Modification of Cr-Mo low alloyed steels by addition of Mn via mechanical milling

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Manufacturing and processing

ABSTRACT

Purpose: The PM industry is in continuous development due to the necessity to increase its potential and competitiveness. This fact and the demand for substituting certain alloying elements used so far, require the addition of new alloying elements and new processes leading to and optimization of costs, strength and tolerances. A different method for introducing Mn into the alloying system is proposed in the present work. Mechanically-blending and mechanically alloying Mn containing master alloys are generated and based on three different steels grades, ASC100.29 (plain iron), Astaloy CrL and Astaloy Mo (pre-alloyed systems).

Design/methodology/approach: To profit Mn sublimation effects, small Mn particles, in order to increase the specific surface available to sublimate, must be homogenously added. Different milling times are considered in order to attain the desired master alloys containing 50% of Mn which is diluted in each base powder by normal mixing. New alloying systems were then pressed to a green density of 7.1 g/cm^3 and sintered at 1120 ºC in 90N$_2$-10H$_2$ atmosphere. STA showed Mn diffusion during sintering and a densification enhancement.

Findings: The sublimation of Mn during sintering provides some specific phenomena which facilitate the sintering of alloying elements with high oxygen affinity. The resulting mechanical properties and the microstructures must be discussed considering the high energy stored in the master alloy which favours the mass transport mechanism during sintering.

Research limitations/implications: Research is being continued with the optimisation of the mechanical properties and the application of heat treatments taking the profit of the increase of the hardenability induced by Mn.

Originality/value: Mn seems a viable substitute for alloy elements used so far in PM, such as Ni and Mo. Following European regulations Ni cannot be used in its elemental powder form because of its effects on health and Mo has increased its price in the last years.

Keywords: Powder metallurgy; Mn addition; Master alloys

1. Introduction

The processing of PM materials demands a high control of the oxidation during the sintering process, because of its critical effects on final properties. This fact, along with the necessity for substituting alloying elements used so far, i.e. Ni and Mo, makes Mn a promising new candidate. Mn has been shown to reduce oxide content during the sintering process by the so-called "Mn self-cleaning effect" [1, 2]. The high vapour pressure of Mn at conventional sintering temperatures for Fe alloys, results in the sublimation of Mn, therefore enables sintering under atmospheres of standard purity, enhancing the continuity of the process and hence its industrialisation.

Since the formation of Mn vapours is a surface phenomenon, the method used to introduce this alloy element is critical. The addition of Mn by elemental blending can result in segregation and an excessive Mn loss. On the other hand, by pre-alloyed systems, Mn activity decreases, as the sublimation. In this work it is proposed an alternative adding method; Mn was added by a master alloy generated by a high energy milling process under an inert atmosphere. The milling process was monitored and two different milling times came out. The purpose of having two different master alloys is to modify the state of Mn in the

latter and hence, make a distinction between solid state or gas-state diffusion and its effect on sintered steels [3, 4].

By the addition of milled powder, in addition to the beneficial effect that Mn sublimation has, the sinterability of the final system is improved. Milled particles have a big concentration of lattice defects; for that reason the mass transport mechanisms are enhanced during the sintering process, resulting in a more effective cohesion between particles. At short milling time, the combination of the addition of "free" Mn which is available for sublimation and deformed particles can be studied, adjusting the alloying system to a sublimation-condensation process provided by the gas-state diffusion. Final particles have homogeneously scattered the Mn into the Fe base powders. On the other hand, longer milling times provide an apparently pre-alloyed powder in which sublimation phenomena are reduced. The remaining Mn as solid solution after sintering strengthens the material, resulting in an important improvement of the mechanical properties [5, 6].

Three different systems are considered ASC100.29, AstaloyCrL or AstaloyMo and master alloys of these were obtained by mechanically alloying with Mn powders in a 1:1 ratio under a static Ar atmosphere [7].

2. Experimental procedure

All the Fe-based initial powders were water atomised and their composition is given in Table 1 Mn powders were obtained via electrolysis with a purity of 99%. The milling process was performed in planetary ball mill at 400 rpm in 15 minutes steps, in order to avoid overheating of the vessel and to refill the process atmosphere. The mill vessel was AISI 316 and the balls of AISI 420. First a thorough study of the milling process was performed. Samples were taken every 15 minutes in order to determine the oxygen content and alloying grade evolution with milling time. The oxygen content was measured with a LECO analyser and the alloying grade was determined via scanning electron microscopy (SEM) and XRD.

In order to prove the improvement on sinterability by the addition of the master alloys into the systems, and the possible modifications of the transition temperatures of steels, several dilatometric analysis of the milled powder were done. These experiments were done in a pushrod 402E Netzsch dilatometer, the heating and cooling rates were 10K/min up to 1275°C with a holding time of 60 min in $90N_2$-$10H_2$ atmosphere.

Once the master alloys were characterised, they were mixed in every case with the corresponding Fe-based powder in order to reach a final Mn content of 1%, thus just 2% of master alloy powder was added. Also 0.8% of amide-wax as lubricant and 0.6% C were added in every case. Subsequently the alloys were pressed to a green density of 7.1 g/cm^3 and then sintered at 1120 °C under $90N_2$-$10H_2$ atmosphere in a belt furnace, with a cooling rate of 0.8°C/s. Spring-back after pressing and dimensional change after sintering was studied in every system.

A metallographic study of the sintered specimens was done with Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) using two different etching agents; Picral and Picral:Na_2SO_5 (1% in distilled water) [8]. Mechanical characterization consisted of the study of the tensile and impact properties as well as the hardness.

Table 1.
Chemical composition in wt.% of initial Fe-based powders (supplied by Höganäs AB)

	Mo	Cr	Mn	Fe
ASC100.29	-	-	-	bal
Astaloy Mo	1.5	-	-	bal
Astaloy CrL	0.2	1.2	0.15	bal

3. Results

3.1. Master alloy characterisation

Since during the milling process a great amount of energy is involved, the temperature of the vessel and therefore that of the powder increases favouring the mass transport processes and oxidation of the surface. Besides, the milling process is generating more surface area which contributes to increase the exposed surface to the oxidative environment. In Fig. 1 is shown the evolution of the oxygen content with milling time. Two different behaviours are seen for the pre-alloyed base powders (Astaloy CrL and Astaloy Mo) [9] and for the plain iron system (ASC100.29) In the case of Astaloy CrL and Astaloy Mo two different stages can be clearly separated. First, the oxygen content follows an increasing tendency which is associated with the plastic deformation processes and the welding of these particles. These phenomena result in increasing the specific area. After 180 minutes of milling the second stage started. The oxygen content decreases until similar values in both systems. This change of the tendency is associated with welding and fracture phenomena with comminution of the particles. Besides, after long milling time, particles are highly activated because of the increase of lattic defects and temperature which could result in the sublimation of the remaining Mn. Sublimated Mn can then react with residual H_2O as proposed by [10] producing H_2 which can reduce the oxide layer previously formed as shown in (1) and (2). In the case of the system ASC100.29 the evolution is different because of the different strength of the powder, which takes to longer milling times the deformation and welding phenomena.

$$Mn(g) + H_2O \leftrightarrow MnO + H_2 \qquad (1)$$
$$MO + H_2 \leftrightarrow M + H_2O \qquad (2)$$

The alloying grade evolution was studied by XRD patterns performed during the whole milling process. As it is seen in Fig. 2 increasing the milling time Mn gets into the Fe base lattice until being
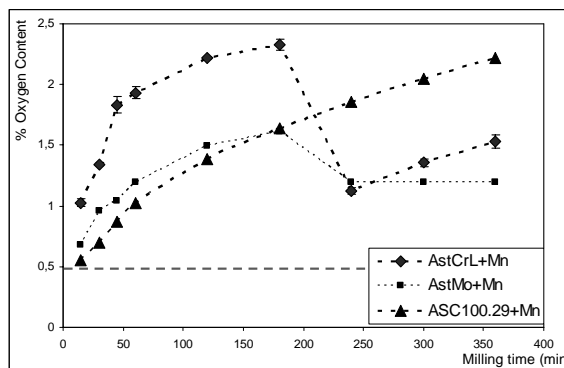

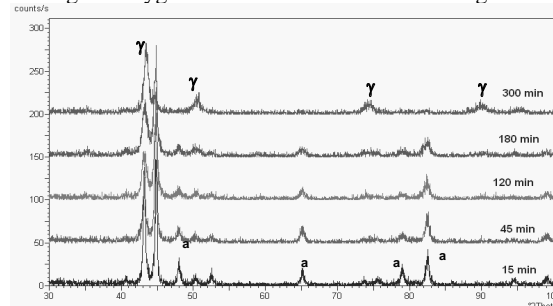Fig. 1. Oxygen content evolution with milling time

Fig. 2. XRD patterns of the alloying grade evolution of system Astaloy Mo
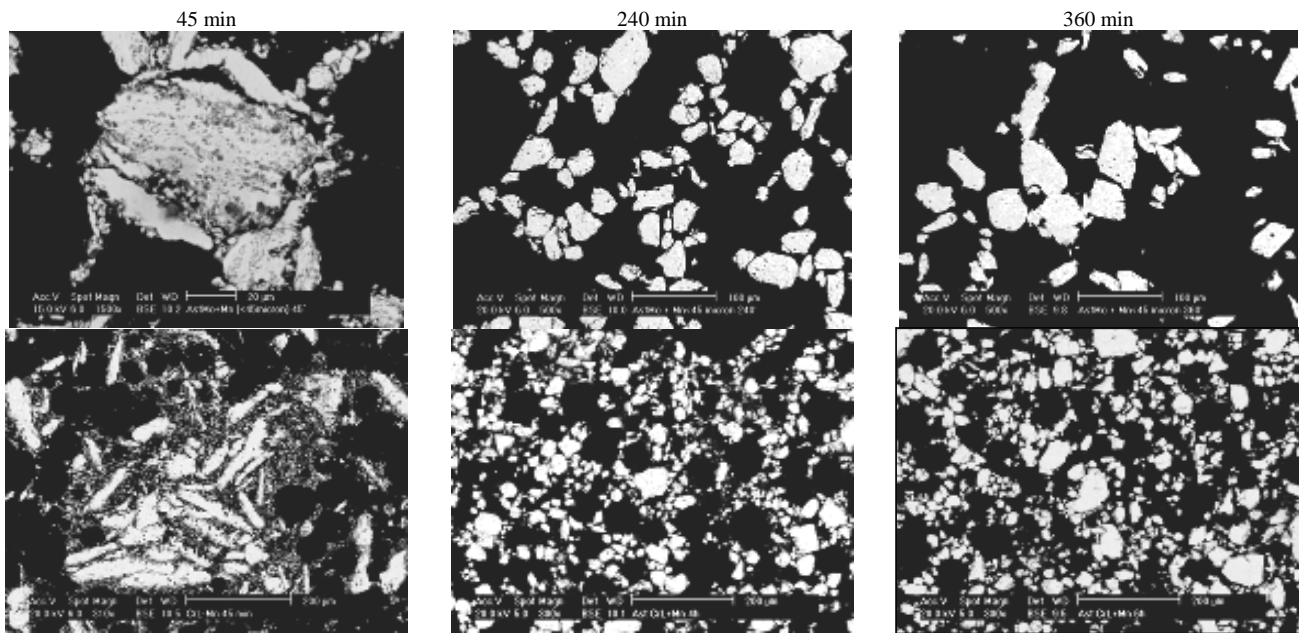
45 min 240 min 360 min

Fig. 3. SEM analysis of the alloying grade evolution with milling time. Upper Astaloy Mo and bottom Astaloy CrL

actually part of the structure and creating a solid solution. The XRD patterns shown in Fig. 2 affirm that the microstructure of the particles changes from ferrite (initial ferrous particles) to austenite after 300 minutes of milling. The austenitic transformation is also favoured by Mn, since it is a γ-stabiliser element.

The behaviour displayed in Fig. 1 is corroborated by the study of the alloying grade evolution shown in Fig. 3. After 45 minutes of milling, Mn was finely dispersed over the Fe-based particles, being more particular in the case of Astaloy Mo where the Mn is already trapped into the deformed iron particles but still free for sublimation.

After 240 minutes, the mechanical alloy was reached and equiaxial particles were obtained with a 50Mn:50Fe-based composition. From this time no trace of free Mn particles was seen, supporting the idea of the reduction of the content of oxygen previously stated. Finally, after 360 minutes of milling only the particle size distribution slightly changes from the results obtained after 4 hours of milling [11].

Therefore, in order to study the situations proposed in this work, the two milling times chosen are 45 and 240 minutes. The master alloy obtained after 45 minutes, MA_1 from now on, contains free Mn and that obtained after 240 minutes, MA_2 from now on, where Mn is homogeneously alloyed with Fe-based particles.

3.2. Thermal characterisation of master alloys

By dilatometric runs it is possible to study the effect of the milled powder addition depending on the milling time. It is necessary to consider two different contributions; the swelling promoted by the Mn additions [4, 12] and the shrinkage provided by the sintering activation. This activation is due to the increase of the crystal defects as milling time is increased.

In Fig. 4 are shown the dilatometry runs for system ASC100.29 and system Astaloy Mo with MA_1 and MA_2. First, it is seen that by the addition of master alloy the shrinkage begins at lower temperatures, besides during the holding time at sintering temperature the contraction

occurred in those systems containing master alloy is greater. Looking at the dilatometry results more carefully it can also be perceived that the combined effect of Mn sublimation and the presence of powder with a high concentration of lattice defects exerts a bigger influence on shrinkage than the solid solution of Mn:Fe, that is, MA_1 produced a bigger contraction than MA_2 [13].

Analysing now Fig. 5 it can be easily understood the difference effect on A_1 and A_3 transition temperatures of adding MA_1, MA_2 and graphite to the alloying system. Since graphite promotes the
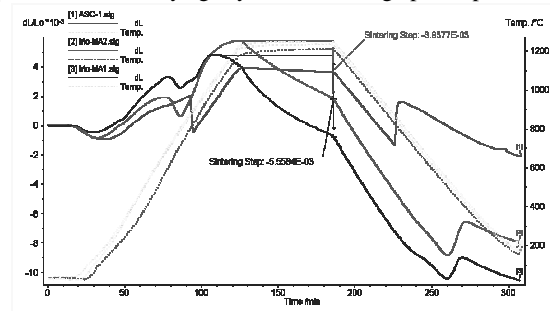

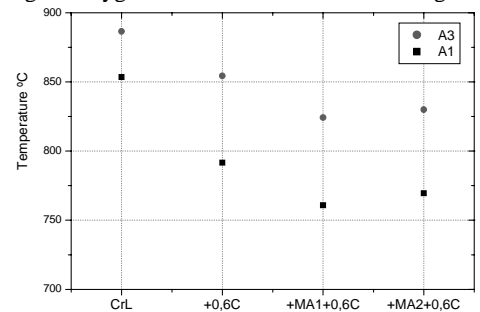Fig. 4. Oxygen content evolution with milling time

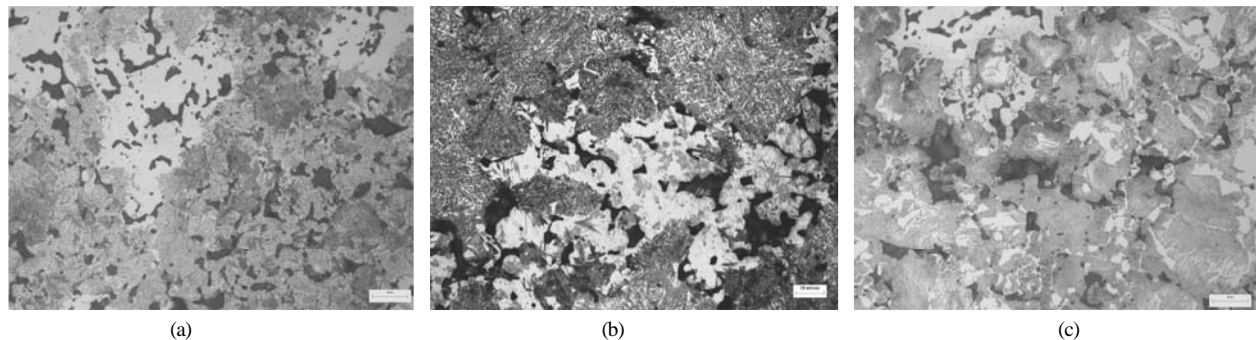Fig. 5. Effect on A_1 and A_3 of the addition of MA_1 and MA_2 or sheer activated base powder

(a) (b) (c)

Fig. 6. Micrographs of systems (a) ASC100.29+MA$_1$ picral (b) Astaloy CrL+MA$_1$ picral and (c) Astaloy Mo + MA$_2$ picral: Na$_2$SO$_5$ C content after sintering: (a) 0.5975% (b) 0.601% and (c) 0.558%

Table 2.
Micro-hardness (HV$_{0.1}$) of studied systems

	+ C	+C + MA$_1$	+C + MA$_2$
ASC100.29	122	163	154
Astaloy Mo	255	290	283
Astaloy CrL	246	320	313

carbothermic oxide reduction, a due to its γ stabilising character, C lowers A$_3$ and A$_1$ temperatures compared to plain iron. Moreover, if MA$_1$ or MA$_2$ is introduced, Mn also contributes to lower these transition temperatures.

3.3. Metallographic study of as-sintered

The addition of master alloys to the starting systems has resulted in a microstructural change. Fig. 6 shows details of these modifications. The original microstructures have changed by the presence of martensitic islands in areas with a higher content of Mn. This change is due to the increase of the hardenability of the system induced by Mn. Moreover, as can be seen in Table 2 the general micro hardness of the systems after the addition of master alloy is considerably greater [14, 15].

4. Conclusions

Mn has been successfully added to the alloying system by generating a master alloy by a high energy milling process. Using this procedure, besides taking the advantage of Mn sublimation which reduces considerably the formation of oxides during the sintering process, this process is activated by the presence of a percentage of powder with a high concentration of lattice defects, enhancing the mass-transport mechanisms.

Moreover, Mn increases the hardenability of the system and this could be proved by the presence of martensitic areas in which the master alloy particles were located. This way, the original microstructure has been improved resulting in higher values of micro hardness.

Acknowledgements

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