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From sintered iron to high performance PM steels

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Abstract. Since low alloyed sintered steels were introduced in the market of the structural parts, we have followed the evolution of a material with poor mechanical properties and any uniformity (in the sense of reproducibility) to materials that today are produced with high reliability and performance. The working efficiency could be equivalent in many cases with the best wrought steel, and maintaining a good margin in terms of cost and competitively. In this paper a complete review of the topic is accomplished, from the early times when the first parts were made by plain iron or iron-carbon, going through the different alloying systems: Fe-Cu, Fe-P, Fe-Cu-Ni-Mo, and more recently Fe-Cr-Mo and Fe-Mn. The development in processing routes has been considered too. The main milestones in the field of new alloying systems have been: 1) the introduction of Cu in 60-70's, 2) the new complex systems with Cu-Ni-Mo in the 80's and 3) the introduction of alloying elements with high oxygen affinity (in the late 90's). Regarding the milestones in processing could be considered: 1) the development of new mixing procedures, 2) the warm compaction and high velocity compaction, 3) the improvements in sintering control and high temperature sintering. Several decades of research and innovation, acting on the processing system (mixing, pressing, sintering, post-sintering operations,...) and on the alloying system (from the earliest times with plain iron to complex systems used today), has allowed us to have a highly competitive materials, in terms of performance, and processes in terms of cost. The future is still open to new developments.

Keywords: powder metallurgy steels, low alloyed steels, high performance, master alloys.

First sintered steels.

Iron based powder metallurgy (PM), were developed in the previous years to the II World War, being the absence of raw materials the pushing effect, and it was the origin of a new materials family (PM Steels) that today can be considered a high performance materials. The first sintered part was introduced in the car industry by General Motors in 1937 and was an oil gear for oil pump [1]. One of the first components introduced was one iron part for an electrical engine in 1945 [2].

Till late 60's were manufactured by PM simple parts, that were based on Fe-C and Fe-Cu-C systems. The knowledge of these systems was developed from works that analyze the possible formation of liquid phase during sintering with the aim of improving the densification and to promote sintering activation [3] as well the diffusion mechanisms in plain systems and self-diffusion of Fe [4, 5]. To analyze and to understand the sintering steps were use iron wires that can reproduce the sintering model based on spheres [6].

Looking for the improvement in the mechanical properties, at that time considering the available technology two basic requirements for new alloying systems were stated: poor or null affinity for the oxygen –sintering atmospheres were not enough dried [7]- and the possibility of controlling dimensionally the sintered part. Around the middle of the 70's, iron powder contents a high amount of oxygen (that produce a poor compressibility and use most of added graphite as reducing agent); in the furnaces the dew point (as well as the composition of the atmosphere) and temperature were not enough controlled producing temperature gradients in the furnaces' load and high levels of humidity. All these aspects made really difficult to predict the final carbon composition in the steel, the level of oxidation and, as a consequence, the reliability, robustness and final properties of the sintered materials.

First alloying elements

The first alloying element that was introduced to the base systems Fe and Fe-C was copper[8]. Copper could be sintered without problems in the type of atmospheres used in that period (endogas, dissociated ammonia or hydrogen), it could produce a liquid phase during sintering at sintering temperatures (between 1120-1150 °C), and this could allow a good distribution of the alloying element among the iron particles and a good diffusion in the first steps of the process [9, 10]. Nevertheless, the presence of Cu, that apparently produced only benefits due to the presence of a liquid phase, had some associated problems that were early detected. The first one was the growth that was detected produced by copper after sintering [11,12,13]. This phenomenon was carefully studied by dilatometry and that allowed a better dimensional control of the effect [14,15]. The second problem, linked with the copper presence and the liquid phase during sintering, was the secondary pores. When a copper particle melts during sintering, it spread and diffuses leaving a pore with a size proportional to the original size of the copper particle. This phenomenon have been widely studied in different works [16, 17, 18]. The use of copper at industrial level in sintered steels and all the problems linked with the transient liquid phase, boosted several fundamental studies associated with this kind of sintering option [19, 20, 21, 22, 23, 24, 25].

The second important alloying element widely used in PM steels was nickel [26,27]. Nickel has, like Cu and compared with Fe, a low oxygen affinity, but its poor diffusivity in iron requires the use of high sintering temperatures or long sintering times to get a proper diffusion into iron. But if it is introduced with low particle size –like carbonyl nickel [28]- it was stated that besides the poor diffusivity at the low sintering times and temperatures used at that period the presence of nickel improved a lot the mechanical behavior, and as a consequence, started to be widely used. Furthermore, the shrinkage produced by using nickel in the sintering process, partially reduces the growing effect of copper in case of using both alloying elements in the same system [29,30,31]. Simultaneously, and looking for the improvement in the dimensional behavior after sintering, the industry started to use phosphorous as alloying element. This element, fully avoided in wrought steels, in PM can be used due to its important effect on the sintering behavior. Phosphorous produces a highly activated sintering process (thanks to its alpha stabilizers character and the liquid phase sintering) that promotes a highly rounded porosity that improves a lot the ductility in the PM steels [32,33,34].

In the middle of the 70's and till the end of the 80's, the industry started to require more reliability and higher performance in the PM steels. The reliability of specimens progresses through the better control of the chemical compositions, lowering the impurities in the powders, and specially, with the better control in the processing parameters (pressing, sintering atmosphere –dew point and carbon content-, sintering temperature,...) These improvements allowed to manage more complex systems and to introduce molybdenum as alloying element [35,36,37,38,39,40,41], widely used in conventional ingot iron metallurgy and with the requirement of low affinity for the oxygen.

Diffusion alloying

The first formulation of highly complex alloying systems, promotes a decade of production developments, first based in the mixing procedure [42,43,44,45], then in the use of the diffusion alloying methods [46,47], and then the development of complex grades partially alloyed and obtained by diffusion alloying (well known by 'distalloys' and commercialized by Höganäs AB (Sweden) y Hoeganaes Corporation (USA)[48,49,50,51,52,53], and other powder producers [54].

In the 90's, the need for improving the competitiveness of the high performance parts, supports the development of two new improvements lines: by one side grades with high level of alloying element (but still in the system Fe-Cu-Ni-Mo-C) and by other side, the searching of new ways to obtain high density by working on the pressing and sintering steps. Under the scope of the first option, new steels with higher Mo contents (from 0.5 wt. % till 0.85, 1 or even 3 -wt.- %) were developed. All of these materials were developed in premix powder grades too [55]. In Fig. 1 can be seen the improvements in UTS and yield strength achieved with these PM grades.

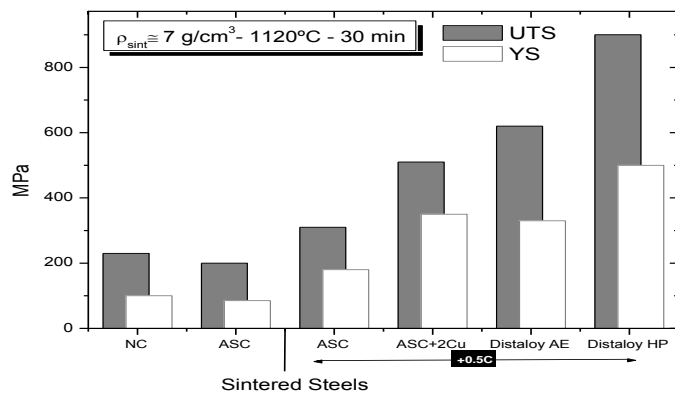


Figure 1. Evolution of conventional PM steel grades

Nevertheless, the high density manufacturing process in the pressing step was highly improved with the development of the warm compaction system [58,59,60,61]. Working on relatively low temperature (in the order of 150 °C), the use of preheated powders and a preheated die reduce the yield strength of the powders, that can reach with same level of compacting pressure, much higher densities. Through this system the concept of uniaxial pressing change, because can be reached enough green densities for green machining. Besides, the pore system was substantially modified into more rounded pores that allow better fatigue performance. Till the design of warm compaction technique, the unique way to reach high densities in conventional PM was by double pressing double sintering cycles.

The next technological advance, under the point of view of pressing, is the high velocity compaction, or pressing by impact waves [62,63,64]. The idea of densification by compressive shock waves produce by the impact of a hammer, comes from explosive compaction method (still considered in the 80's). It is based on the permanent deformation and cold welding between the metallic powder particles by the expansive wave, that provides to the green compact even higher densities and strength higher than warm compacted samples [65,66].

But high densities systems can be reached not only by pressing. For the first time of iron base powder metallurgy, high sintering temperature appears as the natural way to activate the sintering phenomenon [67,68,69] but, taking into account that till mid 90's was not used at the industry [70]. At high temperature, not only self diffusion of iron is improved, but all alloying elements increase their diffusion improving all their features as alloying elements. At high temperature sintering mechanical properties can be improved in terms of 20-30% with better fatigue response and corrosion behavior [71,72].

High oxygen affinity alloying elements

From the first periods of using PM steels, there were many attempts to introduce elements such as Cr, Mn or Si. They are cheap materials, abundant, easy to recycle and improve the properties of steels as alloying elements. Their high affinity for the oxygen and the poor control in the atmospheres till mid 90's, most of these trials have tested through the additions of ferroalloys [73,74,75,76] or master alloys [77,78,79,80,81,82] to reduce their activity during sintering.

In the case of chromium, and being a big difference the Mo base steels of similar characteristics, it can be obtained special steels devoted for carbonitriding or nitriding [83,84]. But the implementation of Cr or Mn in large scale production, despite their fantastic effect on hardenability [85,86], has been limited by their high affinity for the oxygen and the difficulties to reduce de amount of this element. The high stability of their oxides makes highly important to know exactly which reducing agents are playing in each step of sintering, because is well known how these agents change with temperature. Atmospheres of hydrogen or artificial mixes of N₂-H₂ are mandatory for the correct sintering process at large scale. To sinter chromium steels are needed highly pure

Improvements in processing

From 1965 and till the middle of the 80's, the improvements in density were achieved thanks to the development of high compressibility powders [56, 57]. Later on, new generations of lubricants (among those the kenolube), and the use of higher compacting pressures (between 600 and 1000 MPa) allowed to reach a wider values of densities.

atmospheres of N₂-H₂ with oxygen partial pressures lower than 5·10⁻¹⁸ atm [87, 88]. It has been demonstrated that carbon acts as main reducing agent at sintering temperature over 1200°C. But the oxygen partial pressure control, the hydrogen content of the atmosphere and the rate CO/CO₂ (usually produce when the metallic oxides are reduced) [89, 90, 91] are the main and predominant factors on the reducing reactions in the first stages of sintering, during the cooling and at sintering temperatures below 1150°C.

The improvements in hardenability or dimensional control are not the main reason to increase the research on these alloying elements and their characteristics. Another important reason is to develop low cost alloying systems with high benefits in sinterhardening operations. In this process, thanks to the proper cooling rate after sintering, can be obtained high values of hardness and strength [92, 93].

The industrial implementation of low alloyed steels powders with Cr, started in the middle of the 80's, thanks to two Japanese's companies. Sumitomo Metals, developed an oil atomization process, and during 1980 it was commercialized powders of the alloying system Fe-Mn-Cr-Mo (1Cr-0,8Mn-0,25Mo) with levels of oxygen under 100-200 ppm [94, 95]. This feature enables good compressibility levels and the final microstructures of those steels lead to good wear properties [96, 97]. The main drawback of these powders was the costs production which it was the main limitation for their implementation. At the same time, Kawasaki commercialized different grades of water atomized powders of Fe-Cr, but the higher oxygen levels demanded sintering in vacuum with high graphite additions [98]. Till 1998 there are no commercial grades, when Höganäs AB commercialize a water atomized powder of Fe-Cr-Mo suitable for large scale production.

The manganese has a different and distinctive behavior during sintering, its sublimation effect [99]. This phenomenon, that occurs at relatively low temperatures, in the range of 700 °C [100]- and its diffusion mechanism in the iron particles, as well as its mass transport mechanism in vapour phase, that has been studied since 1980 [101,102]. Considering the use of this element, it is possible to obtain some interesting advantages that facilitate the sintering process without using sintering atmospheres with an extremely low dew point. The high affinity for the oxygen of Mn, make it a powerful reducing agent, contributing in the reduction of the fine oxide layer that is always present in the iron particles surface. This phenomenon is well known as the "self cleaning effect" of Mn. The remain Mn in vapour state will condense on the surface of the iron particles in the first stages of the sintering process, when the necks are forming, and thanks to the composition gradient will diffuse inside the particles. Then, from the surface of the sample, and using the open porosity, it will be a positive interaction between the Mn and the sintering atmosphere. In this way manganese contributes to reduce the dew point, and improves the sintering process [85,103,104]. Nevertheless, an important aspect should be considered. Being the sublimation a surface phenomenon, the Mn should be added in a very small size (recommended <10 µm) and this can produce segregation problems during the mixing process. In this way, the most recent studies are focused in new effective methods to introduce the Mn in the alloying system [105].

The 'master-alloy' concept

Although the first approach to the "Master Alloy" concept –as a method for considering alloying elements with high oxygen affinity- was done in the 70's, technical limitations decrease the large scale implementation. The first attempt was done by considering carbides of Cr, V or Mo as additives (from 3 to 10wt.%) in the mixture of ferrous powders [106]. Those materials needed sintering temperatures up to 1250°C, but enables UTS in the range of 800 to 900 MPa with an elongation close to 3%. These first studies had given some new ideas concerning to the alloying system. It was identified the synergetic effect that occurs when using at least two alloying elements, allowing the production of steels with better mechanical properties at a lower cost.

The next step was done when the patent of Stadler (GFE) [107] defined new complex carbides compositions (MCM and MVM) to be blended with iron powder with high compressibility. However the high tool wear block up their development [108]. Further studies were aimed at the formation of liquid phases during sintering [109,110,111]. This liquid phase accelerates the mass

transport improving the homogenization of the composition and final microstructures [112,113,114].

Nowadays, more efficient methods and technologies make that the Master Alloys concept was taking up again. New patents of master alloys with Cr, Mn, Si, finely ground or atomized in Kerosene for preventing the oxidation have improved their applications. In 2007, F.Castro et al. [115] developed a gas atomized master alloy, based on a high carbon ferro-manganese composition that produces a liquid phase at the conventional sintering temperature of 1120°C. New approaches are investigated to fulfil new market requirements [116]. This new alloying systems are designed to solve the dependence with some alloying elements, like Ni and Mo, and to open the range of new final applications improving the versatility of powder metallurgy.

Summary

Since low alloyed sintered steels starts to be used as structural parts, we have followed the evolution of a material with poor mechanical properties and any reliability in the sense of reproducibility to materials that are today produced with high reliability, and performance equivalent in many cases with the best wrought steel, and maintaining a good margin in terms of cost and competitively. Several decades of research and innovation, acting on the processing system (mixing, pressing, sintering, post-sintering operations,...) and on the alloying system (from the earliest times with plain iron to complex systems used today), has allow to us to have a highly competitive materials, in terms of performance, and processes in terms of cost. The future is still open to new developments.

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