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FINAL THESIS

IMPACT STRENGTH OF
P/M Fe-Mo-P SINTERED STEELS

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Section 1 THEORETICAL FOUNDATIONS

1. INTRODUCTION

Powder metallurgy is a metalworking process used to fabricate parts of simple or complex shape from a wide variety of metals and alloys in the form of powders. The process involves shaping of the powder and subsequent bonding of its individual particles by heating or mechanical working.

In the traditional process, a metal, alloy or ceramic powder in the form of a mass of dry particles, normally less than 150 microns in diameter, is converted into an engineering component of pre-determined shape and possessing properties which allow it to be used in most cases without farther processing. The basic steps of the production of sintered engineering components are those of powder production; the mechanical compaction of the powder into a handleable preform; and the hitting of the preform to a temperature below the melting of the major constituent for a sufficient time to permit the development of the requires properties. Normally, parts made by pressing and sintering require no further treatment. However, properties, tolerances, and surface finish can be enhanced by secondary operations such as repressing, resintering, machining, heat treatment, and various surface treatments.

Parts fabricated by pressing and sintering are used in many applications. However, their performance is limited because of the presence of porosity. In order to increase properties and performance and to better compete with products manufactured by other metalworking methods (such as casting and forging), several powder metallurgy techniques have been developed that result in fully dense materials; that is, all porosity is eliminated. Examples of full-density processing are hot isostatic pressing, powder forging, and spray forming.

Characteristic advantages of powder metallurgy are close tolerances, low cost, net shaping, high production rates, and controlled properties. Other attractive features include compositional flexibility, low tooling costs, available shape complexity, and a relatively small number of steps in most powder metallurgy production operations. Powder metallurgy is a highly flexible and automated process that is environmentally friendly, with a low relative energy consumption and a high level of materials utilization. It also encompasses an extensive range of ferrous and nonferrous such as iron, copper, molybdenum and tungsten powders and others like ceramic powders, and mixes of metallic and ceramic powders.

By the other side some disadvantages of the powder metallurgy are that sometimes the cost is high relative to conventional processing, tooling strength and stiffness may be inferior to wrought alloys of similar composition, porosity and low ductility may impair durability, fracture toughness and other mechanical properties may be low.

During the last three decades a substantial expansion has ocurred, dominated tonnage-wise by sintered iron and steel products, but also including components in the refractory metals, stailess steel, copper nickel and aluminium alloys.

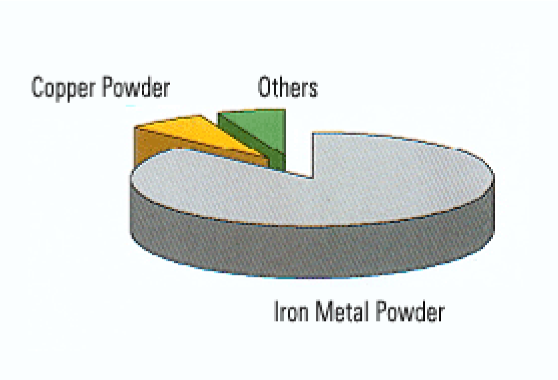


fig (1) global powder material production (%)

Contributing significantly to the growth has been a progressive improvement in the manufacturing technology stimulated by a better understanding of the under-pinning science of the process; improved mechanical properties resulting from the development of more compressible powders which increase the densification of the sintered part; the extention of the materials base to include alloy steels which can be heat treated, and improvements in the control of processing parameters involving the automation of the pressing and sintering operations. Equally important, however, have been the increasingly effective dialogue between the powder metallurgy technologist and the design engineer and the results of their joint efforts in optimizing the use of the process to provide high quality, precision components with a degree of reproducibility, homogeneity and level of properties which often are superior to those achieable in the equivalent cast or wrought product.

Today, the P/M industry is made up of many companies, each with specialization in alloys, applications and production techniques. The largest activity is associated with ferrous alloys, some iron and many steels. Most of P/M products are for applications in structural automotive components based in ferrous alloys. Attainment of the desired mechanical properties requires alloying to form high-strength steels during sintering and the combination of low production costs and high sintered strength dominates de selection criteria, where the trend is toward higher densities to improve the mechanical properties.

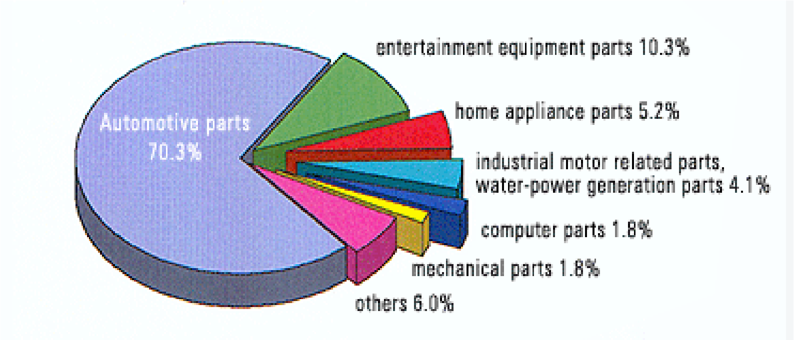


fig (2) Markets for structural parts for P/M

2. POWDER METALLURGY PROCESS

The basic procedure in the manufacture of PM part is:

- The *powder fabrication* and *powder characterization*
- Mix the metal powders with a suitable lubricant.
- Load the mixture into a die or mould and apply pressure. This gives what is called a *compact* which requires only to have sufficient cohesion.
- Heat the compact usually in a protective atmosphere at a temperature bellow the melting point of the main constituent so that the powder particles weld together and confer sufficient strength to the object for the intended use. This process is called *sintering*

2.1. Powder fabrication

Metal powders can be produced by mechanical comminution and first powders were made grinding, filing or hammering a piece of steel. However, it was a poor direct route of powder fabrication and today it is only a rely of the production sequence. Another early technique for fabricating iron powder was in a electrolytic cell but essentialy disappeared from powder metallurgy because of cost and environmental contamination. Today the main industrial processes for powder production are two which together account for more than 90% of the world production of iron and steel powders, the sponge-iron process (chemical process) and the atomization.

2.1.1 Atomization

Powders covering a wide range of alloy steels, copper alloys and light alloys are manufactured in this way. Atomization can be defined as the production of metal powders by the breaking of molten metal into droplets and their subsequent freezing into solid particles. In thus has a fundamental advantage over such techniques as reduction or electrolysis in that it can produce alloy powders of any composition that can be melted. This together with economic factors which have become favourable to atomization.

Water atomization

The level of technology, as evidenced by the yield consistency, quality and costs of the processes used, was very variable, and in many cases poor. The aim of recent developments has thus been two fold: to increase quality and reduce costs. It is generally true to say that advances in understanding of the process of atomization tend to allow both these objectives to be achieved.

A complete plant consists on a source of liquid metal which pours into a tundish to provide a consistent metal supply through a ceramic nozzle to the atomizing jet or jets. There is then a vessel to collect the atomizing fluid and powder following which the powder is separated (e.g. dewatered or filtered from the gas).

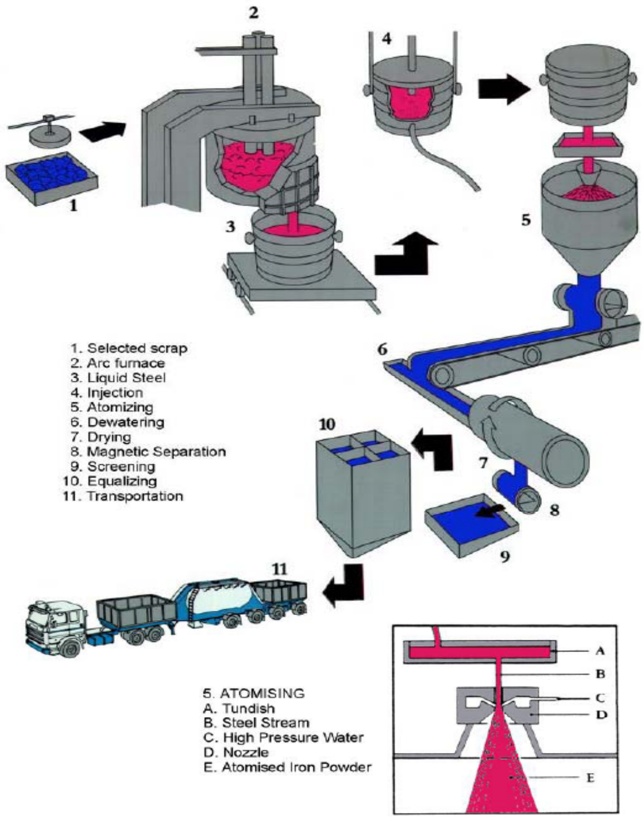


fig (3). Water atomization process

The particle size distribution of a powder is one of its principal qualities. The purity of a powder would be 100% if every particle had the same composition as the ideal specification. Impurities in metal powder, particles with incorrect size or shape and oxide films are the main problem because is incapable of removing impurities dissolved in the molten metal are frequently significant in water atomized powders, but levels of oxide are variable.

Gas atomization

Foe some compositions, especially stainless steels, tool steels, electronic or aerospace alloys the desired particle shape is spherical. Pressurized gas flows out of a nozzle to impact a stream of molten metal to from a droplet spray solidifies into powder. The greater the energy in the gas, the smaller the powder. Most typically the gas is nitrogen or argon.

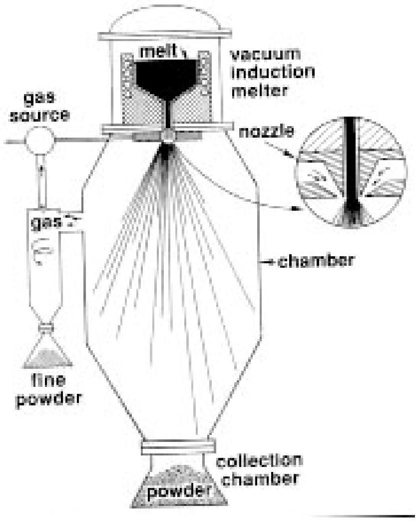
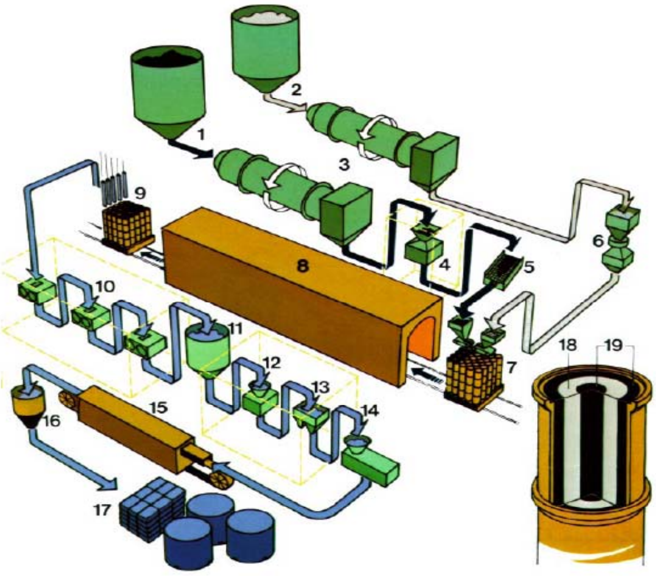


fig (4) gas atomization process

The principal concerns of research have been to produce rapidly solidified and high purity powder. This in turn leads to a need to make finer powders. Increasing pressure does not always give finer, either absolutely, or at a given gas/metal ratio. Much of the details remain propietary but all designs aim to minimize gas use while achieving the correct particle size. This involves getting the gas exit close to the metal and raising gas velocity. Practical problems such as thermal shock, wear, fouling, etc. are very important and reproducible behaviour is vital for commercial success. The incidence of “satellites” is the main variable shape factor. These are caused by collisions between particles in flight and become worse as finer powders are made due to the finest particles being drawn up into the atomizing plume. Costs are very sensitive to output. Automation reduces operating costs but reduces flexibility. In batch melting plants, batch size governs costs to a large extent. The economics of gas atomization when gas recycling is feasible, are quite attractive and close to water atomization. Gas recycling is quite cheap unless purification of the gas is needed. An important extension of rapid solidification technology is that of spray-forming (The Osprey process) in which the atomized metal stream is direct onto a substrate where it solidifies and is allowed to build-up to the required form.

2.1.2 Chemical fabrication (Sponge process)

The sponge iron process, is essentially a chemical process in which finely divided iron ore is being reduced with coke breeze yielding a spongy mass of solid metallic iron, which can readily be comminuted to iron powder. The iron ore used at is a magnetite slick (powdery Fe_3O_4 obtained by selective mining). This magnetite slick, which by nature contains only very small amounts of gang and has extremely low contents of sulfur and phosphorus, is being dressed and concentrated while still at the mining location and then delivered in a highly pure state.



1. Reduction Mix of Coke Breeze and Limestone
2. Iron Ore
3. Drying
4. Crushing
5. Screening
6. Magnetic Separation
7. Charging in Ceramic Tubes
8. Reduction in Tunnel Kilns, Approximately 1200°C
9. Discharging
10. Coarse Crushing
11. Storage in Silos
12. Chrusing
13. Magnetic Separation
14. Grinding and Screening
15. Annealing in Belt Furnace, Approximately 800-900° C
16. Equalising
17. Automatic Packing
18. Iron Ore
19. Reduction Mix

fig (5). Sponge process

The process starts with two raw materials, a ”reduction mix” consisting of coke breeze blended with ground limestone, and a pre-processed magnetite slick. The magnetite slick and the reduction mix are being dried separately in two rotary ovens. The slightly agglomerated dried reduction mix is crushed and screened, and the dried magnetite slick is passed through a magnetic separator. Then, both materials are charged by means of an automatic charging device into tube-like ceramic retorts. These retorts consist of four tube segments of silicon carbide being stacked on top of each other and are standing, on rail-bounded cars which are clad with a thick layer of refractory bricks. These cars are traveling slowly through a tunnel kiln within which the retorts are gradually heated to a maximum temperature of approx. 1200°C. As the temperature inside the retorts increases, the coke breeze begins to burn forming CO which, in turn, begins to reduce the magnetite to metallic iron while itself oxidizing to CO_2. The so generated CO_2 reacts with the remaining coke breeze forming new CO, which again reduces more magnetite to metallic iron. This reaction cycle continues until all magnetite has been reduced to metallic iron and the major part of coke breeze is burned up. Parallel to the reduction cycle, the limestone in the reduction mix binds the sulfur arising from the burning coke breeze.

After completed reduction, the retorts are slowly cooled down again to approx. 250°C before leaving the kiln. Inside each retort, there is now a tube-like sponge iron cake with a porosity of about 75%, a residue of unburned coke breeze, and a sulfur-rich ash. At an automatic discharging station, the sponge iron tubes are pulled out off and the remaining coke breeze and ash are exhausted from the retorts. Thereafter, the retorts are ready to be charged again and go on a new trip through the tunnel kiln. The sponge iron tubes (after having been cleaned from adhering coke breeze and ash) are in several steps crushed and comminuted to a particle size below 3 mm. The so obtained crude powder is intermediately ensilaged before further processing. From the intermediate silo, the crude powder is passed through a specially designed chain of magnetic separators, mills and screens, in order to be refined to a particle size below 150 mm and a well defined bulk density (apparent density). Subsequently, the powder is passing a belt furnace where it is soft-annealed at 800-100° C in hydrogen, and its remaining contents of carbon and oxygen are reduced to a very low level. During annealing, the powder agglomerates to a very crumbly cake which is gently comminuted again in a special mill (not shown on the flow-sheet). The so treated powder has good compressibility and high green strength.

Many belt furnaces are, of course, available to take care of the huge volume of iron powder to be treated. These modern electrically heated belt furnaces are especially designed for the purpose, the belt width being 1500 mm. The powder from several belt furnaces is collected in a special silo, where it is homogenized in lots.

2.2 Powder characterization

It is now well-known that particle size, shape and orientation profoundly influence the characteristics of the final products, while these properties in turn depend strongly on the processes to which the particles have been subjected. Iron powders are generated in many facilities around the world, and at each facility there is a different production concept. Accordingly, a wide array of powder sizes, shapes, chemistries and other attributes are possible. Such a diversity in powders is justified only by the array of applications and their different demands on the powders.

Particle size

Usually particle size is based on a characteristic feature. We accept that particles show spherical shape, which volume or size can be easily determined by its diameter. For non-spherical particles, there is obviously no single definition of diameter and the most appropiate definition depends on the processes to which the particles are subjected. However, quite often it may not be possible to measure this directly, and one of the problems is characterizing the size distribution of particulate materials lies in establishing how different "measures" of particle size obtained by different techniques are related. For any particular size range, the deviation from the standard size is essentially due to the particle shape

For irregular particulate materials the definition of particle diameter must be specified. These are the most accepted theoretical approximations in order to fix this particle feature:

- *Volume- Equivalent Diameter*, d_v this is defined as the diameter of the sphere with the same volume as the particle

- *Projected – Area Diameter*, d_A

  This is defined as the diameter of a circle with the same projected area as the particle

- *Stokes Diameter*, d_s

  The Stokes diameter d_s, is defined as the diameter of a sphere with the same density and settling velocity as the particle in the same fluid.

Most ferrous powders are measured for size by one or two sizing techniques. The classic approach, applicable to larger particles, is termed screening or sieve analysis. A squared grid of evenly spaces wires creates a mesh, just like the screen of a window. Screen analysis begins with a stack of screens with decreasing mesh openings where the smallest are in the bottom. The powder is loaded onto the top screen and the screen stack is agitated and after 30 minutes, the screens are unstacked and the powder in each size interval weighed and the interval percent calculated for each size fraction. Although screening is the most widely recognized particle size technique it has been displaced by automated size analyzers like laser light scattering techniques for automating the measure of particle size that have had the most rapid growth in instrument development in recent years, in spite of the inherent disadvantages that the response depends not only on the particle shape and surface characteristics but also on its optical properties.

The incentive for development of light scattering techniques is obviously their relatively easy of use, automation and capability for on-line size analysis. However because particle sizing depends on the refractive index and absorbance of the particle, it is in general not possible to obtain a unique “light scattering diameter” and to relate it to other particle diameters of interest. Absolute size measurement by light scattering is not simple, and usually other techniques such as sedimentation or ESZ must be used. However, for on-line size analysis and particularly for detection of changes in particle size, it can be convenient to use light scattering techniques.

Particle shape and surface area

Particle shape varies significantly between iron powders. Because measuring particle shape is difficult qualitative descriptors are used to convey the particle shape and these best descriptors are simple words, especially those that invoke wide-spread images such as spherical, angular, irregular, dendritic, sponge, cubic, polygonal, flake, rounded, etc. Particle shape varies with particle size and manufacturing technique. However most particle size analyses assume a spherical shape and this is often invalid.

Surface area is sometimes use to indirectly measure the particle size. However surface area tells nothing about the distribution in particle size or other differences between powders. The two main analysis techniques for measuring surface area are gas adsorption and gas permeability. A knowledge of the composition of the surface and near-surface regions of powders can be of critical importance as far as their subsequent processing is concerned. By near-surface we are generally concerned with the outer 5nm or so of a material surface and the departure of this outer region from the bulk composition. Such changes in composition generally result from one of two processes; they may be a result of the material interacting with the environment; for example, metal powders will always be covered with a thin layer of oxide; or they may result from segregation or other processes that have ocurred during powder production or processing.

Packing and flow

Small powders or irregular shaped particles do not pack or flow very easily. The small particles have a high surface area, and the irregular particles have many surface asperities. Sharp corners are a source of friction between particles that inhibit flow and packing. Both attributes are important to powder shaping, since the powder needs to fill out a die cavity rapidly and uniformly. The packing density decreases because of poor flow past neighboring particles and these parameters are what determinates the apparent density of a powder, the density when the powder is in the loose state without agitation.

2.3 Powder compaction

Iron powder is compressed to high densities by the application of pressure. However, in the as-pressed state the compact has only modest strength and requires sintering to attain strength. Associated with this particle deformation is a decrease in porosity and increase in particle bond strength. Many compaction options exist including hard and soft tooling, heating the die and powder, using rolling mills and even shocks waves. However the most important is die compacting where particles deform into a desired shaped in the die, and mainly under uniaxial stress. Other techniques like powder injecting molding (PIM) can be used depending on operating parameters including pressing directions, shape complexity and relative use.

Die compacting technology

In this technology the forming of a sintered component begins with the densification of the metal powder in a rigid die having a cavity of more or less complicated contour. In this operation, high pressures (usually 650 N/mm^2) are exerted upon the powder in the die cavity, simultaneously from top and bottom, via two or more vertically moving compacting punches. Under the influence of such high compacting pressures, the powder particles are being squeezed together so closely that their surface irregularities interlock and a certain amount of cold welding takes place between their surfaces.

After ejection from the die, if the compacting operation was successful, the compact owns sufficient strength (so-called green-strength) to withstand further handling without damage. In order to facilitate the compacting operation and reduce tool-wear to a minimum, a lubricant is admixed to the powder before compacting.

Powder Compacting in a Cylindrical Die

The strength properties of sintered components increase with increasing density but their economy drops with increasing energy input and increasing load on the compacting tool. Thus, it is most desirable, for both economic and technical reasons, to achieve the highest possible compact density at the lowest possible pressure. Density-pressure curves give information about the frame within which a suitable compromise may be found.

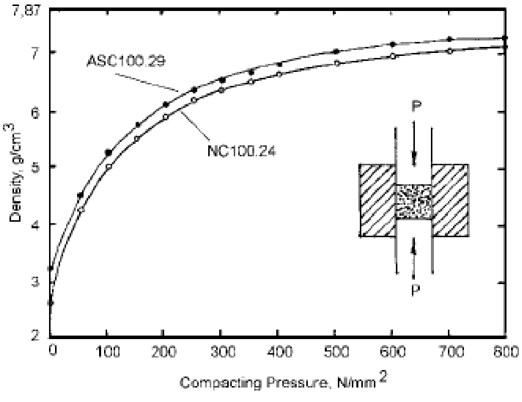


fig (6). Density-pressure for two commercial iron powders compacted in a cabide die.

A striking feature of density-pressure curves is the fact that their slope decreases considerably with increasing compacting pressures, and that the density of massive pure iron (7.86 g/cm3) obviously cannot be reached at feasible pressures. We notice, further, that the two iron powders despite their chemical identity yield different density-pressure curves.

Isostatic Powder Compacting

A powder under isostatic pressure shows a similar densification behavior as in die compacting. Since there is no die-wall friction in isostatic compacting, the powder was not admixed with any lubricants.

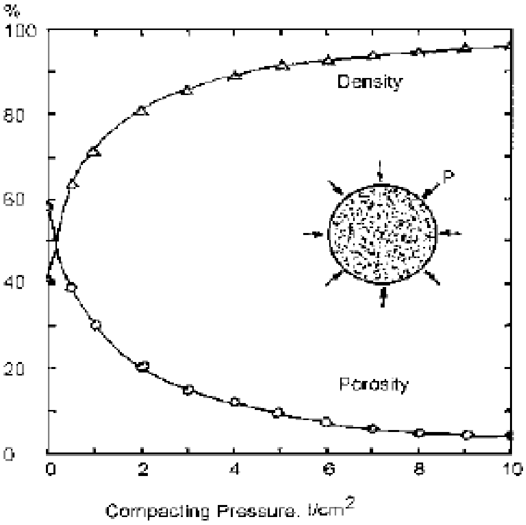


fig (7). Relative density and porosity as functions of isostatic compacting pressure.

Deformation Strengthening of Powder Particles

Disregarding, for the moment, the problem of wall friction in die-compacting and considering isostatic compacting of powder only, we recognize that the problem of powder densification arises from an underlying physical problem which can be defined as follows:

- With increasing densification, the powder particles are plastically deformed and increasingly deformation strengthened, i.e. their yield point is steadily being raised.

- Simultaneously, the contact areas between particles are increasing and, consequently, the effective shearing-stresses inside the particles are decreasing. Thus, at constant external pressure, decreasing shearing-stresses meet a rising yield point, and all further particle deformation ceases, i.e. the densification process stops.

Decrease of Maximum Shearing Stress

In a state of densification where the powder particles are squeezed together to such extend that the initially interconnected pores between them have degenerated to small isolated pores, the stress distribution around each of them can be fairly well approximated by the stress distribution in a hollow sphere under hydrostatic outside pressure P. Let the hollow sphere be of metal having a yield-points0. Let R be the outer radius of the sphere and r its inner radius.

Theoretical Density of Powder Mixes

Sintered components are usually manufactured from mixes of unalloyed or low-alloyed iron powder with additives like graphite, other metal powders and lubricants. Compact densities attainable with such powder mixes are, of course, influenced by the specific weights and the relative amounts of the additives and of impurities if any.

Radial Pressure - Axial Pressure

When the piston of a hydraulic cylinder exerts pressure upon the liquid inside the cylinder, the pressure applied in axial direction is transformed 1:1 to radial pressure upon the cylinder wall. When a powder is being compacted in a rigid cylindrical die, the axial pressure, exerted upon the powder by the compacting punch, is only partly transformed to radial pressure upon the die wall. This radial pressure can be quite substantial, but it cannot reach the level of the axial pressure because a powder is no liquid and has no hydraulic properties.

It is evident that the radial pressure, which a metal plug or a mass of metal powder under axial pressure exerts upon the wall of a compacting die, is the smaller the higher the yield point of the metal is. A metal powder with extremely low yield point and negligible tendency to deformation strengthening, like lead powder for instance, should exhibit an early hydraulic behavior when compacted in a rigid die.

Axial Density Distribution

Frictional forces at the wall of the compacting die restrain the densification of the powder because they act against the external pressure P exerted by the compacting punch. With increasing distance from the face of the compacting punch, the axial stress σ_a, available for the local densification of the powder, decreases. This becomes especially adversely apparent in the manufacturing of long thin-walled bushings which at their waist line show substantially lower densities than at their two ends. Consequently, powder compacts usually have a zone of lower density approximately mid between their end faces. This zone of lower density is often referred to as *neutral zone*. Thus, compacts having thin sections, long in compacting direction, are very fragile before they are sintered.

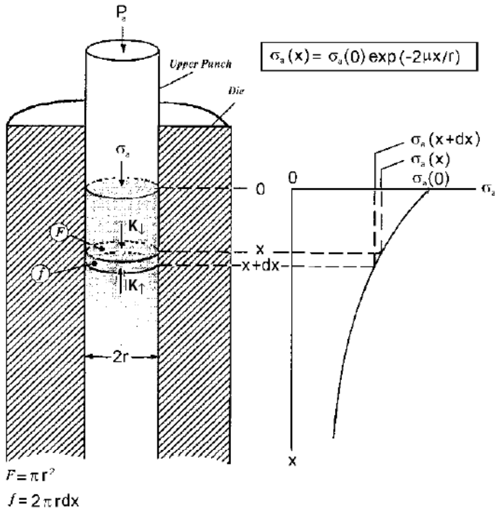


fig (8). Axial stress σ_a as a function of distance x from the face of the upper compacting punch

Ejecting Force and Spring-Back

One direct consequence of the residual radial stress σ_{r0}, is the fact that a substantial force is required to eject a powder compact from the compacting die.

- A certain re-densification effect occurs at the lower end of the compact.

- A long and slender bottom punch, just strong enough to withstand the compacting load, may yield or break under the ejecting load.

If the wall of the compacting die is worn or insufficiently lubricated, it may come to cold-welding effects between the compact and the die wall, recognizable from an excessive increase of the ejecting pressure and a typical stick-slip behavior (creaking noise).

Another consequence of the residual radial pressure becomes apparent at the moment when the compact, on ejection, passes the upper rim of the die. The upper part of the compact, sticking out of the die, expands elastically while the lower part is still under the influence of the residual radial pressure. The horizontal shearing stress arising in this situation may generate horizontal cracks in th compact. In order to diminish the shearing stress and avoid cracks in the compact, it is recommendable to slightly taper the exit of the die and to round the edges of the exit.The elastic expansion of the compact after ejection from the compacting die is called *spring-back*

The spring-back depends of the following parameters:

- compacting pressure, compacting density,
- powder properties,
- lubricants and alloying additions,
- shape and elastic properties of the compacting die,

The powder grade has a strong influence on spring-back. (This must be kept in mind when, in the production of precision structural parts , for one or the other reason, the powder grade is changed).At high densities, a small scatter in density entails a wider scatter in spring-back. (This can turn out to have adverse effects on the final tolerances of the sintered structural parts).

Other powder injection moulding

Metal powder injection moulding

The process of powder injection moulding (PIM) and its application to forming complex shaped, high performance metallic components, allows net shaping of a variety of materials, including metals, ceramics, cermets, intermetallics and composites. In this process a high concentration of powder is mixed with a thermoplastic binder to form a low viscosity slurry when heated. This slurry is shaped using conventional injection moulding practices. Subsequently, the thermoplastic is removed from the compact and the powder sintered to near full density. The process has advantages for the fabrication of complicated shapes for demanding applications. The steps involved in forming a component by powder injection moulding include the following:

- Selecting and tailoring a powder for the process
- Mixing the powder with a suitable binder
- Producing homogeneus granular pellets of mixed powder and binder
- Forming the part by injection moulding in a closed die.
- Processing the formed part to remove the binder (termed debinding)
- Densifying the compact by high temperature sintering
- Post-sintering processing as appropiate, including heat treatment of further densification.

The equipment used in shaping the compact is the same as use for polymer injection moulding. Small particles are used in PIM to aid sintering densification. Powder injection moulding is capable of producing a new range of components from powders.

A main attraction is the economical production of complex parts from high performance engineering materials. Because of the high final density, the PIM products are suitable for high performance levels.

Still it is not cost competitive with traditional die compactation for shapes with relatively simple or axial-symmetric geometries. Also, the availability of suitable powders limits the current materials selection. Other limitations trace to equipment size and sophistication. Large components require larger moulding and sintering devices which prove more difficult to control. Accordingly, PIM is best applied to complex, small shapes.

Finally, some limitations reflect an overall poor understanding of the process. These problems are most acute with the ceramic materials. Microstructural flaws induced during moulding limit the mechanical properies of the final product. Much of PIM´s future growth is linked to solving problems relating to process control, powder availability, powder cost, dimensional control,batch processing, variable thickness, large dimensions, moulding defects, and distortion. Early experience with PIM stablished high production yields with good tolerances. As the engineering community better appreciates these attributes, PIM will continue to grow.

Dynamic compaction technology

Dynamic compaction involves compacting powder by a shock wave which results in work hardened particles bonded by rapidly solidified welds; the technique also has the ability to produce bulk materials which can not be consolidated by other means.

Dynamic compaction offers a means of producing unique materials that in some cases can not be obtained by other techniques. For conventional materials, the shock waves associated with the technique result in high discolation densities, increased hardness and an associacted increase in fatigue strength, while the good contact between particles results in activation of sintering. Also, the interparticle melting that the technique can produce during cold compaction allows the production of many unique alloys of metals, ceramics and plastics which would lose their properties of interest if exposed to a high temperature and thus can be fabricated as 3-D objects only by dynamic compaction.

Dynamic compaction involves the consolidation of powder by discrete shock waves that are created by the impact of a light, high velocity punch or by explosives placed close to the powder, but separated from it. A unique aspect of dynamic compaction, resulting from the compaction being carried out by one or two discrete shock waves, is that it is possible to transform the powder to a solid. This is because the work of compaction is concentrated in the short time that it takes the shock front to pass a point, this results in the temperature rise caused by this work of compaction being sufficient to melt the material and gives strong interparticle bonding. Hence, the technique is of interest for materials which would degrade if exposed to normal sintering temperatures.

The combination of a shock hardened particle surrounded by a rapidly solidified weld zone offers the potential of producing materials with unique property combinations, even when the powders compacted are conventional materials. Obviously, for these properties to be attained, the compaction conditions have to be optimized. Until the optimum conditions are achieved, the properties will vary from those of the powder to those of the a fully bonded compact. The hardness of dynamic compacts is significantly above that of similar alloys produced by conventional compaction or ingot metallurgy. The hardness of dynamic compacts is above that obtained by normal work or shock hardening.

Hot isostatic pressing (HIP)

If the densification is achieved by heating alone, the process is called *sintering*; if it is achieved by pressure alone it is called *cold isostatic pressing*; if by heat and pressure together, then *hot isostatic pressing* (HIPing). In practice a cycle of pressure steps may be used: sintering is often preceded by cold pressing; HIPing may be preceded by sintering , and so forth. The simpler of these processes have been used for decades-some of them for centuries-as a way of making useful components from powders. They, and the more sophisticated HIP and sinter-HIP routes have lately attracted additional attention as ways of fabricating special tool-steels, advanced superalloys, novel dispersion-strengthened alloys and high performance ceramics; in short, for making useful shapes out of materials which are difficult to shape in any other way.

Models are only useful if they have predictive values. In a process as complicated as sintering or HIPing, it is unrealistic to imagine that the models accurately reproduce all the details of the real process. But it is reasonable expectation that they contain the right physical quantities (pressure, temperature, particle size, density and so forth) combined in the correct way; it is the constants of proportionality which are less certain. If valid, the models will then describe the remaining data accurately and can then de expected to predict the outcome of further hypoeutectical o proposed, runs.

There is a further difficulty: it is the imprecision of values for material properties (diffusion coefficients, creep constants and so forth). Powders never have exactly the same properties as the bulk solid from which they were made because of the unusual, often savage, processes used to make them. For this reason, the material property values may have to be "tuned", using information from a small number of sintering or HIPing experiments.

With all these problems, it might be asked wether modelling is worth the effort. But the potential gains in understanding and in the ability to control powder consolidation to give a realiable, high quality product, are enormous. Experiments are currently being conducted to check and refine the calculations. Once this has been done, the remaining problem is that of technology transfer: how can these complex results be presented in a way which helps the materials engineer design HIP cycles and select materials for the HIPing process. The best way of doing this appears to be through the careful preparation of computer software which, for a selected material, will evaluate the consequences of any proposed HIP cycle, showing the operator the final density, other possible changes of structure, and suggesting to him the way in which the process variables can be traded off against each other to optimize the process; it must, however, be recognised that material properties are so variable that a tuning process, in which the equations are calibrated to the results of real HIP runs, will always be necessary.

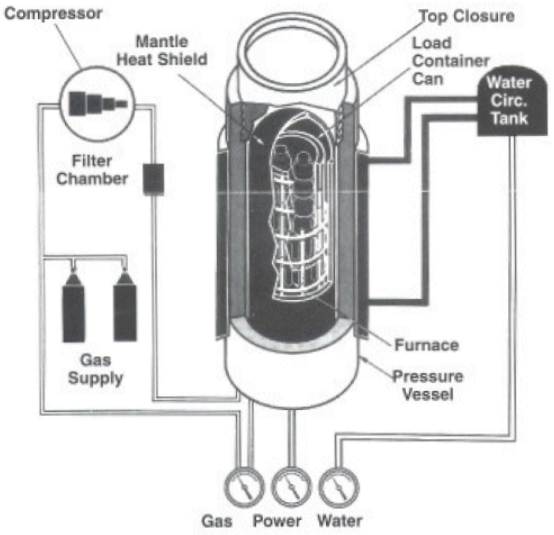


figure (9) hot isostatic pressure

2.4 Sintering

Sintering is the process by which metal powder compacts (or loose metal powders) are transformed into coherent solids at temperatures below their melting point. During sintering, the powder particles are bonded together by diffusion and other atomic transport mechanisms, and the resulting somewhat porous body acquires a certain mechanical strength.

The sintering process is governed by the following parameters:

- *temperature and time,*
- *geometrical structure of the powder particles,*
- *composition of the powder mix,*
- *density of the powder compact,*
- *composition of the protective atmosphere in the sintering furnace.*

Temperature and time

The higher the sintering temperature, the shorter is the sintering time required to achieve a desired degree of bonding between the powder particles in a powder compact (specified e.g. in terms of mechanical strength). This constitutes a dilemma: From the view point of production efficiency, shorter sintering times would be preferable; but the correspondingly higher sintering temperatures are less economical because of higher maintenance costs for the sintering furnace. In iron powder metallurgy, common sintering conditions are: 15 - 60 min at 1120 - 1150°C.

Geometrical structure of the powder particles

At given sintering conditions, powders consisting of fine particles or particles of high internal porosity (large specific surface), sinter faster than powders consisting of coarse compact particles. However, fine powders are usually more difficult to compact than coarse powders, and compacts made from fine powder shrink more during sintering than compacts made from coarse powder.

Composition of the powder mix

The components of powder mixes are selected and proportioned with a view to achieving desired physical properties and controlling dimensional changes during Sintering. When mixes of two or more different metal powders are sintered, alloying between the components takes place simultaneously with the bonding process.

At common sintering temperatures (1120 - 1150°C), alloying processes are slow (except between iron and carbon), and a complete homogenization of the metallic alloying elements is not achievable. If the powder mix contains a component that forms a liquid phase at sintering temperature (e.g. copper in iron powder mixes), bonding between particles as well as and alloying processes are accelerated.

Density of the powder compact

The greater the density of a powder compact, the larger is the total contact area between powder particles, and the more efficient are bonding and alloying processes during sintering. Furthermore, these processes are enhanced by the disturbances in the particles crystal lattice caused by plastic deformation during compaction.

Composition of the protective atmosphere in the sintering furnace

The protective atmosphere has to fulfill several functions during sintering which in some respects are contradictory. On the one hand, the atmosphere is to protect the sinter goods from oxidation and reduce possibly present residual oxides; on the other hand, it is to prevent decarbonization of carbon-containing material and vice versa prevent carbonization of carbon-free material.

This illustrates the problem of choosing the right atmosphere for each particular type of sinter goods. In iron powder metallurgy, the following sintering atmospheres are common:

- Reducing-decarbonizing type: hydrogen (H_2), cracked amonia ($75\%H_2$, $25\%N_2$)

- Reducing-carbonizing type: endogas ($32\%H_2$, 23 %CO, 0-0.2%CO_2, 0-0.5% CH_4, bal.N_2),

- Neutral type: cryogenic nitrogen (N_2), if desirable with minor additionsof H_2 (to take care of residual oxides) or of methane or propane (to restore carbon losses).

At a cursory glance, the choice may seem obvious; A reducing atmosphere for carbon-free materials and a non-decarbonizing or neutral atmosphere for carbon-containing materials. However, apart from economical considerations, there are some technical and thermodynamical problems which complicate both, the choice and the control of the proper atmosphere.

Sintering in presence of a transient liquid phase

In the case of having a compact made from a mixture of particles of two different metals, if one component of the mixture melts at sintering temperature, the arising liquid phase is first being pulled by capillary forces into the narrow gaps between the particles of the solid component, creating the largest possible contact area between liquid and solid phase.

Then, alloying takes place and, if the initial proportion of the liquid phase is smaller than its solubility in the solid phase, the liquid phase eventually disappears. The bulk volume of the compact swells because the melting particles leave behind large pores, while the framework of solid particles increases in volume corresponding to the amount of dissolved liquid phase.

Activated sintering

A special kind of sintering with a transient liquid phase is often referred to as *Activated sintering*. Here, a base powder is admixed with a small amount of a metal or metal compound which, although having a melting point above sintering temperature, forms a low-melting eutectic together with the base metal.

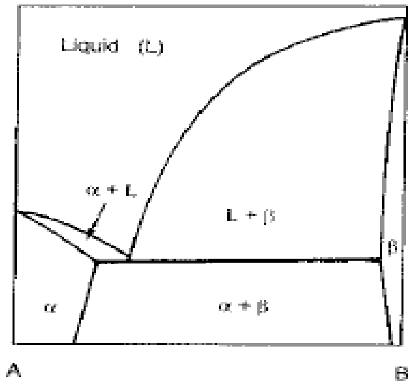


fig (10). Activated sintering by creating a low melting eutectic between base metal and "activator".

The added metal or metal compound is called the *activator*. During sintering, atoms from the activator diffuse into the particles of the base metal until the latter begin to melt superficially. This superficial melting enhances the formation of necks between adjacent particles of the base metal. As the activator continues to diffuse deeper into the particles of the base metal, the liquid phase (eutectic) disappears again. Activated sintering is utilized e.g. in the manufacturing of so called *heavy metal*.

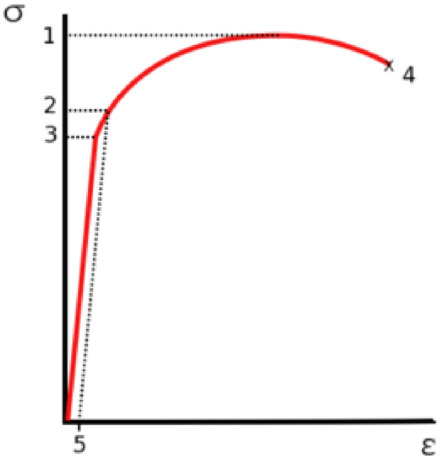
3. MECHANICAL PROPERTIES OF SINTERED STEELS

Iron, as a solid, forms a crystal where the atoms align in periodic structures similar than bricks in a wall. The properties of these structures like periodicity or directionality, phase changes occur in them (polymorphism) and their crystal defects such as dislocations or vacants in lattice sites are the responsible of the mechanical properties of materials. For example, alloying is important because it not only provides strength and corrosion resistance but also allows shifts in the stable crystal structures and properties and dislocations play the most essential part in the plastic deformation.

Since the dominant application of P/M steels are for mechanical components it is important to understand the mechanical properties. Next we will describe them and their most important parameters of influence.

Tensile Strength/ Ductility

strength measures the engineering stress applied at the point when it fails. It is an intensive Tensile property of the material, which not only depends on the type of material but also the preparation of the specimen and the temperature of the test. In other words, the amount of force the material can withstand when being stretched. Tensile test use a sample of sintered materials and pull it to failure. This destructive event measures the force and stretch during testing. Stress is simply the load divided by the cross sectional area at the center of the test bar. Strain is the change in a dimension divided by the original dimension. Metals have a linear stress-strain relationship up to the yield point. For most metals yield point is not sharply defined. Below the yield strength all deformation is recoverable, and the material will return to its initial shape when the load is removed. For stresses above the yield point the deformation is not recoverable, and the material will not return to its initial shape. This unrecoverable deformation is known as plastic deformation. For many applications plastic deformation is unacceptable, and the yield strength is used as the design limitation. After the yield point, steel and many other ductile metals will undergo a period of strain hardening, in which the stress increases again with increasing strain up to the ultimate strength. Ductile metals do not have a well defined yield point. A common measure of ductility is elongation, given as total stretch to failure divided by the initial center test length. It has no unit, so it is given as a percent. Another measure of ductility is the change in cross-sectional area, and it, too, is given as percent.



figure(14) typical curve stress-strain for a ductile metal

Hardness

hardness is the characteristic of a solid material expressing its resistance to permanent deformation. Hardness can be measured on various other scales, like Rockwell, Vickers, and Brinell and they can be compared using practical conversion tables, but Rockwell scales are used more in ferrous P/M. Primarily used in engineering and metallurgy, indentation hardness seeks to characterize a material's hardness; i.e. its resistance to permanent, and in particular plastic, deformation. It is usually measured by loading an indenter of specified geometry onto the material and measuring the dimensions of the resulting indentation. A high hardness gives greater resistance to scratching and wear. On the other hand, a low hardness may suggest easy scratching.

Impact strength/ Toughness

Impact is a very important phenomenon in governing the life of a structure when a material must withstand sudden loading, as might be encountered in accidents. Impact strength is the energy required to fracture a specimen subjected to shock loading, as in an impact test. A concept very closed to impact strength is toughness, the resistance to fracture of a material when stressed. Toughness can be found by taking the area underneath the stress-strain curve. It is defined as the amount of energy per volume that a material can absorb before rupturing. There are two main different kind of impact test, the Izod test and Charpy test. In the Izod test an arm held at a specific height (constant potential energy) is released. The arm hits the sample and breaks it. From the energy absorbed by the sample, its impact strength is determined. The Izod impact test differs from the Charpy impact test in that the sample is held in a cantilevered beam configuration as opposed to a three point bending configuration.

Charpy impact test is a standardized high strain-rate test which determines the amount of energy absorbed by a material during fracture that give us information of material's toughness. The test was developed in 1905 by a French scientist and the apparatus consists of a pendulum axe swinging at a notched sample of material. The energy transferred to the material can be inferred by comparing the difference in the height of the hammer before and after a big fracture.

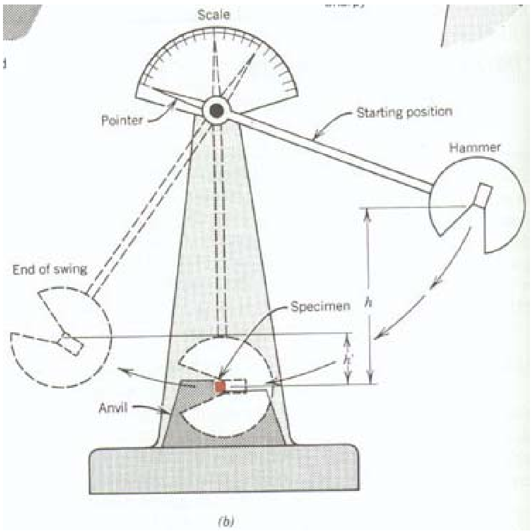


fig [15] Charpy test

Fatigue

An important mechanical property for many ferrous steels is fatigue resistance. This is a measure of the stress that a material can see repeatedly without faliure. he maximum stress values are less than the ultimate tensile stress limit, and may be below the yield stress limit of the material. The process starts with dislocation movements, eventually forming persistent slip bands that nucleate short cracks and go on with the propagation until material failures. Damage is cumulative and materials do not recover when rested. Fatigue strength is important for components that will be in service for long time, such as in automobile engines or office machines.

The properties of sintered steels can approach those observed via other metalworking techniques and there are several ways to achieve desired mechanical properties with iron-based sintered materials, where the most important parameters of influence are:

- Density
- Sintering conditions
- Alloying elements
- Heat treating conditions

These parameters should be controlled to within the closest possible limits, because even small variations may cause an unacceptably wide scatter of dimensional changes during sintering and thus spoil the dimensional stability of the sintered parts.

Density

Porosity and density are important parameters with respect to the physical properties of sintered structural parts. Pores reduced the effective cross-sectional area and negatively affect hardness and tensile properties. Another factor is the stress concentration at each pore. Ductility is also sensitive to porosity and pore shape, as are most other mechanical properties; impact energy, fracture toughness, and fatigue strength have the greatest sensitivities. Even in those materials possessing full density, inferior properties can occur as a result of microstructural defects. Major determinations from quasistatic testing are the transverse rupture strength, yield strength, ultimate tensile strength, elongation to fracture, reduction in area, elastic modulus, and Poisson´s ratio. Likewise, hardness tests are usually done on undeformed portions of tensile samples. Several attempts have been made to find predictive relations between these various measures of mechanical properties. However, such efforts prove invalid. All the quasistatic mechanical properties vary with the density and microsturcture. Furthermore, the presence of defects lowers strength.

Just a porosity degrades strength, it also degrades ductility, but there is an additional sensitive to pore shape and placement. Smooth pores at large spacings are less detrimental than small, closely spaced pores. The negatives effect of pores on ductility is due primarily to the initiation of cracks at the pores. Thus, beyond a porosity effect on ductility, there is a further sensitivity to the pore shape.

Interestingly, cast and wrought materials often posses pores. However, a small level is not detrimental, unlike the situation in P/M steels. This is due to the close spacing of pores in sintered materials. Thus, the shape, spacing, size, and placement of pores contribute to a high level of variability in ductility in P/M materials. With greater than 15% porosity, ductility is often negligible.

Although quasistatic mechanical properties are degraded by porosity, a more severe detriments occurs in the dynamic properties. These are the properties of impact strength, fracture toughness and fatigue strength. They are also sensitive to microstructure. At low sintered densities, it is unwise to subject sintered steel to cyclic stresses or impact loads. At high densities, the behavior depends on the microstructure, and is affected by the pore side and pore spacing.

Pore shape is another factor that can affect sintered properties. Thus as a first point in understanding properties of P/M materials there is a requirement that porosity and pore structure differences are measurable. Creating a favorable pore shape depends on processing conditions. Generally, those actions that improve sintering are favorable to the mechanical properties. At low densities, the strength is limited by the interparticle bond size. For the higher densities, the strength has a complex dependence on the pore structure and the particle boundaries.

Sintering conditions

The followings outcomes depend on what sintering conditions are used:

1. How fast and efficiently powder particles in the compact weld together and pores become rounded.
2. How quickly homogenization of alloying elements takes place.
3. The extend of oxidation of sensitive elements.

In powder metallurgy industry, the efficiency of the sintering process is judged by the quality of the physical properties it lends to the sintered parts in relation to its processing costs. Thus, in the manufacturing of structural parts based on iron powder, a prime interest is to achieve optimal strength and dimensional stability at lowest possible sintering temperatures and shortest possible sintering times.

The are big evidences about the influence of sintering time and temperature on density on tensile strength and elongation of iron powder compacts

- Tensile strength and elongation adopt noticeable values first at sintering temperatures above 650 and 750°C respectively. From there-on, they increase almost exponentially until reaching an intermediate maximum at approx. 900°C. Just above 910°C, where the crystal structure of iron changes from ferrite to austenite, the values of tensile strength and elongation suddenly drop a little and then increase again, but more slowly than below 910°C.
- The temperature dependence of the self-diffusion coefficient of iron, drawn in the same diagram for comparison, drops dramatically as ferrite changes to austenite (Dg»Da/300).

The parallelism between these two features is not incidental. To the contrary, it is strong evidence of the predominant role which volume diffusion plays in the sintering process of iron. The effect of the drastic change of the diffusion coefficient on tensile strength and elongation is muffled by the following circumstance: sintering begins already during the heating-up period, while still in the ferrite state, and those which are heated up to higher temperatures have already acquired a certain level of strength before they change from ferrite to austenite.

Heat-treating conditions

Approximately 60% of the current P/M steel production uses a heat treatment after sintering to attain the desired final strength and hardness. Sometimes the heat treatment can be performed as part of cooling from the sintering temperature. More commonly is a separate operation that occurs after sintering to produce the desired phases of metal giving the microstructure and properties required for successful service.

The simplest postsintering heat treatments are annealing, normalizing and solutionizing. They involve heating the compact to a high temperature to remove residual stresses from machined or deformed components and to stabilize the microstructure. The important details in determining a heat treatment are as follows:

- Heating rate, this is seldom critical
- Soak temperature and time
- Cooling rate and atmosphere or quenching fluid used for cooling
- Intermediate hold temperatures and times during cooling
- Reheat temperatures and time
- Final cooling rate and medium

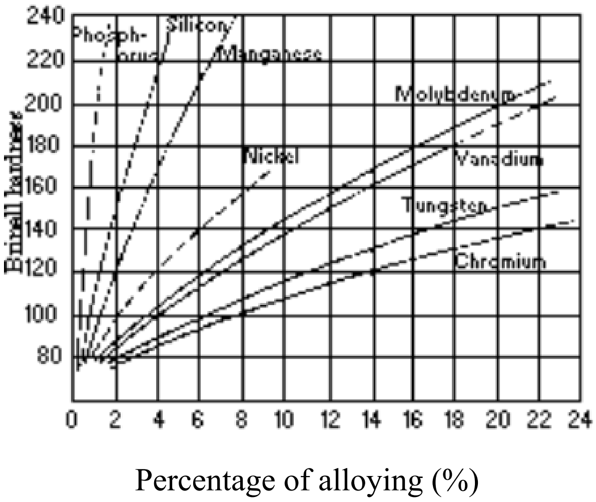
A successful heat treatment cycle depends on identification of each of this parameters and effective decisions required knowledge of the alloy, carbon level, porosity and desired properties.

4. INFLUENCE OF ALLOYING ELEMENTS ON SINTERING AND PROPERTIES OF SINTERING IRON STEELS

Alloying elements, dissolved in a base metal, give rise to the formation of various microstructures and increase the materials resistance to the formation.

In principal alloying elements have the same effects on sintered steels as on conventional steels. However, not all elements commonly alloyed with conventional steels can be used on sintered steels. Some of them (e.g. Mn and V) are to easily

oxidized in commercial sintering atmospheres. On the other hand elements undesirable in conventional steels (e.g. Phosphorous) can have beneficial effects in sintered steels.
Alloy compositions of sintered steels for structural parts have to be careful not only with respect to desire strength, but also with respect to dimensional stability during sintering. With alloy composition yielding hardness levels above 150-180 HV, it is important that dimensional changes of the structural parts during sintering are as small as possible and, even more important that the scatter of these dimensional changes in kept within the closest possible limits.
The microstructures produced with additions of different amounts of alloying elements have influence in mechanical properties and parameters such as grain size will influence too. With decreasing grain size, strength increases, but with increasing grain size ductility is improved. A very efficient way to boost tensile strength and hardness of sintered iron is to alloy it with carbon. Being an interstitial alloying element, carbon dissolves rapidly in the lattice during sintering.



Fig(16) Alloying effect on hardening

Next we are describing the most important alloying elements in based iron system.

Phosphorous

In conventional steel making, phosphorus is a most undesirable element since it provokes irreparable segregation during solidification, making the steel brittle. In iron powder metallurgy, however, phosphorous has shown much potential as a strengthening alloy. It is normally added to iron powder as a very finely ground Fe_3P. Phosphorus alloyed sintered steels are characterized by a unique combination of strength and ductility. The beneficial effect of alloying with phosphorus and then the activated sintering that takes place can be explained by the following three mechanisms:

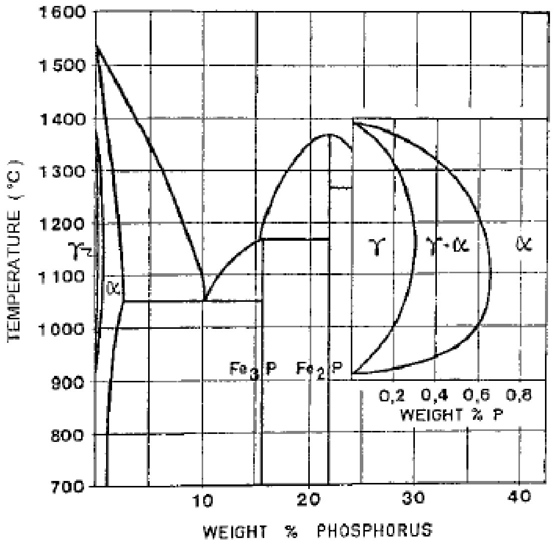


fig (17). Fe-P Phase Diagram

a) *Liquid phase sintering* - a transient liquid phase is formed at 1050°C by the peritectic reaction $Fe_3P + \alpha \rightarrow L$, which facilitates diffusion and densification during sintering.

b) *Ferrite stabilization* - phosphorus stabilizes ferrite and thereby a transformation from austenite to ferrite occurs as phosphorus diffuses into the iron particles during sintering. Since the diffusivity in ferrite is much higher than in austenite, the sintering gets more effective leading to reduced porosityand rounder pores.

c) *Solid solution hardening* - small amount of phosphorus in iron has a strong solution hardening effectand contributes to the high strength of phosphorus alloyed sintered steels.

Molybdenum

Addition of molybdenum or pre-alloyed (0,85-1,5%) to iron alloys has only a minor effect on compressibility compared to plain iron. The advantages are increased dimensional stability and hardenability and in molybdenum-phosphorous system the embrittlement cause by phosporous additions can be avoided by molybdenum additions, because at low phosphorus contents it prevents segregation to grain boundaries. At higher phosphorus contents both molybdenum and phosphorus are enriched in the grain boundaries, but the effect on mechanical properties is limited. The beneficial effect of molybdenum is however suppressed by the presence of carbon in the material. molybdenum stabilizes ferrite and contributes to the solid solution hardening in the samenway as phosphorus. It amplifies the positive effects of phosphorus and suppresses the negative effect of grain boundary embrittlement. It is also important to put emphais in the fact that molybdenum has limited affinity to oxygen and dosen't cause problem during sintering.

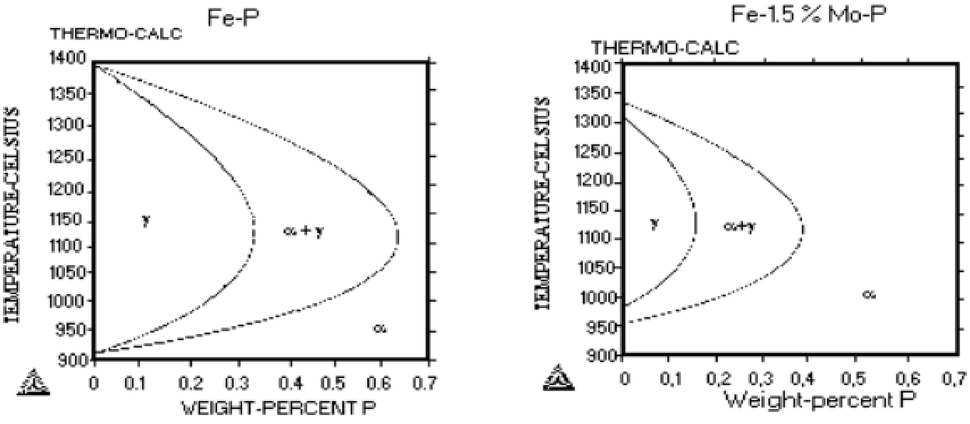


fig (18). Movements into the transition γ-α nose with Mo additions

Copper

Copper is added to the basic iron-powder usually in amounts from 1.5 to 4 wt % and have a two fold benefit:

-Copper melt at 1085ºC (below sintering temperature) and rapidly infiltrates the pore system of a compact powder, from where it diffuses relatively easily into the iron particles.

-Copper is dissolvable in austenite up to approximately 9 wt %, but only up 0,4 % wt in ferrite, consequently iron copper alloys can be precipitation-hardened by low temperature annealing after sintering , and they actually do so to a certain extend anyway , when passing the cooling zone of the sintering furnace.

Section 2 EXPERIMENTAL PROCEDURE

5. AIM OF WORK

In this research we have tried to analyse the results obtained for the impact strength of sintered Fe-Mo-P steels, as well as some related characteristics and parameters like density, the dimensional behaviour, microstructure and fractured surface . In order to be successful in our study we had to develop an appropriate method based in the following steps.

First, we had to prepare a suitable numbers of samples that ensured us enough data for our investigation. In this way forty samples were made in the laboratory, two for each one of the two different sintering temperatures, 1120º and 1200º, and each one of the ten different composition. We have used sponge iron base powder NC 100.24 (supplied by Höganäs AB) and amounts of Mo and Fe_3P powder were added to get the composition we needed. Mo powder additions of 1.5 wt % and phosphorus in the form of Fe_3P as a fine grained (mean size 10 μm) containing 15,6 wt % P, in different amounts to obtain varying phosphorus content in mixtures, namely; 0.0; 0,3; 0.4; 0.5; 0.6 wt %. The powders were mixed and after compacted at 600 MPa in uniaxial hydraulic press. The specimens were sintered under pure hydrogen atmosphere conditions with a heating rate to isothermal sintering temperature was 10^{o}C/min and cooling rate 20^{o}C/min.

Secondly we had to calculate the density of each sample by geometrical method, both of green and sintered density, taking the measures of the weight, length, wide and high. Once done we tested the specimens in Charpy test and get the energy absorbed that provide us an idea about the toughness of the material. For both of these aspects, porosity and energy, the role of phosphorus and molybdenum is very important and one of our main goal will be determinate those roles. It is well known that alloying elements have a strong effect in sintered steels, improving density and mechanical properties. Porosity and pore size and shape have also a big influence in impact strength and we will try to describe them. Along of our investigation we will determinate and analyze other sintering phenomenon and the behavior of phosphorus as *activator* and its ferrite stabilizing effect. Addition of molybdenum to phosphorous system may have three main benefits; avoiding the embrittlement caused by phospohorus grain boundary segregation, improving hardenability and dimensional behavior. For all these reasons we may expect improvements for levels of density and absorbed energy in the impact test.

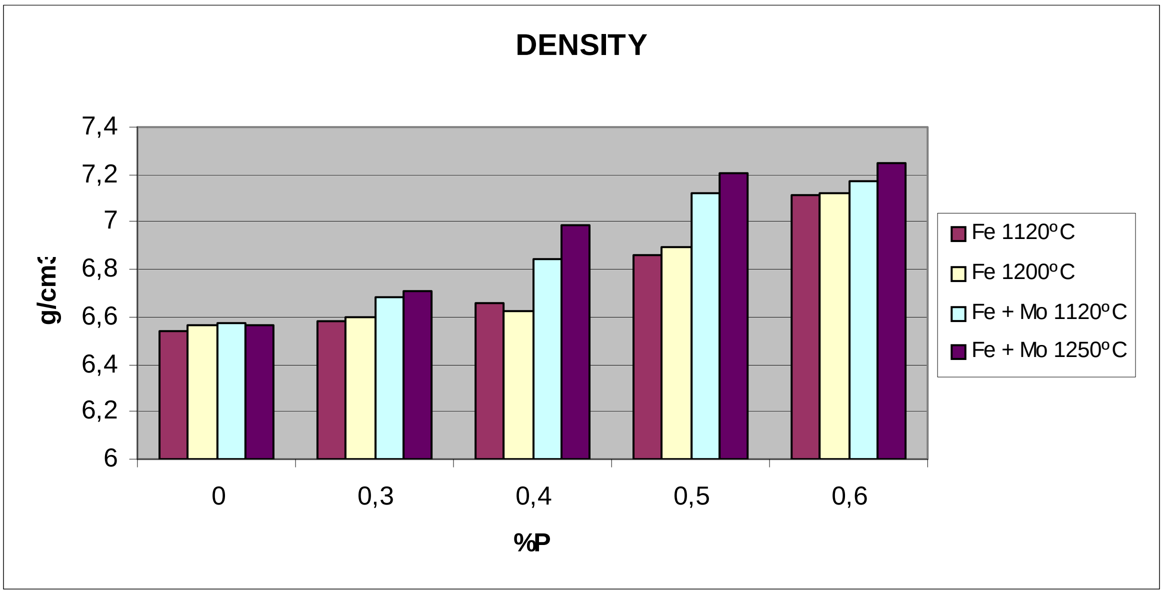
Finally we will try to corroborate our outcomes characterizing those samples that can be more useful for our research. Looking to the microestructure we can compare level of porosity, pores shape and size, distribution and scanning electron micrograph (SEM) will help us to analyze the fracture surface, in order to be able to check cohesion in particles, strain hardening caused by deformation and possible embrittlement due to segregation to grain boundaries caused by phosphorus.

5. ANALYSIS OF DENSITY, DIMENSIONAL BEHAVIOR AND MICROESTRUCTURE

5.1 Analysis of porosity

Pores degrade the mechanical properties, partly because of the reduced area supporting the load. Another factor is the stress concentration at each pore. Impact strength and energy absorbed as most other mechanical properties, are also sensitive to porosity and pore shape. Even in those materials possessing full density, inferior properties can occur as a result of microstructural defects. The presence of defects and its influence in impact energy will be discuss in great detail later in point 6 of this document. By now we will pay attention to density, porosity and pore shape.

The following chart show density after sintering for all specimens function of composition and temperature. As we told before density is calculated by geometrical method.



Fig(19) Density obtained after sintering

As we can see in the graphic density increase with both of alloying elements, molybdenum and phosphorus due to they have a strong effect on the sintering mechanism. During sintering at 1120ºC, the phosphorous acts like an activator when concentration at the surface of the iron powder particles temporarily are higher and the particles melt superficially, enhancing the formation of necks between adjacent particles of iron. Then, a second benefit of phosphorous becomes effective: Surface regions of the iron particles have changed from austenite to ferrite, where the coefficient of selfdiffusion for iron is much greater. Consequently, at equal temperature, sintering proceeds faster in ferrite than in austenite, achieving a higher densification.
Molybdenum has also a important role during the sintering: in combination with phosphorus has a strong effect on the sintering mechanism moving both the γ / (α + γ) and (α + γ) / α phase boundary for the lower phosphorus content as compared to material without molybdenum addition.

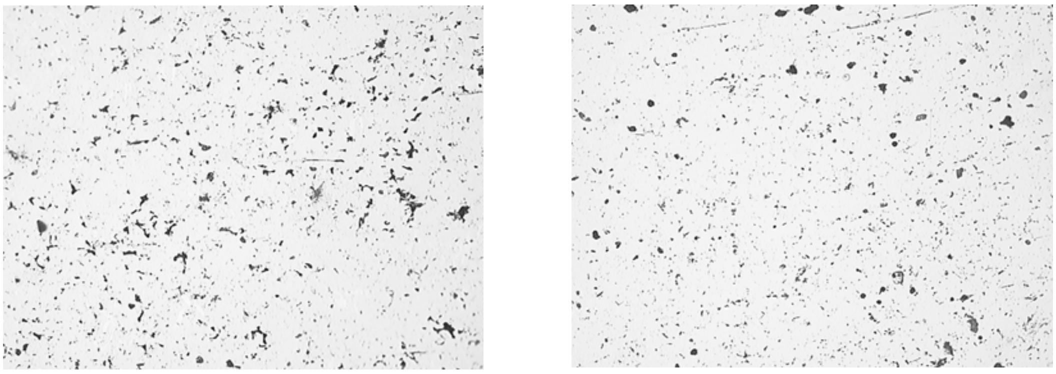
The effect of phosphorus, without presence of molybdenum, is clearer as bigger is its amount, achieving the highest densification and most important gaps for 0,5 and 0,6 percentage of phosphorus where we get 6,89 and 7.12 g/cm3 respectively. The presence of molybdenum also increases the densification in all the compositions but it has strongest effect for the range of 0,4 and 0,5 % of phosphorus where the gap of density is higher between those samples without this element.

The influence of temperature is also important and we can observe in the graphic a greater values for density in almost all the specimens for the higher temperature specially under molybdenum influence.

5.2 Metallography

A good way to certificate the level of densification, pores shape and size and the influence of phosphorus and molybdenum in porosity is studying the metallographic features of the sintered specimens. This will help us to understand in a better way their dimensional behavior during sintering and the final influence in the impact strength.

In the fig (20) the influence of phosphorous in the porosity becomes obvious; under the effect of this alloying element level of porosity is lower and pores are mainly rounded meanwhile than for reference material sponge iron they partially are. This kind of porosity shape is beneficial to improve mechanical properties like impact strength.

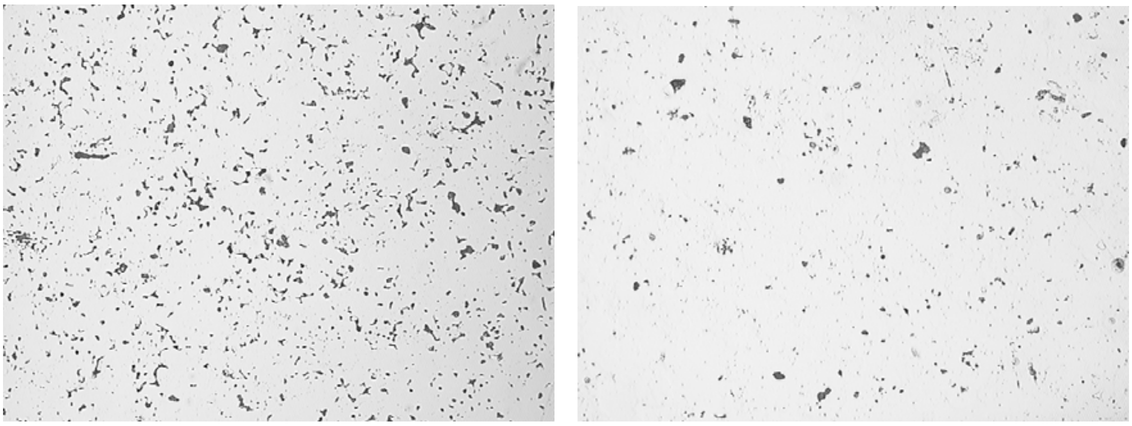


Fe 1120ºC

Fe + 0.4 % P 1120ºC

Fig (20). Porosity microscope photography

The addition of molybdenum does not make any change in the porosity- shape evolution with the raising content of phosphorous but it does in its global amount adding the final density of the specimens. The addition of this ferrite stabilizer improves specimens properties increasing their final density and therefore decreasing their porosity, fig (21).

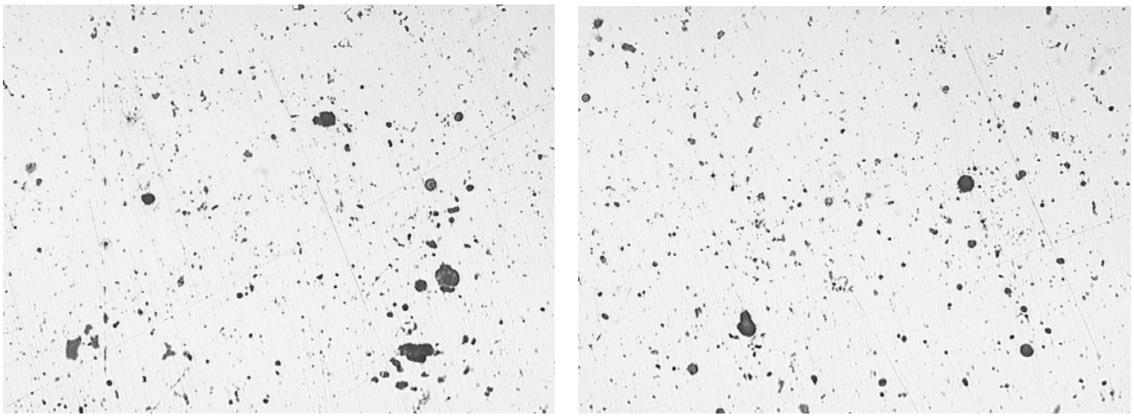


Fe + 0.6 % P 1120ºC

Fe + Mo + 0.6 % P 1120ºC

Fig (21). Porosity microscope photography

If we try to carry out the same comparison done for the first two specimens but in this case for the highest sintering temperature 1200ºC we realize about some changes in the porosity evolution. An increase in the sintering temperature improves diffusion processes that finally give us higher density and lower porosity values. Therefore porosity is lower compared to low isothermal holding specimens value and it gets lower as greater is the amount of P. Paying attention to its shape, the presence of rounded pores is very clear in both of these micrographies. fig (22)

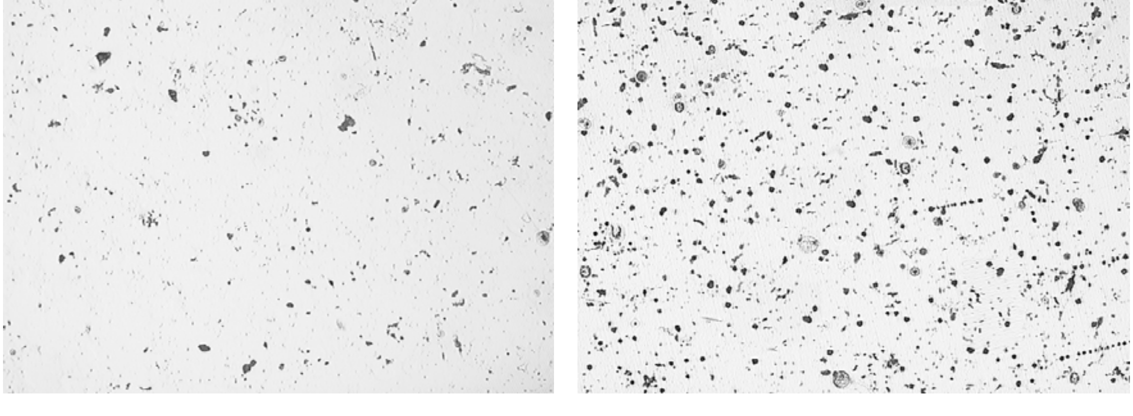


Fe + 0.4 % P 1200ºC

Fe + 0.6 % P 1200ºC

Fig (22). Porosity microscope phtography

In the next photographies we can appreciate more clearly the differences in the microstructure and porosity between two specimens sintered at different temperature, as previously commented, higher isothermal holding ensures higher final density and lower porosity specially under molybdenum influence, fig (23).



Fe + Mo + 0.6 % P 1200 ºC   Fe + Mo + 0.6% P 1120ºC

Fig (23). Porosity microscope photography

5.3 Analysis of dimensional behavior

When the phosphorous is present in the base materials, their thermal behavior experiment some important changes. In order to better appreciate the evolution of that behavior considering the increasing percentage of phosphorous, we will pay attention to the time scaled dilatometric curves [fig(24)]. It is easy to notice a softening phenomenon at the transition stages during heating and cooling processes which becomes stronger as bigger is the amount of the added substance due to its dissolution in iron. By the way, transitions during heating and cooling stages are respectively and progressively postponed and advanced which as it was mentioned before, will lead to a longer stay under ferrite diffusion conditions. As the added percentage increases, a bigger quantity of phosphorous dissolves in iron, which means less part of the crystaline structure changes its configuration due to this presence. By keeping ferrite optimum diffusion conditions, the shrinkage during the isothermal step adquires greater speed conditions which as bigger is the amount of phosphorous, closer they will be to the cooling step shrinkage speed conditions. Furthermore, and after the typical thermal expansion, for a quantity of 0,6 %, sintering shrinkage starts slighty below the isothermal holding and continuous up to the end of the whole process. Final shrinkages increase gradually obtaining notable values and observing a little gap between the first four samples and that one with the biggest amount of alloying element.

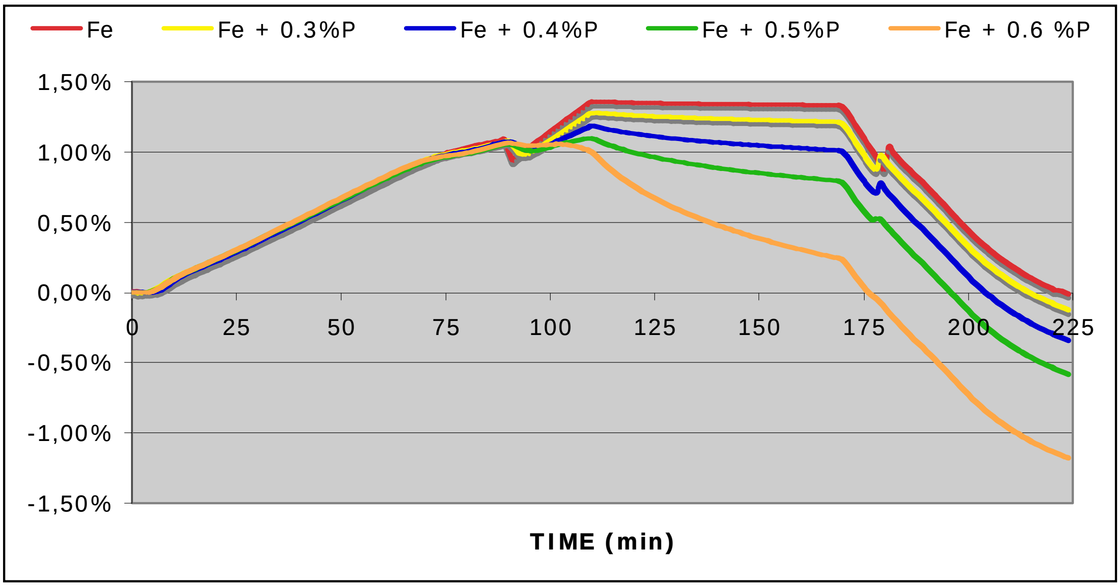


fig (24). Fe time scaled dilatometric curves

When analyzing the importance of an addition of a ferrite stabilizing element as Molibdenum, there is a clear analogy attending to the evolution of the thermal behavior of the different specimens, compared with the previous ones. However, some effects related to the influence of the Molibdenum can be appreciated [fig (13)]. The softening phenomenon the phosphorous causes is well amplified by this element during heating but specially during cooling where becomes invaluable for just 0,5 %. After a typical thermal expansion, shrinkage normally begins once the isothermal step has started, but for a 0.6 wt.% content, it does slightly below this change of stage. Final shrinkage increases gradually but in this case without any noticeable gap.

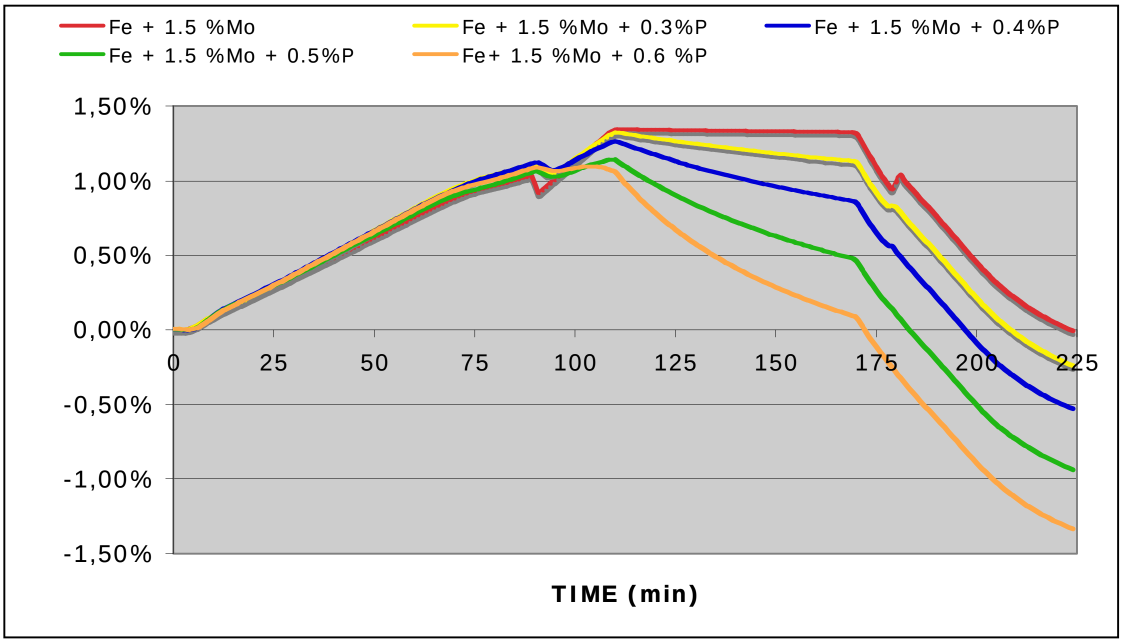


fig (25). Fe-Mo time scaled dilatometric curves

Other type of dilatometric data comparisons may help us to understand some peculiarities and the real role of the presence of P and Mo as well as the selected sintering temperature into the final steel features. Fig (26) show the maximum dimensional change obtained after the whole process and its evolution related to the fixed composition. This final dimensional change increases as the content of phosphorous does. The Molibdenum increases P power specially for the highest sintering temperature and with medium percentages of phosphorous, at which a great qualitative change is visible. The best sintering conditions are offered by adding 0,6 % of Phosphorous to the steel base and under Molibdenum stabilizing conditions in the highest isothermal holding temperture. However and attending to the chart, the most significant improvements are obtained in the highest sintering thermal state and for 0,4 – 0,5 % of added Phosphorous under Mo influence.

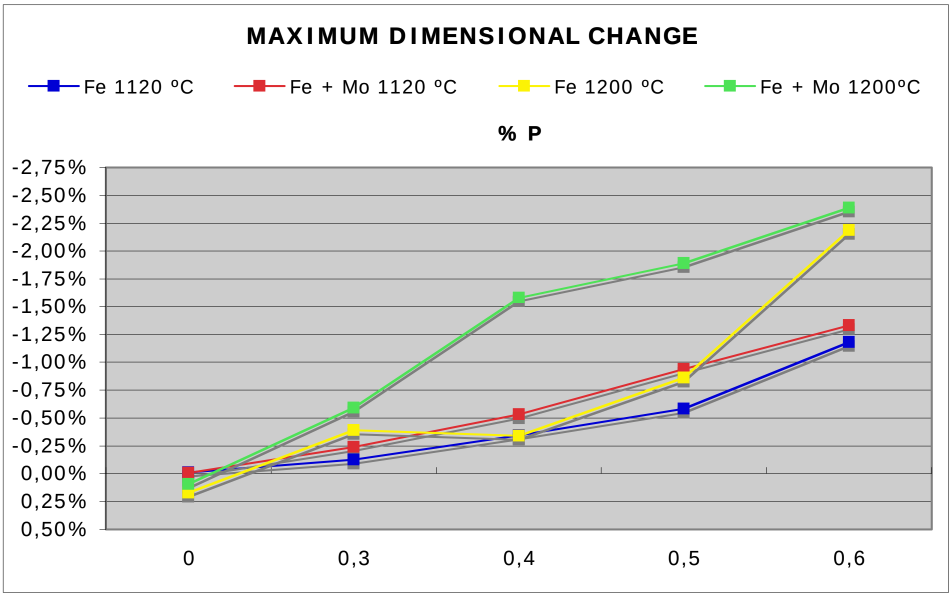


fig (26). Final dimensional change

The behavior of the sample during the isothermal holding can perfectly explain the role of the added substances into the diffusion processes and therefore most of its final properties directly related to the amount of shrinkage experimented. Next figure tries to explain the importance of the dimensional reduction that happens along the heating time. As the chart shows, this dimensional reduction increases with the amount of added phosphrous. Nonetheless the evolution for the different specimens finally stablish a bigger contraction during the heating step for the highest sintering temperature samples, showing a qualitative gap for 0,6 wt%. Those samples containing Molibdenum offer slight worse sintering behavior during heating that means Molibdenum addition just improves dimensional behavior along the isothermal step.

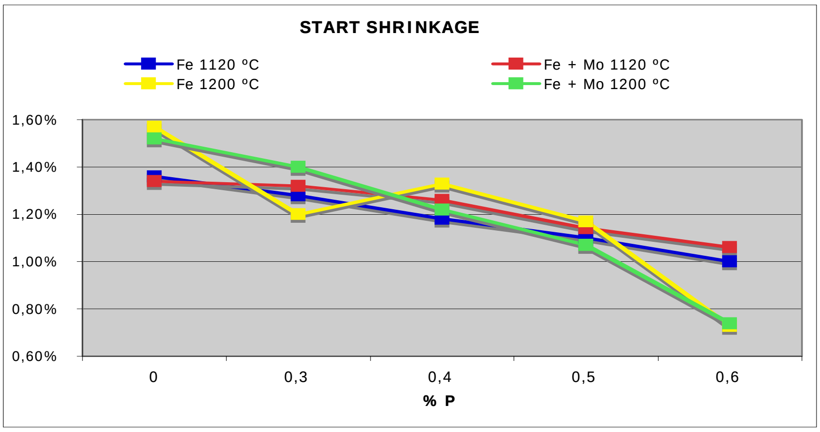


fig (24). Start in dimensional reduction after typical expansion during heating

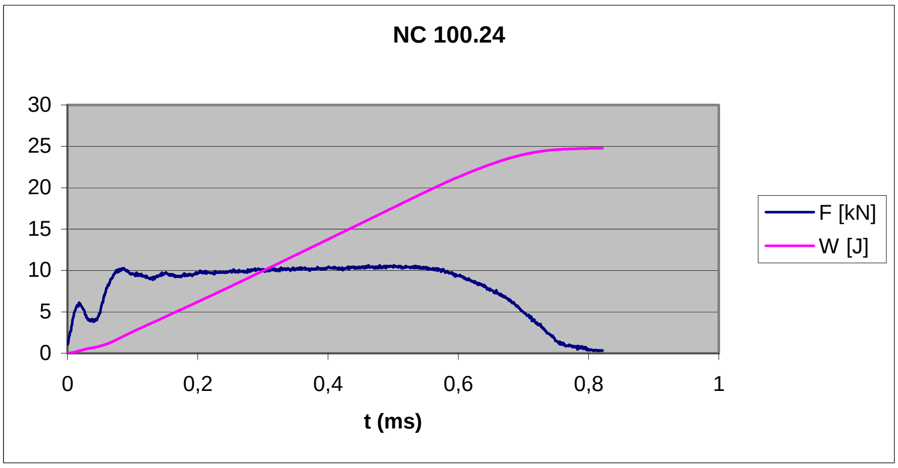
6. IMPACT PROPERTIES

After evaluate some important aspects like density, porosity and dimensional features we are in conditions to do a deep analyze of impact behavior and its relation with the parameters studied before, but first we will describe slightly how the test was carried out and under which conditions.

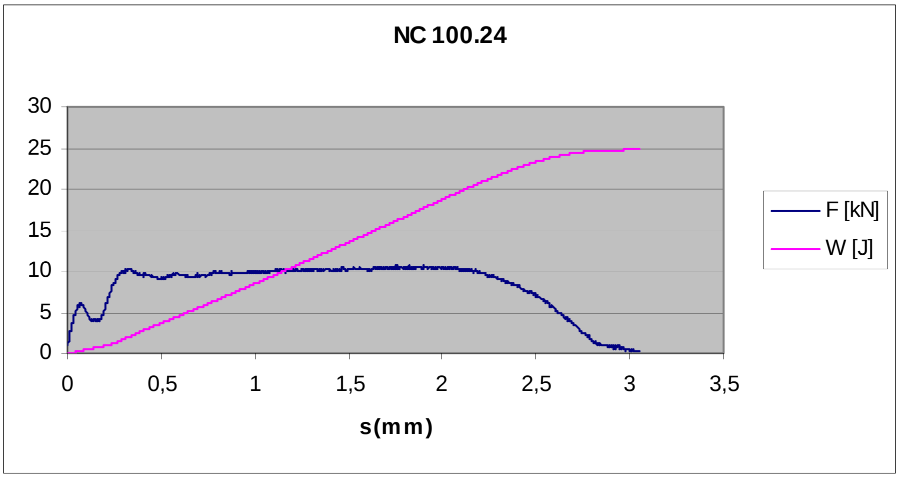
In order to get the impact properties forty samples were tried out in Charpy test. According to ASTM A370, standard untouched specimen for Charpy impact test is 10mm×10mm×55mm. The conditions under were carried out the samples were:

Angle of rise (ß)	81°
Hammermass	19,69 kg
Velocity	3,903 m/s
Room temperature	

The curve taken from the Charpy impact test are shown in the next chart, fig(). It gives us information about the evolution of load and energy absorbed like function of time and elongation for the base material, in our case sponge iron powder NC 100.24.



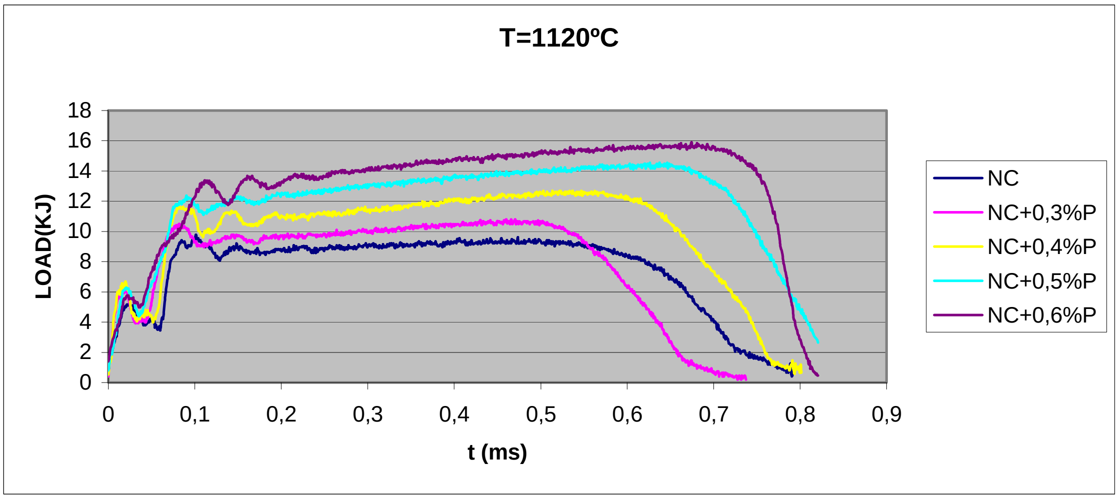
fig()Charpy impact curve for reference material



fig(27) Charpy impact curve for reference material

Looking at its curve we can appreciate typical behavior for ductile materials where we can differentiate three main stages. First a quickly increase in the load applied until it reaches a pick close to maximum. This load and energy supplied during this moment is that are necessary to start the plastic deformation of material, making possible the movement of dislocations on their slip planes. Then the load keep with a very soft increasing for a long time until it gets the maximum. In this period of time is when the material absorbs the most amount of energy in its plastic deformation. After, in the last stage, the load decreases quickly due to the fracture of material. This last stage gives us an idea about how the fracture is, ductile, brittle or mixed. If It is ductile the curve will fall down slowly and material still absorb a quite big amount of energy in this stage but it is brittle, the slope will be very high and low the energy absorbed.   At the same time we get the total energy absorbed by the sample during the impact just like the area under the load line. We can calculate it integrating the load curve along the elongation.

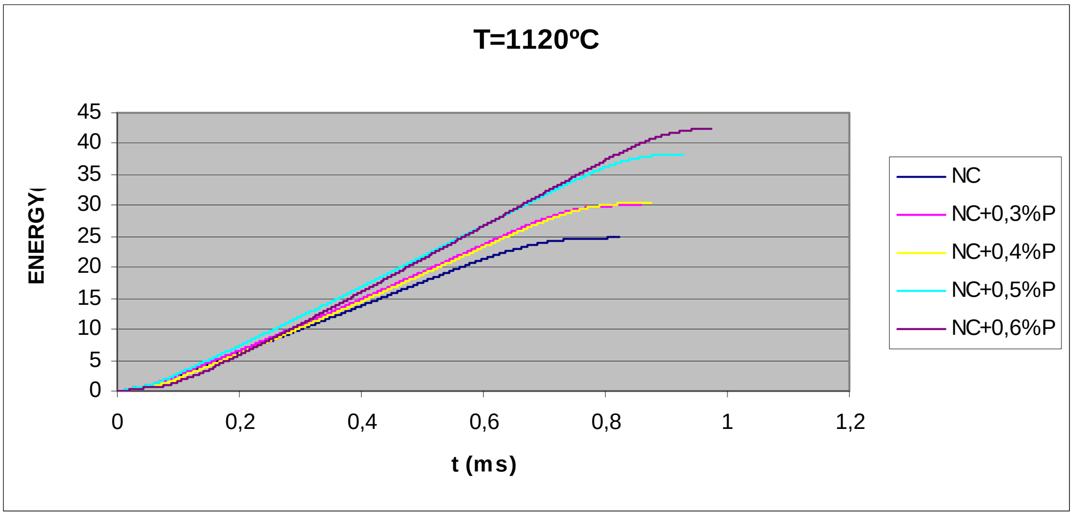
Next step in our investigation will be to analyze the influence under different amounts of phosphorus, molybdenum and sintering temperature in impact properties of our reference material iron powder NC 100.24



figure(28)Influence of phosphorus in Fe NC 100.24

Graphic shown in figure (28) gives the evolution of the load applied in the specimens during the impact test. As we may wait, values of maximum loads are higher as bigger is the amount of phosphorus added. Also the time during the samples support loads just before the fracture is longer that means greater absorbed energy and toughness.

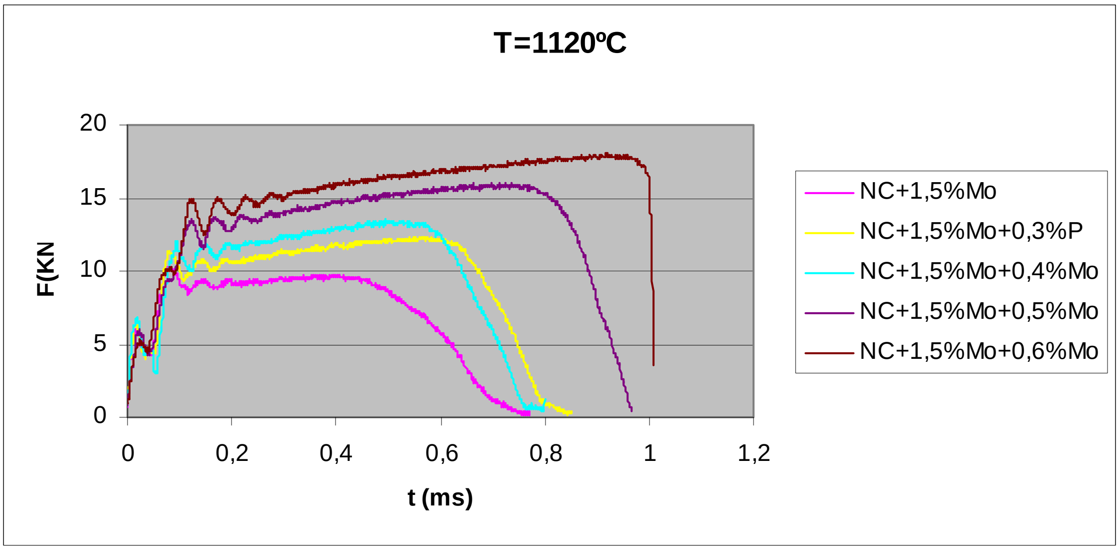
Precisely, this energy is given by the test and we show its variation under different percentages of phosphorus in figure (29).



figure(29)Influence of phosphorus in Fe NC 100.24

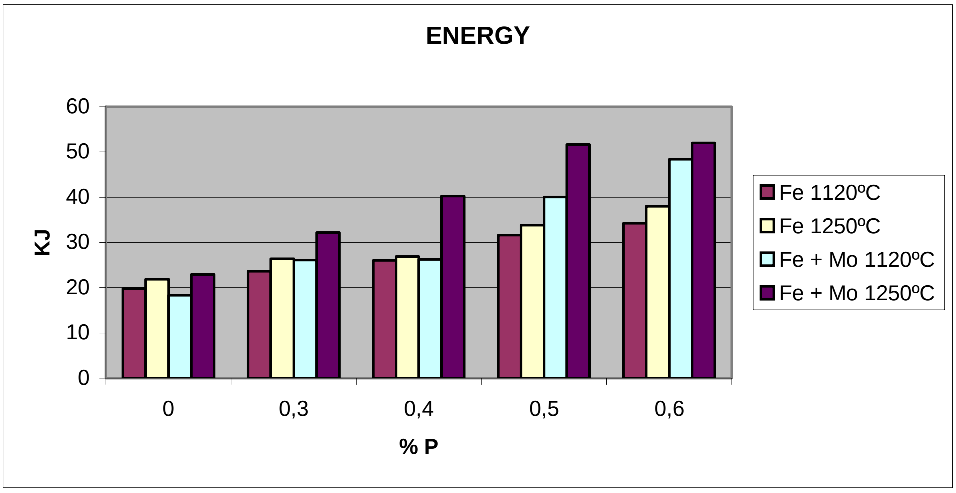
As we told before when we analyzed density, phosphorus has influence in the mechanism of sintering achieving lower levels of porosity and specific pores shape and size. Porosity reduces the amount of metal actually present in a given section of the part and when it is loaded the pores themselves can act as stress raisers. For this reason we get greater energy in those samples with higher amount of phosphorus. Looking to the charts we can conclude that addition of phosphorus, due to its activator effect during sintering, achieves good cohesion between particles improving the impact behavior of specimens.

In fig (30) we can observe the same curves obtained from the test but in this case for specimens containing molybdenum. The tendency is very similar to the lower temperature, increasing the energy as higher is amount of phosphorus. We can realise for sample with 0,6%P the load go down very quickly with almost vertical slope after cracking what makes us wonder in brittle fracture.



figure(30) Impact curves for NC 100.24+Mo

It will be more useful and easy to analyze the influence of different sintering conditions and compositions if we show the obtained data from the impact test all integrated in the same graphic like in fig (31) where are represented total absorbed energy for all studied specimens.



fig(31) Energy absorbed

If we observe outcomes for samples without phosphorus content we may conclude that molybdenum has no influence by itself in density and toughness, only powers the activator effect of phosphorus when it is present in higher amounts avoiding segregation and improving its properties. In any case, the effect of segregation is difficult to appreciate since as specimens without molybdenum improve their impact properties even for the highest amount of phosphorus, although is true not so much as those that contents molybdenum. Temperature has always good benefits for density and impact strength supplying more energy to sintering and improving diffusion process specially under molybdenum influence where the gaps between two isothermal holding are significant.

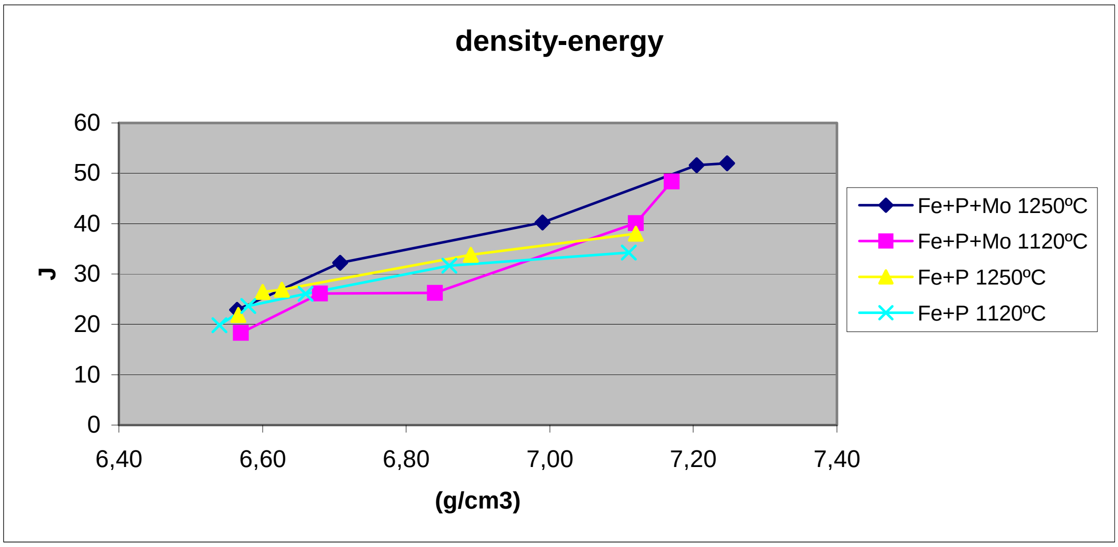


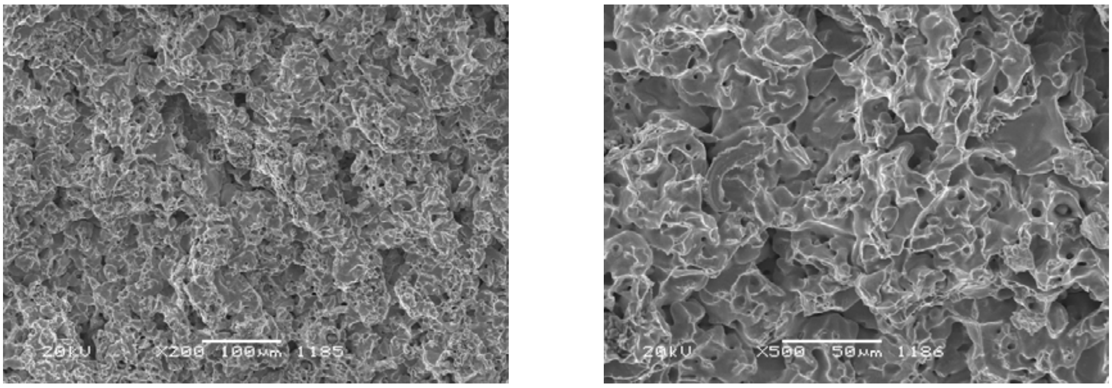
Fig (32) energy in function of density

In this chart, fig (32) we can observe the correlation between energy absorbed and density. We have already emphasize several times the strong influence that porosity has in the toughness of materials. Here the trend is clear and is easy to notice that energy absorbed increases when density does. However, it is important to pay attention in those samples with great percentages of phosphorus and high density do not achieve to absorb such energy as we could wait, meanwhile those with molybdenum get much higher energy during the impact even for similar level of density. If we look the chart we can see energy absorbed by those specimens without molybdenum keep stable and they do not get above 40 jules even for high densities. This fact may due to border grain segregation of phosphorus what makes not to reach so high energy levels and produces embrittlement.

7. FRACTURE OF SINTERED MATERIALS

Scanning electron micrograph of surface fracture will give us important and useful information to clarify the cause of fracture. Depending on the composition and sintering temperature we can get ductile or brittle cracking, intergranular or transgranular fracture just as possible segregation and strain hardness.

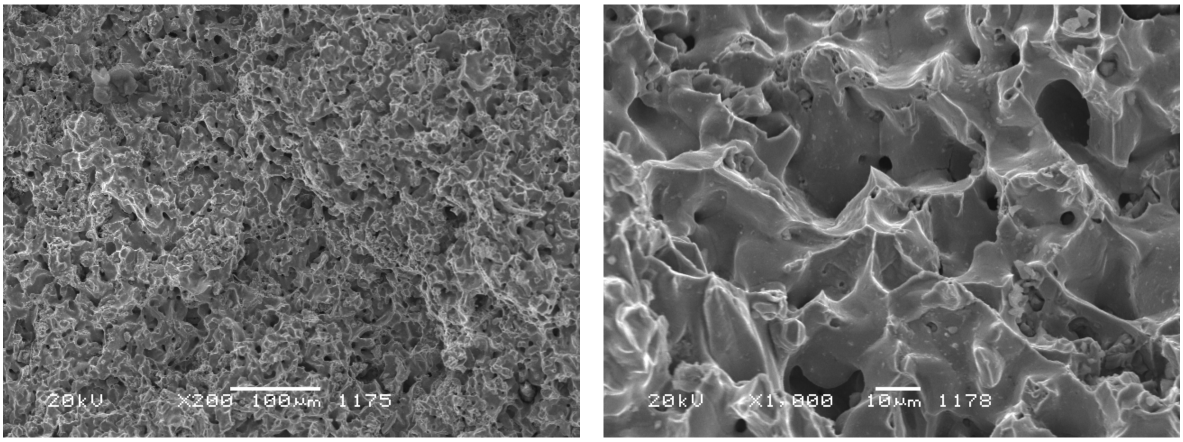
First two photographs shows fracture surface of our base material, sponge iron NC 100.24, fig (33)



Fig(33) micrographs for sponge iron NC 100.24

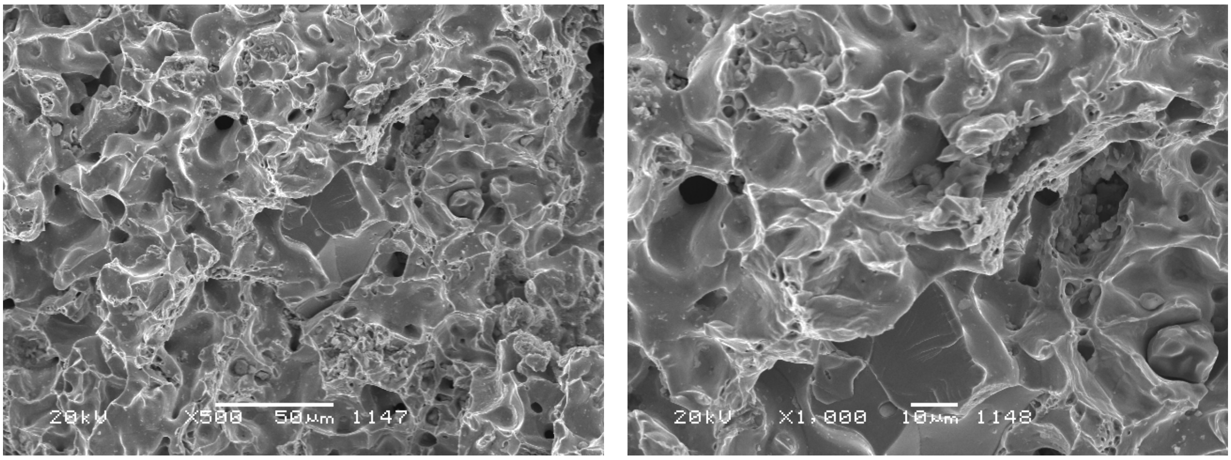
We can observe here a typical ductile fracture formed by rounded and heterogeneous shapes. There are some places where great amount of material was pulled out that may give us an idea about certain weakness and low cohesion in bonds in this sample. In any case it was we could wait from this specimen that was sintered under lower temperature and no alloying elements.

In next pictures, fig(34) we can see the micrographs for iron under P influence. It presents a ductile fracture too, characterized by spherical and deep cavities similar to volcanos. However there are some important difference to pure iron. Here we can appreciate a greater cohesion, less porosity and more homogeneous surface between particles that proves more efficient bonding during sintering. By other hand some small and no developed grains appears in border grain that makes us wonder in phosphorous segregation. Anyway, it does not detrimental so much iron properties since as we got higher absorbed energy during the impact.



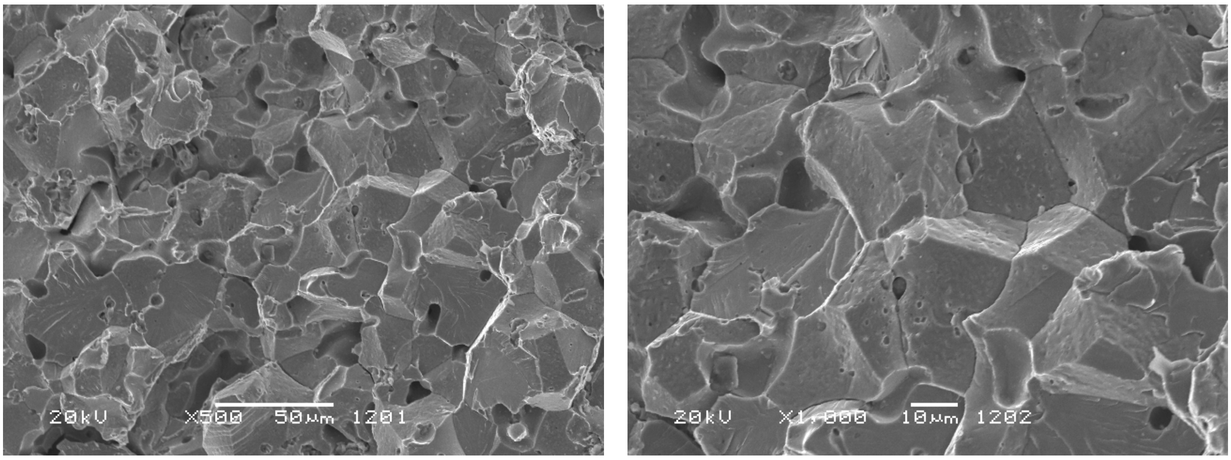
Fig(34) micrographs for Fe+0,4%P

In next pictures for highest percentage of phosphorus and temperature difference becomes clear. In this case the fracture is a mix of ductile and brittle and is easy to appreciate specific zones of flat surfaces that means transgranular cracking and others spherical and rounded typical of ductile cracking with intergranular crack propagation. In these ductile areas appears a different phase in border grain, despite of it is difficult to appreciate and to determinate exactly the role it played since as the toughness of this sample is quite high.



Fig(35) micrographs of Fe + 0,6%P 1200ºC

Clear examples of brittle fractures are shown in next charts, fig (36) where flats areas are predominant. Typical grooves into the grains appear like consequence of strain hardness during deformation in this kind of surfaces. The high cohesion achieved during sintering causes this transgranular cracking and sign of this is the great amount of energy necessary to broke this sample, that gets the best impact properties.



Fig(36) micrographs for Fe+Mo+0,6%P 1200ºC

After this scanning characterization we can conclude that fracture surface features are agree with previous obtained outcomes for density and toughness. Ductile fracture characterized by an intergranular cracking occurs in samples with low amounts of alloying element, in this case P and Mo, and brittle fractures associated with high absorbed energy and toughness for those samples with grater percentages of P and Mo, powering this effect by the higher isothermal holding temperature, 1200ºC. Possible embrittlement caused by border grain segregation is not present very clearly since as specimens with big amounts of phosphorus and no molybdenum achieved good impact properties.

8. CONCLUSIONS

In current research were carried out different analysis in order to obtain impact strength and other features of sintered Fe-P-Mo steels with sponge iron NC 100.24 as reference material. Addition of phosphorous as alloying element improves the impact properties and dimensional behavior mainly due to two different aspects. First benefit as an activator, forming a low melting eutectic phase enhancing the formations of necks between adjacent particles during sintering favouring the cohesion; by the other hand, phosphorus acts as a ferrite stabilizer where diffusion is much faster than in austenite. These mechanisms during sintering improves dimensional behavior and densification what is directly related with better properties. One more positive aspect has to be emphasized since as phosphorus gives to pores an specific rounded shape which is very positive for impact properties. Addition of molybdenum has no effect by himself but powers the phosphorous effect increasing density and energy absorbed during impact. This alloying element is also a ferrite stabilizer and changes the ferrite-austenite to the left in the phase diagram Fe-P. Possible embrittlement caused by border grain segregation of phosphorous does not become very evident since as specimens with highest amount of phosphorus and no molybdenum absorbed high levels of energy and achieve good properties. The sintering behaviour of the different compositions is improved with higher isothermal holding temperature, supplying more internal energy to the system favouring diffusion processes and achieving important results specially for the highest percentage of phosphorous and under Mo influence.

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