance of the steel.

The critical parameters for designing low melting point compositions are analyzed in this work by combining the use of thermodynamic software tools, wetting angle/infiltration experiments, and advanced thermal analysis techniques. Due to their low ability to dissolve iron, Cu-based liquids present remarkable infiltration properties that provide homogeneous distribution of the alloying elements. Dissolutive liquids, on the other hand, tend to render more heterogeneous microstructures, rapidly solidifying in contact with the matrix. As a consequence of their lower infiltration capacity, dimensional changes upon liquid formation are significantly lowered. When using master alloys with high content in oxidation-sensitive alloying elements, the differences in oxygen affinity cause an oxygen transfer from the surface of the iron base particles to the surface of the master alloys. The change in the surface chemistry modifies the wetting capability of the liquid, and the dimensional stability becomes increasingly sensitive to the processing atmosphere.

KEY WORDS

master alloys, liquid phase sintering, oxygen-sensitive alloying elements, dimensional stability, wetting/infiltration

1 Introduction

The so called “master alloys” emerged in the very early seventies as a vehicle to introduce in low alloyed sintered steels elements with high oxygen affinity. The combination of these elements with others with lower sensitivity for oxygen - such as Fe - reduced the risk of oxidation during the early stages of sintering[1-5].

A master alloy could be defined as a powder with a high concentration of alloying elements that is designed to be mixed with a base iron powder in order to provide the desired final composition of the steel after the sintering process. Compared with the use of fully prealloyed steel grades, the master alloy route presents interesting advantages such as preserving the compressibility of the base powder, and yielding flexibility in the selection of the final composition. But probably one of the most interesting benefits of using master alloys is the fact that their composition can be specifically designed to promote the formation of a liquid phase that enhances the distribution of alloying elements and accelerates the sintering mechanisms.

Several authors have considered the use of master alloys specifically as a means of activating sintering through the formation of a liquid phase with specific characteristics. For instance, Cu-based master alloys provide a liquid with the ability to distribute through the pore network and penetrate the iron grain boundaries, reducing the diffusion distances needed to homogeneously distribute other alloying elements[6-8]. The diffusion of elements like Si is considerably faster than that of Cu, the latter one being mainly used as a mean of having a liquid phase with enhanced penetration capacity that acts as a vehicle to homogenize the distribution of the alloying elements.

Mocarski et al.[9-12] carried out a systematic study to find Mn-based alloying systems with low melting points and narrow melting ranges. The liquid formed dissolved high amounts of iron, which the authors claimed could be used to protect the alloying elements against oxidation. The addition of small amounts of Si or rare earth elements in the composition of the master alloy yielded more

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homogeneous microstructures by improving the wetting behavior of the liquid and eliminating the oxide diffusion barriers (since these elements act as oxygen traps).

Nowadays, one of the most promising developed Mn-master alloys for liquid phase sintering is a gas atomized Fe-Mn-C master alloy with a high carbon content[13-16]. Thermodynamic calculations performed with a software tool allowed to identify the composition Fe-35Mn-4.4C (w.%), which melts at approximately 1077 °C and, due to the limited Mn content, prevents to some extent Mn losses in the surface by evaporation. Although the vapor pressure of Mn is reduced, there is still some sublimation that allows Mn redistribution over the iron base particles Furthermore, the high carbon content is claimed to provide an effective self-protection against oxidation[13-16].

Thus, in the last years, the use of thermodynamic and kinetic software tools has triggered interesting developments in the design of liquid phases, by allowing the identification of low melting point compositions[17-19]. However, further advances in the design of master alloy compositions cannot be limited to the study of low melting point compositions, but should aim to provide tools for predicting – from the early stages of the design- important features of the liquid that affect the properties of the final sintered component[20-22].

This paper shows how the combination of thermodynamic software tools with advanced thermal analysis techniques and macroscopic wetting/infiltration experiments, can help to anticipate from the early stages of the design process critical characteristics of the liquid that affect both the microstructural development and the dimensional stability of the sintered part.

2 Experimental Procedure

A summary of the equipments and the characteristics of the experiments presented in this paper are gathered in Table 1, together with some relevant references in which the experimental procedures are explained with more detail.

The search of compositions with low melting points was carried out using ThermoCalc Software with the databases TFCE5 (for Fe-based compositions)[23] and SSOL4 (for Ni and Cu based compositions)[21,22].

Macroscopic experiments for wetting/infiltration evaluation were performed in a DSAHT furnace (KRÜSS) equipped with an observation window and a video recording system to monitorize the wetting/infiltration processes[20-22]. In these experiments a liquid phase former (an ingot with the composition of the master alloy) is placed on top on an iron substrate and continuously heated up to the sintering temperature to follow the phenomena taking place after the formation of the liquid. The difference between wetting and infiltration experiments is the type of substrate, which is dense for wetting experiments and porous for infiltration tests[20,21,24-26]. Dense substrates consist on either pure iron (Cometal S.A. grade EFP) or wrought steel with 0.5 wt.% C (Standard AISI 1050). Infiltration experiments require porous substrates prepared from water atomized powder (grade ASC100.29 from Höganäs, Sweden) pressed at 600 MPa. The liquid phase formers were either Cu or master alloys with the compositions presented in Table 2, which were prepared as ingots from high purity Fe, Mn, Si, Cu and Ni powders melted in an electric arc furnace under He atmosphere.

Master alloys with the compositions selected after the design were produced in the powder form by gas atomization. The compositions and melting temperatures of the three master alloys selected for this study are presented in Table 2. Master alloys MA1 and MA2 were gas atomized in N_2 by Höganäs AB, and MA3 was produced at Universidad Carlos III by gas atomization in N_2 in a lab scale atomizer from the company Atomizing Systems Ltd (Sheffield, UK).

Sinterability of steels modified with small additions of master alloy particles was studied with advanced thermal analysis techniques. Dilatometry and step sintering experiments were carried out on green samples obtained by pressing (at 600 MPa) mixes of base iron powder (water atomized plain iron grade ASC100.29 from Höganäs Sweden), 0.5 wt.% graphite (grade UF4 from Kropfmühl) and 4 wt.% of either Cu or master alloys MA1, MA2 and MA3. Simultaneous Thermal Analysis (STA) experiments were performed on mixes of loose powders instead of green compacts, and were coupled with Mass Spectrometry (MS) measurements that allow identifying the degassing behavior during

Table 1 Summary of the different experimental techniques, equipment and characteristics of the experiments.

Technique	Equipment and Characteristics of the experiment	Ref
Thermodynamic Calculations	ThermoCalc® software. Databases: TCFE5 for Fe based master alloys, and SSOL4 for Ni and Cu based master alloys.	21-23)
Wetting Experiments	DSAHT furnace (KRÜSS) equipped with an observation window and a recording system. Atmospheres: Ar and N_2-5 %H_2 (Purity 99.9 %). Videos recorded during continuous heating at 5°/min heating rate up to 1200 °C.	20-22, 24-26)
STA: Differential Thermal Analysis and Thermogravimetry	Netzsch STA 449 C Experiments in Ar atmosphere. 1500 °C, Heating/Cooling rate 20°/min	27,28)
Dilatometry	Netzsch 402 C dilatometer Experiments in Ar, H_2 atmosphere. 1300 °C, Heating rate 10°/min	
Mass Spectrometry	Quadrupol mass spectrometer Netzsch QMS 403 Aeölos Coupled by a quartz capillary with STA and dilatometer. Allows the analysis of the gaseous species evolved during the thermal treatment	
Step Sintering Experiments	DT1000 Adamel Lhomargy quenching dilatometer Atmosphere: He, Heating rate 10°/min, Cooling rate ~ 100°/s	21,22,29)

Table 2 Characteristics of the MA compositions used as liquid formers. $T_{sintering}$ represent the expected sintering temperature. $T_{solidus}$ and $T_{liquidus}$ were measured by DTA (in Ar)

MA1	Cu-2Ni-1Si (wt.%), Fraction < 45 µm $T_{solidus}$ = 1073 °C, $T_{liquidus}$ = 1091 °C, $T_{sintering}$ = 1120 °C
MA2	Ni-4Cu-12Si (wt.%), Fraction < 45 µm $T_{solidus}$ = 1084 °C, $T_{liquidus}$ = 1127 °C, $T_{sintering}$ = 1250 °C
MA3	Fe-40Mn-15Si-1C (wt.%), Fraction <45 µm $T_{solidus}$ = 1060 °C, $T_{liquidus}$ = 1072 °C, $T_{sintering}$ = 1250 °C

sintering. The masses registered in these experiments were 12(C), 14(N), 15(CH_3), 16 (CH_4, O), 17(OH), 18(H_2O), 28(CO, N_2), 32(O_2) and 44(CO_2).

Interrupted sintering experiments were carried out in a quenching dilatometer (DT1000 Adamel Lhomargy) with the aim of analyzing the microstructural evolution during the formation of the liquid phase. The samples were held for 2 min at the target temperatures and rapidly cooled in order to freeze any liquid phase formed. After the experiments, the samples were examined by optical microscopy.

3 Results and Discussion

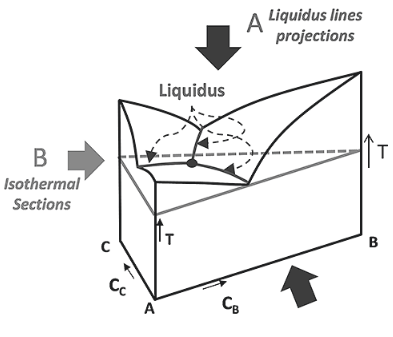
3.1 Design of low melting point compositions using thermodynamic software tools

The first approximation to the design of new alloying compositions can be made with a thermodynamic study of the systems of interest using software tools such as ThermoCalc. This tool offers the possibility to represent multi-component phase diagrams using the information available in commercial databases, such as TCFE for Fe-based systems and SSOL for general alloys.

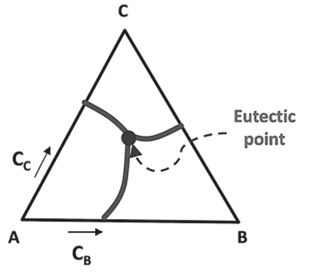
Identification of the minimum melting points in a specific system can be made by finding the eutectic compositions. Considering a ternary diagram such as the one in Fig. 1, the projection of the liquidus lines into Composition-Temperature and Composition-Composition planes show possible eutectic compositions in the confluence of the liquidus lines (Fig. 1-a). Another possibility is to calculate isothermal sections at the temperatures of interest – for instance at the sintering temperature- in order to observe the compositional range for which the liquid phase is stable (Fig. 1-b). The possibility to calculate several isothermal sections allows observing the evolution of the melting ranges for different compositions. Narrow melting ranges simplify the study, especially if considering that dissolutive and diffusion processes can importantly modify the composition of the liquid in contact with the iron particles which might change the melting temperature or cause the solidification of the first liquid formed blocking the access of the liquid to the pores network.

Possible changes in the melting point as a consequence of the inter-diffusion of elements between the master alloy and the other constituents of the powder mix (such as iron base powder and graphite) can be anticipated during the design. For instance Fig. 2-left shows an isothermal section at 1100 °C in the ternary phase diagram of the Fe-Mn-Si system. Compositions within the liquid field indicated in the diagram yield a liquid phase at temperatures below 1100 °C. It is evidenced in the diagram that, while the Si content should be maintained around 10-15 wt.% in order to stay into the liquid region, there is more flexibility regarding the Mn content for which it is enough to have a composition over 20 wt.% Mn, as long as the Si content is kept around 10-15 wt.%. This in turn means that the liquidus temperature of this alloy will be less sensitive to variations in Mn content than in Si content.

In a similar way, the influence of carbon in the liquidus temperature of the master alloy can be predicted from the phase diagrams. The diagram in Fig. 2-right is built up for a starting composition



(a) A: Projection of liquidus lines



(b) B: Isothermal Sections

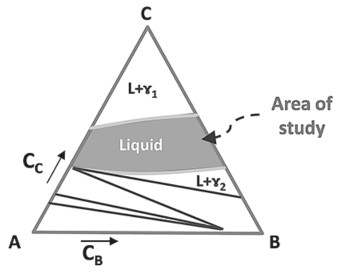


Fig. 1 Methods used for designing low melting point compositions: based on (a) the projection of liquidus lines, or (b) the calculation of several isothermal sections.

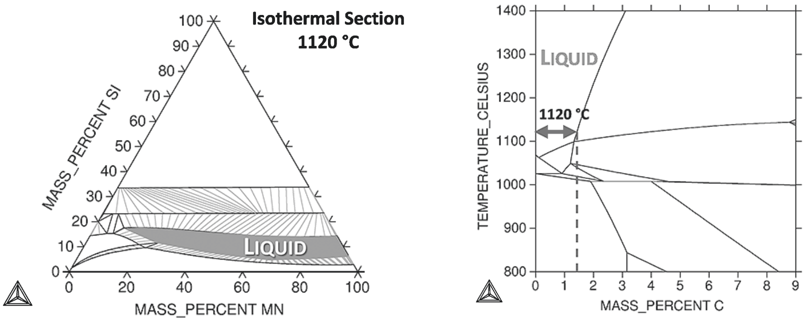


Fig. 2 Phase diagrams (obtained with ThermoCalc software) used to predict the sensitivity of the melting point to changes in the composition.

Fe-40Mn-15Si (wt.%) from which the amount of carbon is increased while keeping the ratio of alloying elements equal to that in the starting composition. According to the phase diagram, the formation of a liquid phase at temperatures below 1120 °C is possible as long as the carbon content in the master alloy is kept below 1.5 wt.%. This condition should be easily fulfilled in low alloyed sintered steels where the typical graphite additions are below 1 wt.%. The information provided by this type of diagrams can therefore be useful to understand how sensitive the melting point of the master alloy is to the diffusion of graphite.

3.2 Solubility features in the liquid-solid system

An important aspect to consider during the design of liquid phases is the solubility condition between the liquid phase and the solid base powder. Solubility will determine whether the liquid phase will have a persistent or transient character. If the liquid-forming constituent is soluble in the solid and its amount contained in the mix is below the solubility limit at the sintering temperature, the liquid will eventually disappear due to diffusion of the elements into the solid particles. In this case the phenomena associated to the liquid phase formation - such as enhancement in the diffusion mechanisms - will be promoted only during the time the liquid phase is present. Moreover, the solubility condition affects as well the tendency of the green compact to shrink or swell upon formation of the liquid. A tendency for swelling is associated to low solubility of the main constituent in the liquid combined with high solubility of the liquid-forming constituent in the solid. On the contrary, high solubility of the main constituent in the liquid and low solubility of the liquid-forming constituent in the solid promotes persistent liquid phases, which renders favorable conditions for particle rearrangement that can cause shrinkage of the green parts and provide high degrees of densification30).

Fig. 3 illustrates the (pseudo)binary phase diagrams of the three master alloys considered (with increasing wt.% Fe) and the phase diagram for Cu-Fe. Two families can clearly be recognized: both Cu and MA1 present lower solubility of Fe in the liquid (highlighted as $S_{S \to L}$ in the graph) and lower solubility of the liquid-forming elements in the solid ($S_{L \to S}$ in the graph) than MA2 and MA3. The solubility values are presented Table 3. Due to their lower ability to dissolve iron, these two systems will be referred as "low dissolutive" systems. MA2 and MA3 which can dissolve up to 46 wt.% and 29 wt.% of Fe at 1300 °C will be considered as "high dissolutive" systems.

Table 3 Solubility condition of the systems at 1300 °C: $S_{S \to L}$ is the solubility of iron in the liquid, $S_{L \to S}$ the solubility of the liquid forming elements in Fe, and R_s the ratio. Calculations are made with ThermoCalc software (TCBIN and SSOL5)

	$S_{S \to L}$	$S_{L \to S}$	R_s
Fe-Cu	8 %	10 %	0.87
Fe-MA1	6 %	9 %	0.68
Fe-MA2	46 %	40 %	1.15
Fe-MA3	29 %	20 %	1.45

Fig. 4 depicts the results from infiltration experiments on porous substrates using as liquid either Cu (low dissolutive) or MA3 (high dissolutive). The graph on the top row shows the evolution of the "normalized drop height" which is calculated by dividing the drop height measured at each instant by the drop height immediately after its formation. The bottom row shows the cross section of the samples after the infiltration experiments. While liquid Cu infiltrates completely the pore network, the dissolution of the iron substrate by liquid MA3 has stopped the infiltration of the liquid, creating also an effect of porosity closure in the vicinity of the infiltrated liquid. The differences in solubility between these two liquids is therefore enough to determine the ability of the liquid phase to penetrate the pores and distribute the alloying elements in the green compact.

3.3 Wetting behavior of the liquids

Another important feature in the design of liquid phases is the ability of the liquid to wet and spread over the surface of the iron base particles. Macroscopic wetting angle measurements have shown how the wetting behavior is affected by the efficient reduction of the oxide layers present on the surface of the metals in contact20,21). Thus, the characteristics of the liquid-solid-atmosphere interaction dictate the wetting behavior of the liquid.

Fig. 5 shows an explicative example of the influence of liquid-solid- atmosphere interaction in the wetting behavior24). An experiment in which no reducing agents are available in the system is considered as the reference: liquid Cu on a solid plain Fe substrate under Ar

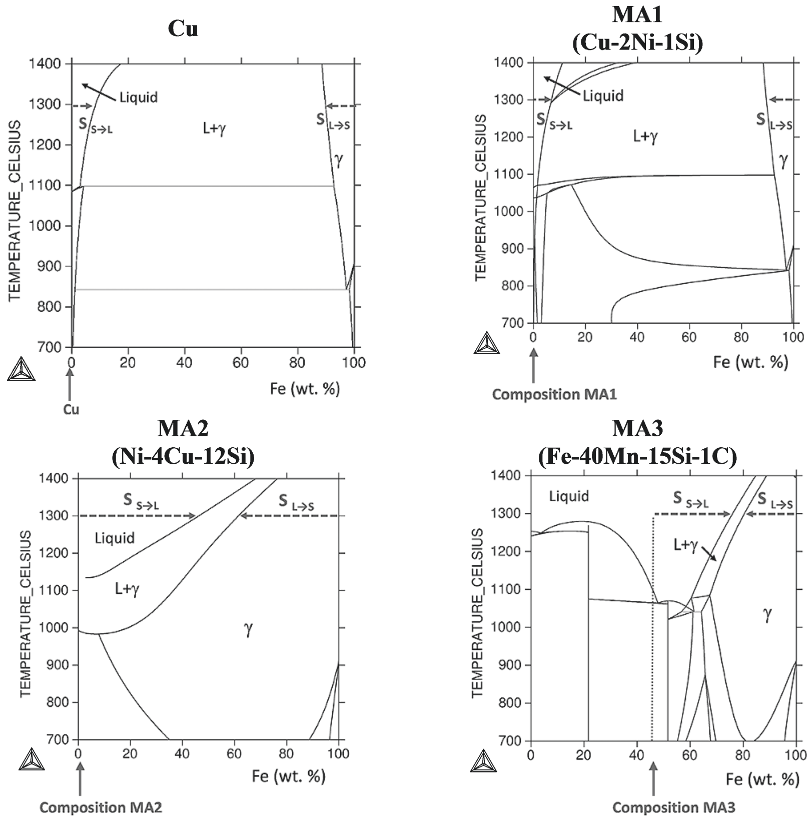


Fig. 3 Phase diagrams representing stable phases as a function of T and wt.% Fe calculated for Cu, MA1, MA2, MA3 using the databases SSOL4 and TCFE5 in ThermoCalc software.

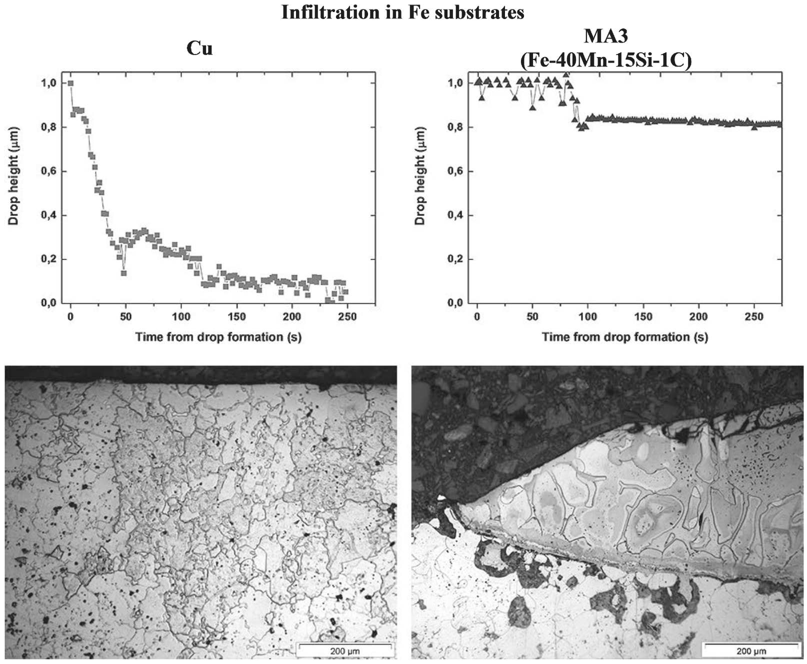


Fig. 4 Evolution of drop height and micrographs of the cross sections of samples after infiltration of liquid phases in porous iron substrates: left-Cu, right-MA3.

atmosphere. As shown in Fig. 5, under the conditions mentioned -indicated as "reference"- liquid Cu is not able to wet the iron substrate (wetting angle above 100°). However, the addition of reducing agents either in the atmosphere -H_2 in Fig. 5 (a)-, or in the substrate composition – Fe-0.5 wt.%C substrate in Fig. 5 (b)- or even in the liquid composition – Cu-2Si liquid in Fig. 5 (c)- radically changes this behavior and decreases the wetting angle to values below 30°. In the latter case, the improvement in the wetting behavior is favored by the presence of small additions Si in the liquid, which acts as an oxygen trap.

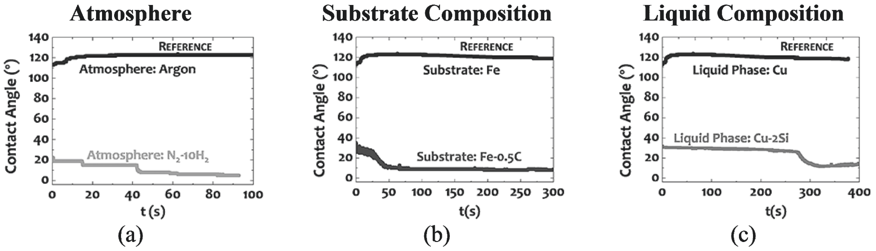
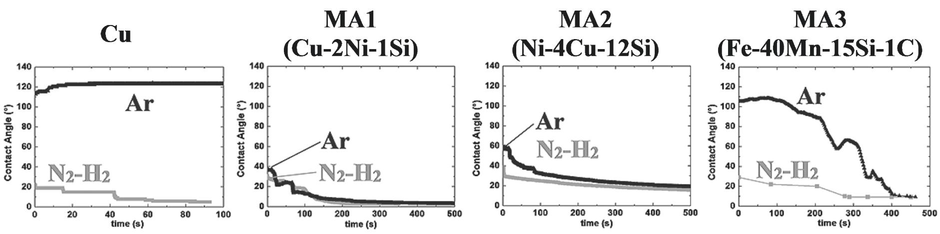


Fig. 5 Macroscopic wetting angle experiments in the Fe-Cu system. Reference experiment: Fe substrate, Cu liquid in Ar atmosphere. Influence of changes in (a) Atmosphere, (b) Substrate composition, (c) Liquid composition.

Wetting on Fe Substrates



Wetting on Fe-C Substrates

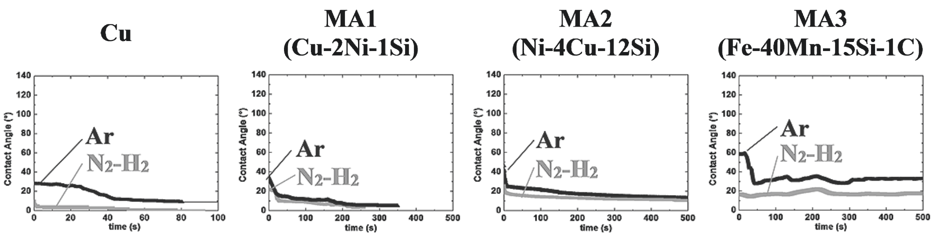


Fig. 6 Wetting experiments on Fe and Fe-0.5C substrates carried out in inert – Ar - and reducing - N_2-10 % H_2-atmospheres using Cu, MA1, MA2 and MA3 as liquid phase formers.

The graphs in Fig. 6 show the evolution of the wetting angle for the different liquid phase formers analyzed in this study (Cu, MA1, MA2 and MA3) on substrates with and without carbon, and using different atmospheres.

The wetting behavior of Cu is considerably improved when using MA1, which is a Cu based master alloy that contains 1 wt.% of Si. In this case, the liquid master alloy wets the surface of a plain Fe substrate even under an inert atmosphere. As indicated before, this behavior can be explained considering that Si can act as an oxygen getter and promote - at least locally - the silicothermic reduction of surface oxides.

Favorable wetting characteristics are observed also in MA2 - with 12 wt.% Si - which presents an initial wetting angle around 60° in the less favorable conditions (Ar atmosphere and plain iron substrates), that evolves to values below 20° when the temperature is increased.

A different scenario is found when a high amount of oxygen sensitive alloying elements are included in the master alloy composition, as is the case with MA3 containing 40 wt.% Mn and 15 wt.% Si. The wetting behavior of this liquid is very sensitive to the presence of reducing agents either in the atmosphere or in the substrate. A non-wetting condition - with wetting angles above 100° - is observed for MA3 after melting when using Fe substrates and Ar atmospheres. In this case, in contrast to Cu, the dissolutive character of the master alloy allows the evolution of the wetting angle to lower values, as a result of the dissolutive processes taking place in the solid-liquid interface[31-33]. Excellent wetting properties are observed however when the experiment is carried out in N_2-10 % H_2 - with initial wetting angles around 20° - and also a significant improvement is observed in Fe-0.5C substrates which provide initial values around 60° in Ar atmospheres. The best conditions for wetting are found when combining carbon containing substrates and reducing atmospheres.

In general, the results of the wetting experiments underline the importance of the presence of reducing agents that assist the removal of the oxide layers covering the metallic surfaces in contact. Such reducing agents efficiently affect the wetting behavior when they are introduced either in the atmosphere or in the composition of the substrate or even as alloying elements in the master alloy that is used as liquid phase formers. In this latter case, however, it is noteworthy that the master alloy with the highest content of oxidation-sensitive alloying elements exhibits - as in the case of Cu - a high sensitivity to the presence of reducing agents either in the atmosphere or in the substrate composition. The combination of substrates containing carbon with reducing atmospheres provide excellent wetting conditions (wetting angles

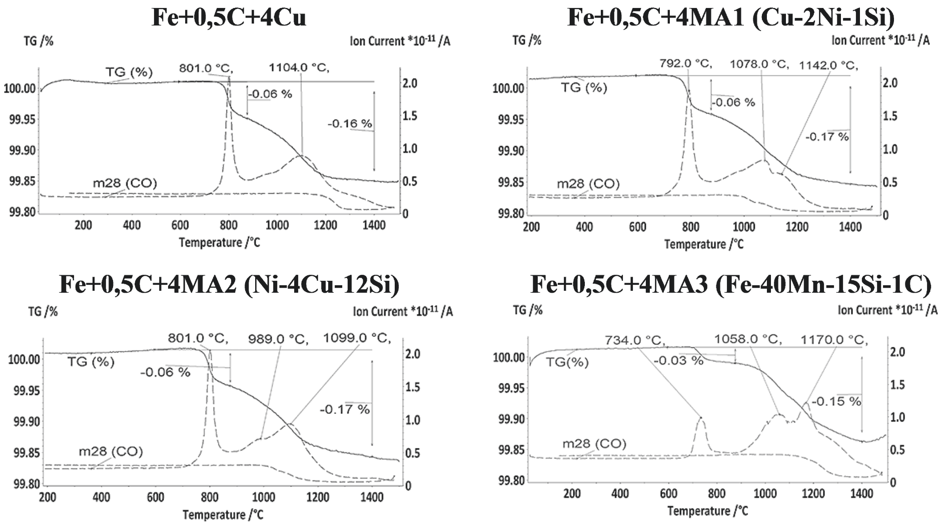


Fig. 7 Thermogravimetry and degassing/reduction curves for experiments in Ar with powder mixes containing Fe + 0.5 wt.% C and 4 wt.% addition of Cu, MA1, MA2 or MA3.

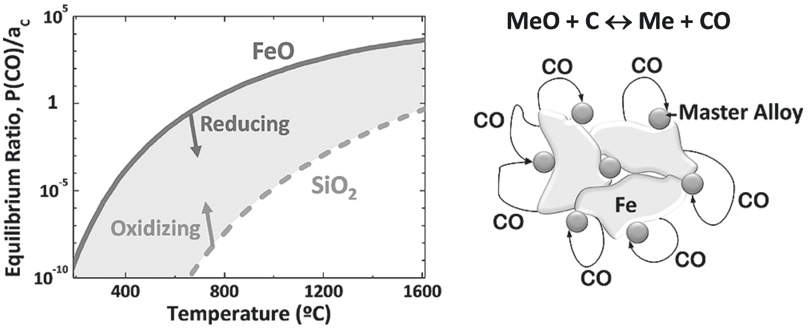


Fig. 8 Schematic of the “internal getter” effect exemplified for the direct carbothermal reaction.

below 20°) for all the liquid phases studied.

3.4 Oxidation/Reduction reactions in steels containing master alloy additions

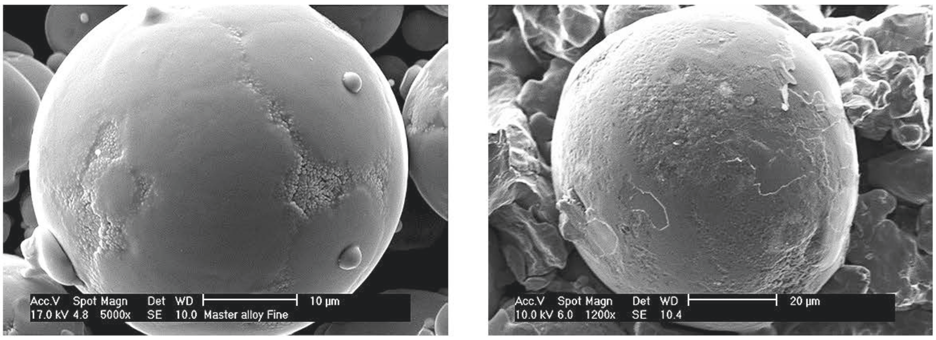
Removal of the oxide layers covering the surfaces of the powder particles is essential to activate the diffusion processes and create strong sintering necks. Additionally, according to the macroscopic wetting experiments previously shown, oxide removal has a significant effect on the wetting behavior of the liquid phases. Therefore, evaluation of the temperature ranges within which the reduction of the different oxides present in the starting powders takes place can provide very important information for designing the optimum sintering conditions.

Fig. 7 shows the thermogravimetry and degassing curves for experiments in Ar atmosphere with powder mixes containing base iron powder, 0.5 wt.% graphite and 4 wt.% master alloy additions. In these experiments, carbothermal reduction processes are identified by a mass loss in the thermogravimetry curve accompanied by a simultaneous peak in m28 (CO).

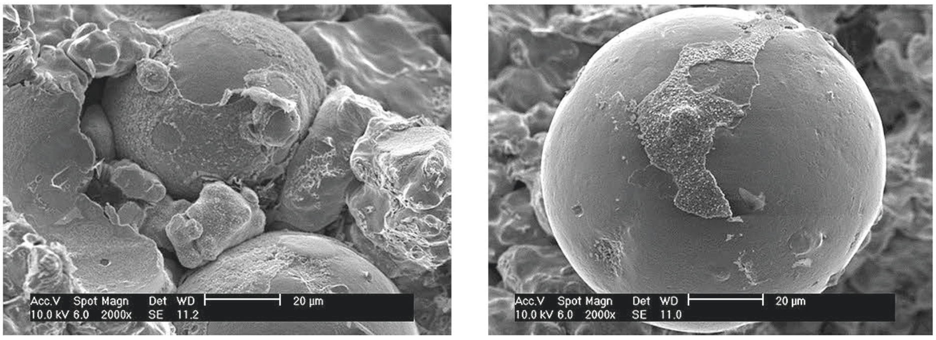
As described in previous studies[34,35)], the reduction of the oxides present in Fe powders takes place in two stages: a peak in m28 at approximately 700-800 °C indicates the reduction of less stable surface iron oxides by carbothermal reactions, and a peak at higher temperatures (~1100 °C) shows the reduction of more stable oxides or internal oxides.

As can be observed in Fig. 7, the evolution of the reduction processes described for Fe powders does not seem to be affected by the addition of Cu or master alloys MA1 and MA2, in which case the reduction stages are very similar to those reported for iron powders[34,35)]. However, only 4 wt.% additions of MA3 cause a significant change in the reduction process. In this latter case, the mass loss associated to the reduction of the surface oxides decreases from 0.06 % to 0.03 %, and the intensity of the m28 peak in this first stage is considerably lowered.

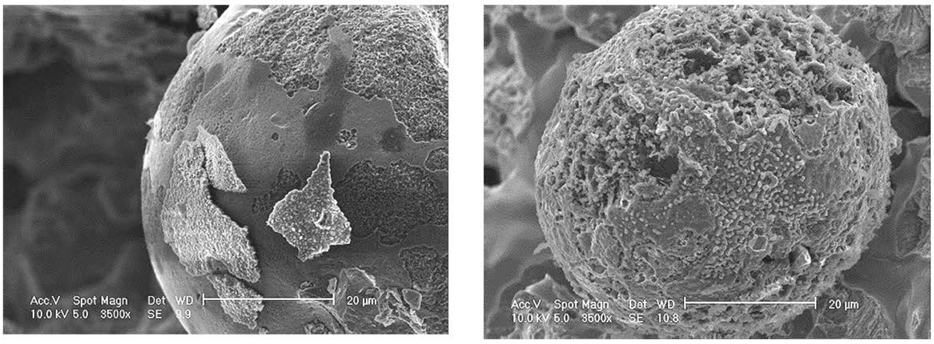
The effect observed with MA3 can be attributed to the fact that a master alloy with a high content of oxidation sensitive elements can act as an “internal getter” agent. At those temperatures where the reduction of iron oxides is possible, the conditions of temperature and P_{CO}, P_{CO2} might be still oxidizing for the oxygen-sensitive alloying elements present in the master alloy -Fig. 8- and due to the increased temperature they are also especially avid for oxygen. This implies that the gaseous products from the reduction of iron oxide layers (CO and CO_2) react with those elements for which the conditions are still oxidizing. The mass loss is then lowered, or even completely avoided, because the oxygen is only transferred



a) As atomized Master Alloy MA3 b) Fe-0.5C-4MA3 600°C



c) Fe-0.5C-4MA3 700°C



d) Fe-0.5C-4MA3 800°C e) Fe-0.5C-4MA3 1000°C

Fig. 9 a) As atomized MA3 powder particles. Fracture surface of Fe-0.5C-4MA3 sintered for 30 min in Ar at b) 600 °C, c) 700 °C, d) 800 °C, e) 1000 °C.

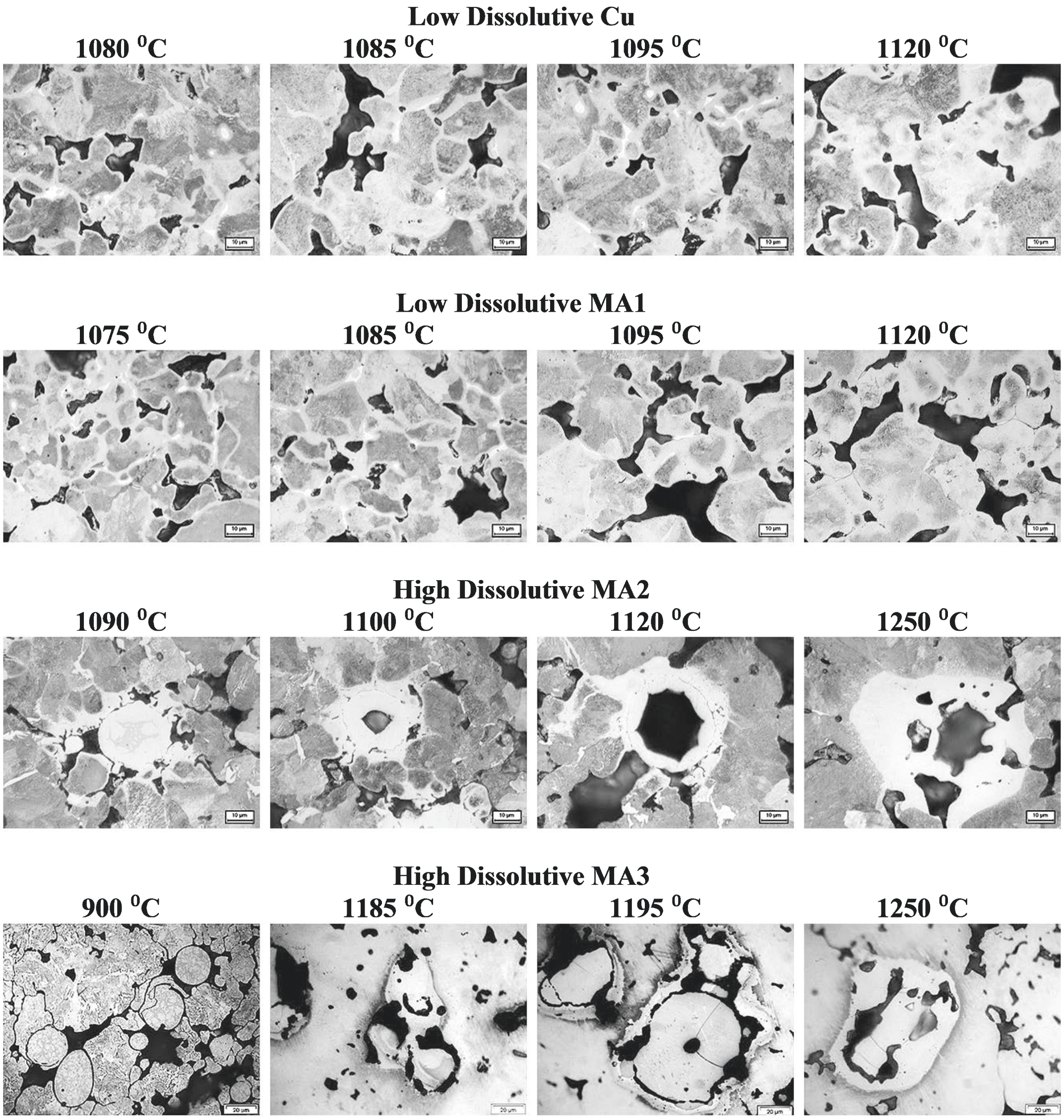
from the surface of the iron base powders to the oxidation sensitive elements present at the surface of the master alloy particles.

Microstructural evidences of the consequences of the internal gettering effect are clearly observed in Fig. 9 which shows the progressive formation of an oxide scale on the surface of the master alloy particles at temperatures between 600 and 800 °C, as a consequence of the oxygen transference from the base iron particles through the gaseous species[27,36-38]. The adherence of such oxide layer seems to be poor, as it was peeled off when breaking the specimens. Incipient melting of the master alloy particles at 1000 °C causes dissolution of this oxide layer on the liquid. As suggested by the macroscopic wetting experiments -shown before- it might be expected that the presence of an oxide on the solid-liquid interface would have a detrimental effect on wetting and spreading of the liquid at least during the first stages after melting.

To reduce the intensity of this internal getter effect, the reduction of Fe oxides should take place at temperatures as low as possible, at which the reactivity of Si and Mn present in the master alloy is still low. The use of H_2 containing atmospheres allows the reduction of iron oxide layers from the base powders at temperatures around 400 °C[35] at which the oxidation sensitive elements are still not so avid for oxygen. This can minimize the oxygen transference phenomena at least in the areas of the green compact where the atmosphere has good accessibility[27]. Reducing the risk of forming oxide layers on the surface of the master alloy particles can improve the wetting characteristics of the liquid upon its formation.

3.5 Microstructural evolution

The solubility condition between liquid and solid phases and the wetting properties of the liquid affect the microstructural evolution during sintering. Microstructural evolution of steels containing master alloy additions was observed by performing step sintering experiments at different stages of the heating process (Fig. 10).



Low Dissolutive Cu

1080 ^{0}C 1085 ^{0}C 1095 ^{0}C 1120 ^{0}C

Low Dissolutive MA1

1075 ^{0}C 1085 ^{0}C 1095 ^{0}C 1120 ^{0}C

High Dissolutive MA2

1090 ^{0}C 1100 ^{0}C 1120 ^{0}C 1250 ^{0}C

High Dissolutive MA3

900 ^{0}C 1185 ^{0}C 1195 ^{0}C 1250 ^{0}C

Fig. 10 Microstructure evolution in steels containing Fe + 0.5 wt.% C with 4 wt.% addition of Cu, MA1, MA2 or MA3. Experiments in static He atmosphere.

Clear differences are observed between non-dissolutive liquids - Cu and MA1 -, and dissolutive master alloys MA2 and MA3. Non dissolutive Cu and MA1 infiltrate and distribute through the pore network immediately after melting. An excellent distribution of the liquid through the green compact promotes the development of homogeneous final microstructures. In this case, the particle size of the master alloy powder used should mainly affect the size of the secondary porosity in the final microstructure, as homogenization of the microstructure is assisted by the good infiltration capacity of these liquids.

On the other hand, with liquids MA2 and MA3 dissolution of the surrounding Fe base particles changes the composition of the liquid causing an increase in the solidus temperature that eventually leads to solidification and thus blocks the access to the interconnected porosity. This is a well-known effect, very welcome for liquids used as reactive fillers[39,40]. The alloying elements remain concentrated in the vicinity of the places where the original master alloy particles were located. Dissolutive liquids have therefore a tendency to provide heterogeneous microstructures unless the particle size of the master alloy is small enough, and/or the sintering temperature/time is high enough to provide homogenization of the alloying elements by solid state diffusion after the liquid phase has been consumed. The final microstructures obtained in these steels - and therefore the expected mechanical properties - should be more sensitive to the particle size of the master alloy powders, and to the proper distribution of the alloying particles within the mix. Studies on steels containing fine Mo elemental powders have shown that the use of fine alloying powders does not ensure homogenization of the microstructure by solid state sintering only, which then renders the use of fine powders somewhat ineffective. However, formation of a transient liquid phase by sintering above the critical temperature - 1230 °C - strongly affected homogenization of Mo in the steel[41]. This, in turn means that even if the infiltration capacity of these liquids is lower than that of Cu, they can still be advantageously used for improving the homogenization of the microstructure, if the particle size used is fine enough (while only using fine alloying particles - without liquid formation - does not ensure correct homogenization).

It is noteworthy how the microstructures of the steels containing MA3 heated at 1185 °C - first stages after melting - show remains of liquid phase which tend to be locally concentrated on specific areas of the pore surface. After further heating to 1195 °C, the liquid seems to be better distributed over the surface of the pore, most likely because spreading of the liquid has been favored by the dissolutive processes. However, the liquid formed with MA2 seems to be well distributed on the surface of the pore already in the first stages after melting at 1100 °C. Such differences in the distribution of the liquid present in the secondary pores right after melting might be a consequence of the different conditions in the surface of the master alloy particles upon melting. As it was shown in Fig. 9, the internal getter effect causes the formation of an oxide layer on the surface of MA3 particles. Presence of such oxides in the solid-liquid interface - or even partial dissolution of the oxides in the liquid- might have a detrimental effect on its wetting capabilities at the early stages after liquid formation.

3.6 Dimensional stability

In order to investigate how the characteristics of the liquid phases affect the dimensional stability during sintering, dilatometry studies were carried out in inert – Ar- and reducing - pure H_2-atmospheres, using green compacts with a composition Fe-0.5C-4MA (wt.%). Fig. 11-a, shows the full dilatometric runs for the experiments in Ar, and Fig. 11-b presents the derivative of these dilatometry curves.

Dilatometry curves obtained when sintering steels containing master alloys which form transient liquid phases -such as the ones described in this paper- typically feature a swelling phenomenon upon liquid formation. The ability to compensate this swelling phenomenon with the shrinkage obtained during isothermal holding will determine the final dimensional behavior as well as the final density.

The differences in the magnitude of such swelling phenomena are visible in the heating stage of the dilatometry curve (Fig. 11-a), and are more clearly evaluated by studying the intensity of the peaks in the derivative curve (Fig. 11-b). Besides, in order to quantify the magnitude of such swelling, the dimensional change has been summed up for a temperature range - between 950 and 1370 °C- within which all the master alloy particles melt (Fig. 12).

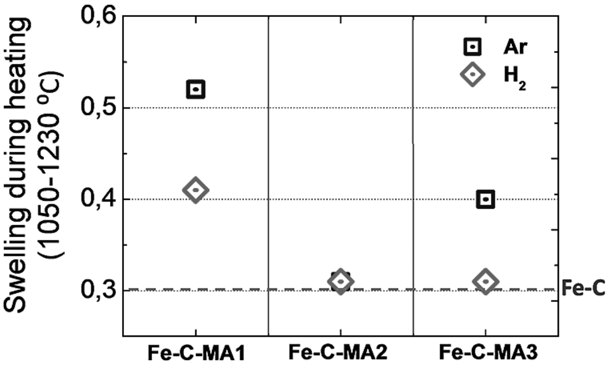
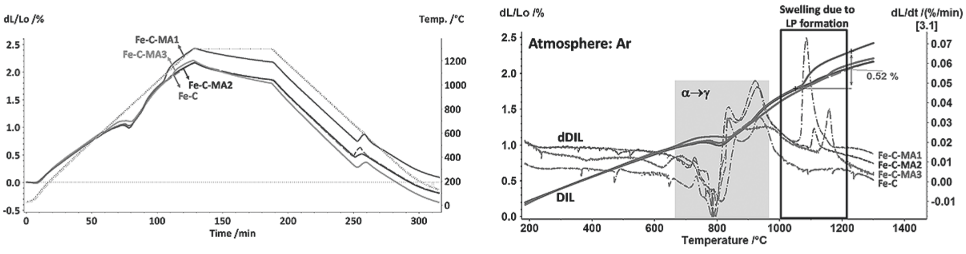


Fig. 12 Magnitude of swelling in the temperature range of liquid formation (1050-1230) Calculated from the dilatometry curves obtained in Ar and H_2 atmospheres.

The most evident feature observed in these experiments is the effect of the dissolutive capacity of the liquids. Non-dissolutive (infiltrating) liquids - MA1 - cause an intense swelling upon formation of the liquid phase (see Fig. 11). This is a consequence of the excellent penetration through the pore system and the distribution of the liquid over the surfaces of the iron base particles and inside the iron grain boundaries. The presence of reducing agents in the atmosphere – which help to reduce the oxides present on the surface when the liquid is formed-decrease considerably the magnitude of swelling (see results for MA1 in Fig. 12).

The swelling effect is lowered in a great extent when using dissolutive (non infiltrating) liquids - MA2 and MA3 - because the liquid phase tends to remain locally concentrated inside the secondary pores, and therefore its influence in the dimensional behavior is decreased (of course at the expense of microstructural homogeneity).

Even though dissolutive master alloys present a considerably lower tendency for swelling, MA3 causes a higher degree of swelling than MA2. Besides, the type of atmosphere (Ar or H_2) is also relevant for the reduction of swelling in MA3-steels (see results for MA3 in Fig. 12). A possible explanation for the sensitivity of the swelling condition to the atmosphere in case of steels containing MA3 can be a consequence of the internal gettering effect described during the study of the reduction/ oxidation phenomena. The internal gettering effect observed when sintering in Ar causes the formation of an oxide layer on the



(a) (b)

Fig. 11 Dilatometry curve (a) and derivative of the dilatometry curve in the heating stage (b) for steels containing MA1, MA2 and MA3 sintered in Ar atmosphere.

surface of the master alloy particles. Once the master alloy particles melt, the presence of such oxide in the liquid-solid interface can have an effect in inhibiting spreading and wetting of the liquid (as confirmed by macroscopic wetting experiments). Thus, reduction of the oxides present in the different surfaces in contact can cause differences in the wetting behavior of the liquid and this can affect the dimensional behavior upon formation of the liquid. This effect seems to be particularly relevant for liquids with a high infiltration capacity (MA1), as well as for liquid formers containing high amounts of oxidation-sensitive elements (MA3). In the latter one the main reason would be the risk of forming oxides on the surface of the master alloy particles, as a consequence of the internal gettering effect.

It is impossible to directly extrapolate the influence of the reducing agents observed in macroscopic wetting experiments to the conditions in a green compact. Especially in the case of the atmosphere, it should be considered that in a green compact the atmosphere has only limited access to the internal porosity, and a microclimate is created inside the closed pores. Carbon is therefore an essential additive, on one hand because it can promote the reduction by carbothermal reactions even inside the microclimate created inside the isolated pores. And on the other hand because reduction of more stable oxides - for which higher temperatures are needed - will always be assisted by carbon, which is the most effective reducing agent at higher temperatures.

4 Conclusions

Thermodynamic modeling software tools, macroscopic wetting angle/infiltration experiments and thermal analysis techniques have been combined to assess the design of master alloys for liquid phase sintering. The design methodology proposed considers not only the melting point of the master alloy, but also the consequences of its interaction with the other elements that will be present during sintering: base iron powder, graphite and sintering atmosphere. Such interactions determine dissolutive processes, and affect the wetting behavior of the liquid especially as a consequence of the modifications in the surface chemistry of the powder particles. All these features will have a significant influence on dimensional behavior and microstructural development and therefore it is interesting to consider them already from the early stages of the design.

The study of three different master alloy systems presented in this paper allow drawing the following conclusions:

- Non-dissolutive or low dissolutive liquids (liquid phases which dissolves only small amounts of iron) present a high ability to infiltrate and distribute through the iron pore skeleton, giving an optimum distribution of the alloying elements and very homogeneous microstructures. The excellent infiltration ability of these liquids causes a significant swelling effect upon liquid formation which is sensitive to those parameters that affect the wetting behavior of the liquid, such as the sintering atmosphere or the presence of carbon.
- Liquids with a highly dissolutive behavior tend to remain locally concentrated around the location of the original master alloy particles. Dissolution of the surrounding iron base particles decreases its ability to distribute through the pores, which lead to heterogeneous microstructures. In this case, the final properties could be expected to be more sensitive to the use of fine and well dispersed master alloy powders in the mix. In contrast to low dissolutive (infiltrating) liquids, dissolutive master alloys provide significantly lower dimensional changes upon formation of the liquid phase. Dissolutive master alloys might as well be very suitable for brazing applications where the interconnected porosity may be a problem since the capillary forces in the pores tend to pull brazes away from the joint interface.
- Special attention should be paid when using master alloys with a high content in oxidation-sensitive alloying elements. Despite the dissolutive behavior of MA3, the dimensional stability in Fe-C-MA3 steels is sensitive to the atmosphere. With this type of master alloys, the differences in chemical activity between base iron powders and master alloy powders can cause an oxygen transfer from the surface of the iron base particles to the surface of the master alloys. The change in the surface chemistry of the master alloy particles can modify the behavior of the liquid - in particular its wetting capability - which in turn can affect the sensitivity of the dimensional stability to the processing atmosphere.

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