Surface engineering of ferrous sintered materials

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Ferrous sintered parts can be mass produced at low cost by powder metallurgy technology. The possibility of increasing the wear and fatigue resistance of some sintered structural steels by surface treatment, particularly ion-nitriding, gas nitriding and steam treatment are discussed. However, the base material must have a chemical composition suitable for fully exploiting the positive effect of thermochemical treatments of the surface layer. The work of various authors is examined here to determine which surface treated sintered materials are most successful in high wear resistance applications.

Key words: *sintered parts, thermochemical treatments, wear resistance*

1. Introduction to manufacture of sintered components

The traditional powder metallurgy (PM) process and industrial variation on it are well-documented and will not be described in detail here [1]. In the traditional process, a metal, alloy or ceramic powder in the form of a mass of dry particles, normally less than $150\,\mu m$ 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 further processing.

The basic steps in the manufacture of PM parts is [2]:

1. Mix the metal powder or powder with a suitable lubricant.

2. Load the mixture into a die or mould and apply pressure. This gives what is called compact which requires only to have sufficient cohesion to enable it to be handled safety and transferred to next stage. Such compacts are referred to as green, meaning unsintered: hence the terms green density and green strength.

3. Heat the compact, usually in a protective atmosphere, at a temperature below the melting point of the main constituent so that the powder particles weld together and present sufficient strength to the object for the intended use. This process is called sintering hence the term sintered parts. In certain cases a minor constituent becomes molten at the sintering temperature in which case the process is referred to as liquid phase sintering. The amount of liquid phase must be limited so that the part retains its shape. In certain special

cases stages 2 and 3 are combined i.e. compaction is done at an elevated temperature such that sintering occurs during the process. This is termed hot pressing, or pressure sintering.

In many cases the sintered part is subjected to additional post sintering operation and these will be dealt with the appropriate sections below. However, in certain cases, for example in the manufacture of filter elements from spherical powder, no pressure is used, the powder being placed in a suitably shaped mould in which it is sintered. This process is known as loose powder sintering.

There are a number of reasons for making engineering components by powder metallurgy and these lead to the grouping below:

- Refractory metals, particularly those with very high melting points, are very difficult to produce by melting and casting, and also are frequently very brittle in the cast state. Tungsten, molybdenum, tantalum and related metals come into this category. A sintered powder compact having a relative density of less than 90% can be mechanically deformed at a suitably elevated temperature, and gradually develops a microstructure with preferred orientation that gives the now dense material useful ductility even at ambient temperatures.

- Composite materials, consist of two or more metals which are insoluble even in the liquid state, or of mixtures of metals with non-metallic substances such as oxides and other refractory materials. In this class appear:

  - electrical contact materials such as copper/tungsten, silver/cadmium oxide.

  - hardmetals, i.e. cemented carbides, used for cutting tools, wear parts such as, for example, wire-drawing dies, and tools for the hot forging of metals. Tungsten carbide bonded with cobalt was the first of this class of material and still has the majority of the market, but other carbides and, more recently, nitrides, carbo-nitrides and borides are being used in increasing quantities, and substitutes for the relatively scarce and expensive cobalt are being tried. These include: Ni, Ni-Co, Ni-Cr, nickel-based superalloys, and complex steels.

  - friction materials for brake linings and clutch facings in which abrasive and other non-metallic materials are embedded in a copper or other metallic matrix.

  - diamond cutting tools especially grinding wheels in which small diamonds are uniformly dispersed in a metal matrix bedded in a copper or other metallic matrix.

  - in recent years several wrought products containing finely dispersed non-metallic phases have been developed and put into service. These dispersion-strengthened materials, referred to as ODS materials if the strengthening particles are oxide, have strength especially at elevated temperatures superior to that of case and wrought metal of similar basic composition. As in the case of refractory material it is difficult if not impossible to make these composite products except by PM.

- Porous materials; most forms of metal are porous to some extent, sintered metals more so than most, but here we are concerned with the production

of parts having a significant carefully controlled porosity designed to serve a useful purpose. The chief products in the group are filters and oil-retaining bearings often referred to as self-lubricating bearings. The latter is one of the major PM products. Again the above products cannot readily or satisfactorily be produced by alternative processes.

- Structural parts; by any reckoning, this is by far the largest group. The bulk consists of iron-based parts, but significant tonnages of copper, brass, bronze and aluminium parts are produced, as well as some rarer metals such as beryllium and titanium. In general such parts do not have mechanical properties superior to those of equivalent parts made by forging or machined from wrought bar, often the reverse, but they are entirely suitable for the required duty. They often have advantage over forgings in dimensional accuracy, but in a large number of cases, the main justification for their use is economic – i.e. PM is a cheaper production process. Recently, however, developments have taken place that will require revision of the foregoing. It is now possible to produce sintered parts with properties equal to and even superior to those of parts made by more traditional routes.

- Special High-Duty Alloys; an area that is growing very rapidly is the production from powder of high strength materials – high speed steels and so-called superalloys based on nickel and (or cobalt) to give a product having superior properties to those achieved by casting and forging. In general the powder is compacted into a blank or billet which is then subject to forging, or extrusion followed by forming in traditional ways. The advantages of the powder route are higher yield or usable material, and a finer, more uniform microstructure that confers improved mechanical properties, and, in the case of cutting tools and wear parts, longer life. The PM process has also allowed the development of new types of materials based on powders having micro-crystalline or even amorphous (glass like) structures produced by cooling droplets of molten metal at very high rates. The final consolidated product is characterised by very high strength, ductility, and thermal stability.

1.1. Powder manufacture

There are many ways in which metals may be produced in powder form, comminution of solid metal - precipitation from solution of a salt; - thermal decomposition of a chemical compound; reduction of a compound, usually the oxide, in the solid state, - electrodeposition, and the atomisation of molten metal. Of these the last three account for the bulk of the powders used [2].

1.1.1. Solid state reduction. This has been for long the most widely used method for the production of iron powder. Selected ore is crushed, mixed with carbon, and passed through a continuous furnace where reaction takes place leaving a cake of sponge iron which is then further treated by crushing, separation of non-metallic material, and sieving to produce powder. Since no refining operation is involved, the purity of the powder is dependent on that of the raw materials. The irregular sponge-like particles are soft, and readily compressible, and give compacts

of good green strength. Refractory metals are normally made by hydrogen reduction of oxides, and the same process can be used for copper.

1.1.2. Electrolysis. By choosing suitable conditions – composition and strength of the electrolyte, temperature, current density, etc., many metals can be deposited in a spongy or powdery state. Extensive further processing – washing, drying, reducing, annealing and crushing may be required. Copper is the main metal to be produced in this way but chromium and manganese powders are also produced, by electrolysis. In these cases, however, a dense and normally brittle deposit is formed and requires to be crushed to powder. Electrolytic iron was at one time produced on a substantial scale but it has been largely superseded by powders made by less costly processes. Very high purity and high density are two distinguishing features.

1.1.3. Atomisation. In this process molten metal is broken up into small droplets and rapidly frozen before the drops come into contact with each other or with a solid surface. The principal method is to disintegrate a thin stream of molten metal by subjecting it to the impact of high energy jets of gas or liquid. Air, nitrogen and
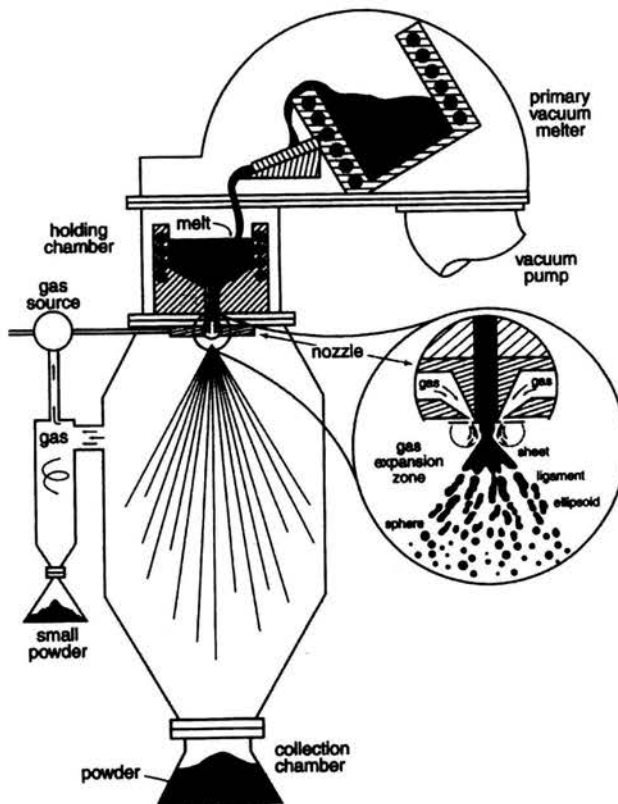
FIGURE 1. Gas atomised process [2].

argon are commonly used gases, and water is the liquid most widely used (Fig. 1). A commercial scale plant was set up in Japan to produce iron powder using paraffin as the atomising liquid the object being to keep the surface oxygen content as low a possible. The process was technically successful, but the advantages did not justify, in commercial terms, the extra cost involved. However, interest has not entirely evaporated and work is going on elsewhere.

By varying several parameters: design and configurations of the jets, pressure and volume of the atomising fluid, thickness of the stream of metal etc., it is possible to control the particle size distribution over a wide range. The particle shape is determined largely by the rate of solidification and varies from spherical (Fig. 2), if a low heat capacity gas is employed, to highly irregular if water is used (Fig. 3). In principle the technique is applicable to all metals that can be melted, and is commercially used for the production of iron, copper, including tool steels, alloy steels, brass, bronze and the low-melting-point metals, such as aluminium, tin, lead, zinc, cadmium.
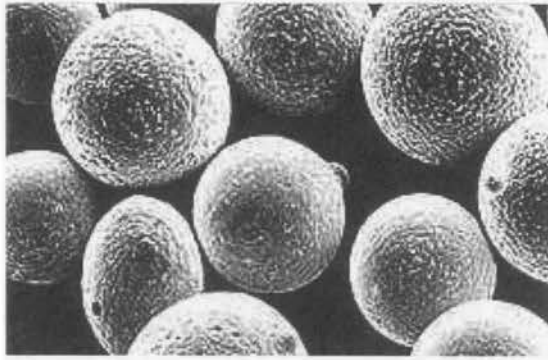
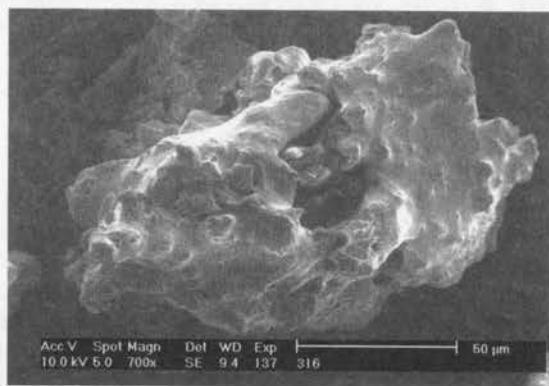FIGURE 2. Argon atomised aluminium powders [2].

FIGURE 3. Water atomised austenitic stainless steels powder AISI 316L.

Atomisation is particularly useful for the production of alloys in powder form, since the constituents metals are fully alloyed in the molten state. Thus each powder particle has the same chemical composition. Additionally the process is used to produce compositions such as copper-lead, in which the lead, though soluble in the liquid state, comes out of solution on solidification. If a casting of such an alloy is made, serious segregation of the lead results, but if the liquid is atomised, the end product is copper powder containing a very fine and uniform distribution of lead inclusions within each powder particle.

1.1.4. Mechanical comminution. Brittle materials such as inter-metallic compounds, ferro-alloys – ferro-chromium, ferro-silicon, etc., are pulverised mechanically in ball mills, and a process known as the Coldstream. Process is finding increasing application for the production of very fine powders such as are required for injection moulding (qv). In this process, granular material, which may be coarsely atomized powder, is fed in a stream of gas under pressure through a venturi and is cooled and thereby embrittled by the adiabatic expansion of the gas before impinging on a target on which the granules shatter.

1.1.5. Chemical processes. Thermal decomposition of a chemical compound is used in some cases, a notable one being nickel carbonyl. This Carbonyl Process was originally developed as a means of refining nickel, crude metal being caused selectively to react with carbon monoxide under pressure to form the carbonyl which is gaseous at the reaction temperature and which decomposes on raising the temperature and lowering the pressure. The same process is used for iron, and carbonyl iron powder finds small scale application where its very high purity is useful. Recently, demand for very fine powders for the injection moulding process has given a considerable impetus to the carbonyl process. Typically the particle size of carbonyl iron powder is 1-5 m, but, as in the case of nickel, it can be tailored to suit particular requirements. Another case of thermal decomposition is platinum powder of which is made from sponge produced by heating salt – platinum ammonium chloride. In the Sherritt-Gordon process, nickel powder is made by hydrogen reduction of a solution of a nickel salt under pressure. Chemical precipitation of metal from a solution of a soluble salt is used in other cases – e.g. silver, powder of which is produced by adding a reducing agent to a solution of silver nitrate. This is, of course, the same basic process as is used to produce black and white photographs.

1.1.6. Powder characteristics. The further processing and the final results achieved in the sintered part are influenced by the characteristics of the powder: particle size, and size distribution, particle shape, structure and surface condition. A very important parameter is the apparent density (AD) of the powder, i.e. the mass of a given volume, since this strongly influences the strength of the compact obtained on pressing. The AD is a function of particle shape and the degree of porosity of the particles. The choice of powder characteristics is normally based on compromise, since many of the factors are in direct opposition to each other. An increase in the irregularity and porous texture of the powder grain, i.e. decrease in apparent density, increases the reduction in volume that occurs on pressing and

thus the degree of cold-welding, which, in turn, gives greater green strength to the compact. This increase in contacting surfaces also leads to more efficient sintering.
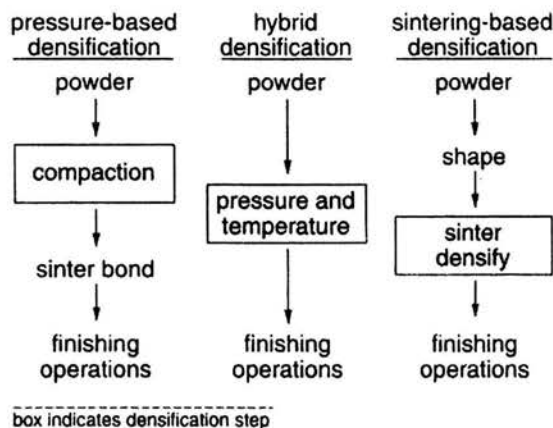
Additionally the greater reduction in volume necessary to give the required green density may require greater pressure and consequently larger presses and stronger dies. The ease and efficiency of packing the powder in the die depends to a large extent on a wide particle size distribution. So that the voids created between large particles can be progressively filled with those of smaller size. Fine particle sizes tend to leave smaller pores which are easily closed during sintering. An excess of fines, however, reduces flow properties with the results already detailed above.

The purity of the powder is critically important. Impurity levels which can be tolerated depend to a large extent on the nature and state of combination of the substances concerned. For example, the presence of combined carbon in iron tends to harden the matrix so that increased pressures are required during compaction. Free carbon, however, is often an advantage, acting as a lubricant during the pressing operation. Most metal powder grains are coated by a thin oxide film, but in general these do not interfere with the process, since they are ruptured during the pressing operation to provide clean and active metal surfaces which are easily cold-welded.

Their final reduction under the controlled sintering atmosphere is essential for complete metal bonding and maximum strength. Stable oxide films or included oxide particles, such as SiO_2 and Al_2O_3 are more serious, since these are generally abrasive and lead to increased tool wear. Furthermore they cannot be reduced during subsequent sintering and their presence may adversely affect the mechanical properties especially impact strength of the finished part. This is of major importance when high integrity, high density part are required.

1.2. Production of sintered parts

The general sequence of operations involved in the powder metallurgy process is as follows.

pressure-based densification	hybrid densification	sintering-based densification
powder	powder	powder
↓	↓	↓
compaction		shape
↓	pressure and temperature	↓
sinter bond	↓	sinter densify
↓	finishing operations	↓
finishing operations		finishing operations

box indicates densification step

Component powders are mixed, together with lubricant, until a homogeneous mix is obtained. The mix is then loaded into a die and compacted under pressure, after which the compact is sintered. An exception is the process for making filter

elements from spherical bronze powder where no pressure is used; the powder being simply placed in a suitably shaped mould in which it is sintered. This process is known as loose powder sintering [2].

1.2.1. Mixing.

1.2.1. Mixing. The object of mixing is to provide a homogeneous mixture and to incorporate the lubricant. Popular lubricants are stearic acid, stearin, metallic stearates, especially zinc stearate, and increasingly, other organic compounds of a waxy nature. The main function of the lubricant is to reduce the friction between the powder mass and the surfaces of the tools – die walls, core rods, etc. – along which the powder must slide during compaction, thus assisting the achievement of the desired uniformity of density from top to bottom of the compact. Of equal importance is the fact that the reduction of friction also makes it easier to eject the compact and so minimises the tendency to form cracks.

It has been suggested that an additional function of the lubricant is to help the particles to slide over each other, but it seems doubtful whether this factor is of much significance – good compacts can be obtained without any admixed lubricant, e.g. using die wall lubrication or isostatic pressing. Care in the selection of lubricant is necessary, since it may adversely affect both green and sintered strengths especially if any residue is left after the organic part has decomposed. Over-mixing should be avoided, since this increases the apparent density of the mix. Additionally, over-mixing usually further reduces the green strength of the subsequent compacts probably by completely coating the whole surface of the particles, thereby reducing the area of metal to metal contact on which the green strength depends. The flow properties also are impaired and good flow is essential for the next step, i.e. loading the powder into the die. In the special case of cemented carbides, the mixing process is carried out in a ball mill, one of the objects being to coat the individual particles with the binder metal, e.g. cobalt, but as the very fine powders involved do not flow, the mixture is subsequently granulated to form agglomerates [2].

1.2.2. Pressing. The mixed powders are pressed to shape in a rigid steel or carbide die under pressures of 150-900 MPa. At this stage, the compacts maintain their shape by virtue of cold-welding of the powder grains within the mass. The compacts must be sufficiently strong to withstand ejection from the die and subsequent handling before sintering. Compacting is a critical operation in the process, since the final shape and mechanical properties are essentially determined by the level and uniformity of the as-pressed density. Powders under pressure do not behave as liquids, the pressure is not uniformly transmitted and very little lateral flow takes place within the die. The attainment of satisfactory densities depends to a large degree on press tool design.

The basic parts of a tool set are the die in which the powder is contained, and punches which are used to apply the compacting pressure (Fig. 4). If, as is frequently the case, the part has holes running through it, these are formed by core rods located in the die before the powder is introduced. Multiple punches acting independently are used if the component being pressed has different levels. The die and core rod(s) from the contour of the compact parallel to the direction of pressing, and must, of course, be free from projections and re-entrants at right angles to the
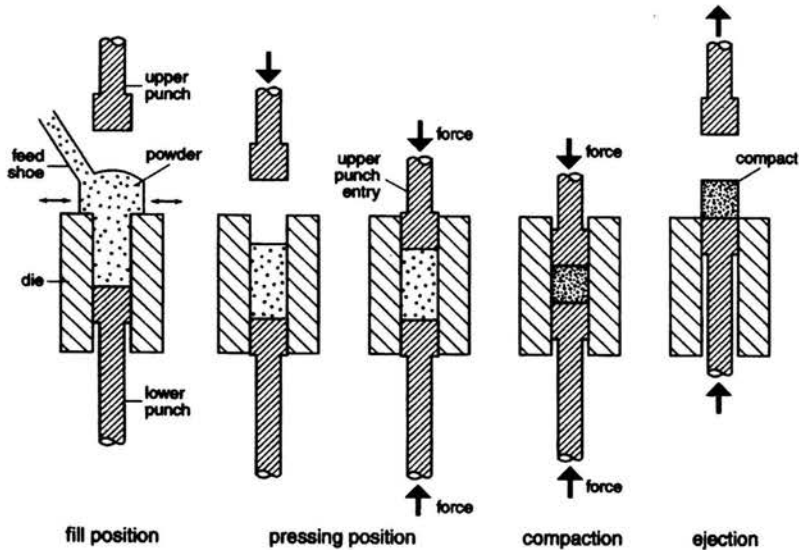
FIGURE 4. Die compaction cycles [3].

pressing direction; otherwise it would be impossible to eject the compact from the die. Materials used are hardened tool steels or hardmetals (cemented carbides). The use of the more expensive carbide is increasing because of the greater life it affords, and the increasing cost of tool changes both in lost production and toolsetters' wages. PM high-speed steels are finding increasing application in this field. For short runs, ordinary steel dies may, of course, be more economical. The importance of precise dimensions and high quality of the surface finish scarcely needs emphasis bearing in mind that one of the major features justifying the use of sintered parts is the ability to produce such parts accurately as regards size and with a surface finish that obviates the necessity for subsequent machining operations. Die life is another important aspect, and here it is impossible to give more than an indication. The life depends not only on what material is being pressed, and to what density, what lubrication is provided and the degree of die wear that can be tolerated, but also on the skill of the toolsetter, and the complexity of the tools. With steel dies up to about 200 000 compacts can be achieved, with carbide dies 1 000 000 parts or more are possible.

It has already been stated that because of the frictional forces set up between the powder grains and die wall, there is a progressive reduction of pressure transmitted and thus of density achieved through the length of the component. It will be obvious that this factor increases in importance as the size of the compact increases, and is one of the factors limiting the size of sintered part that can be produced economically. These effects are minimised by improved lubrication and by double-ended compaction, and many presses incorporate multiple punch motions operating from above and below the die. The same general results can be obtained with the single-

acting press using a floating die assembly (Fig. 5). It is possible to continue the downward movement of the die after compaction, thereby withdrawing the die from the component rather than ejecting by an upward movement of the bottom punch. The dependence of green density upon compacting pressure follows an hyperbolic relationship and there is therefore a practical optimum pressure above which further densification is negligible and tool wear becomes severe. Another feature that limits the density that can be achieved is the presence of the lubricant. Although this is normally present in no more than 1% by weight, the volume can be 5% or more, so that even if there are no voids in the compact, the density could not exceed 95%. The use of die wall lubrication using unlubricated powder mixes overcomes this problem, but the practical difficulties of applying the lubricant which must be renewed before each die fill have, so far, limited the use of the process to a few special cases where high density is a must [2].
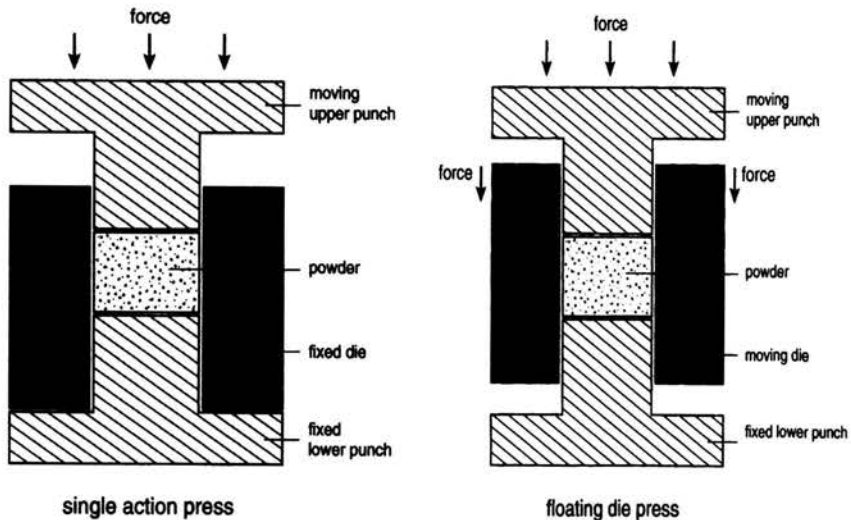

FIGURE 5. Single and floating die compaction [3].

1.2.3. Warm compaction. The effect of density has a great influence on the performance of structural PM parts and generally speaking most mechanical properties are improved as density is increased. Normal powder pressing at room temperature is relatively inexpensive for a wide range of shapes, but it has limited density capabilities. Double pressing and double sintering produces higher density PM parts but part shape is limited and double processing is expensive. Powder forging can produce PM parts to near or full density but this process is also expensive. Warm compaction provides a new way of achieving high density parts capable of competing with existing wrought steel products at only a marginal cost addition to normal PM processing. The warm compaction process uses conventional powder compaction presses and is applicable to most ferrous PM material systems. The process requires that both the powder mix, upper punch and core rod assemblies,

and die are heated to temperatures in the range of 130 to 150°C. A new pressing lubricant allowing the lubricant content in the mix to be reduced to 0.6 wt % was developed to operate successfully at warm compaction temperatures. The result is an increase in green density of 0.2 grams per cubic centimetre for a standard powder grade for example Höganäs AB as Distaloy AE containing 0.3% carbon - when this is compacted at 600 MPa. There is also a dramatic increase in green strength of the warm compacted parts which offers the benefits of limiting damage in the handling of green compacts and thereby reducing scrap, or even machining in the green state. When sintered at 1120°C in endogas for 30 minutes, the tensile strength properties for this grade of powder increase by around 10% to 720 MPa and there is almost zero dimensional change [2].

1.2.4. Hot pressing. While the bulk of sintered parts is made by pressing the powder mix at ambient temperature followed by sintering, hot-pressing is used in certain cases. At elevated temperatures metals are softer, and, therefore, it is usually possible to press to a much higher density without increasing the pressure required. It may be possible to dispense with a separate sintering operation, but this is not general because hot pressing is only justified by the significantly better properties obtained and a subsequent sintering step almost invariably improves the properties. The use of the process is limited by the much greater cost: special heat-resistant dies are required, a controlled atmosphere may be needed and production rates are, relatively, very slow: but it is used for the production of hardmetal, and diamond cutting tools, both of which are, in any case, expensive materials [2].

1.3. Other powder shaping method

1.3.1. Rapid Solidification. Another class of wrought sintered material that is beginning to make an impact is based on particulate material – powder or chopped ribbon – that has been solidified and cooled at a very high rate such that metastable non-equilibrium microstructures result. They may be microcrystalline or amorphous. The process is applicable only to certain alloys, and one important feature is that the matrix metal can retain in solid solution a much higher than the equilibrium percentage of the alloying element. Providing that the densification and mechanical working is carried out at a temperature low enough to avoid destroying the non-equilibrium structure, remarkably enhanced mechanical properties can be achieved. A major development programme is underway with alloys of aluminium, titanium, and magnesium, the hope being that their use in aircraft structures will significantly reduce the weight and increase the payload [2].

1.3.2. Isostatic Compaction. A technique which is coming increasingly into use is isostatic pressing. In Cold Isostatic Pressing (CIP) the powder is contained in a flexible mould commonly of polyurethane, which is then immersed in a liquid, usually water, which is pumped to a high pressure. Thus the powder is compacted with the same pressure in all directions, and, since no lubricant is needed, high and uniform density can be achieved. The process removes many of the constraints that limit the geometry of parts compacted unidirectionally in rigid dies. Long thin-walled cylinders and parts with undercuts present no problem. The process is being

increasingly automated with consequent improvements in productivity, and production rates are in some cases comparable with die pressing. Cold isostatic pressing is now firmly established as a production tool not only in powder metallurgy, but also in the manufacture of ceramics [2].

1.3.3. Hot Isostatic Pressing (HIP).

Also finds extensive use for the compaction of powders. In this case it is not possible to use a liquid pressure medium and argon is normally used. Furthermore, the material used for the container cannot be an organic elastomer, and in general a metal container, referred to as a can, is used. Since at the temperatures involved sintering takes place, the question of green strength does not arise, spherical powders which have the highest AD are favoured. The process is used in the production of billets of superalloys, high-speed steels, titanium, ceramics etc. where the integrity of the materials is of prime consideration [2].

1.3.4. Sinter-HIP.

With sintered metals a relative density of about 92% is sufficient to ensure that open porosity – i.e. surface-connected porosity has been eliminated and if vacuum sintering has been used so that there is no gas in the pores, such parts may be HIPed to full density without canning. In a recently developed process, sintering followed by HIPing in the same vessel is achieved. The vessel is evacuated, raised to sintering temperature, and then, at a predetermined stage, high pressure argon is introduced. This process, called Sinter-HIP or Pressure Assisted Sintering (PAS) is rapidly superseding the two stage process of vacuum sintering followed by HIPing in a separate apparatus for hardmetal cutting tools, and it can be expected to find increasing application more generally [2].

1.3.5. Powder rolling.

This term is applied to the process, now established on an industrial scale, in which a metal powder is fed continuously into a rolling mill which may be heated, and compacted between the rolls into strip. This strip is then passed through a sintering furnace and rerolled to finished size. In general the product does not have any advantage over strip produced by rolling cast billets, although in some cases superior homogeneity can be demonstrated as well as freedom from laminations that can arise from ingot defects.

Powder rolling is economical, therefore especially in cases where the metal is produced cheaply as a powder directly during the extraction process, e.g. nickel, and in the case of a material that work-hardens rapidly and, therefore, requires many intermediate annealing and pickling operations during reduction of a rolling slab, e.g. stainless steel. The production of small quantities of special materials by powder rolling is increasing for applications such as cobalt- or nickel-base alloy strip for welding, nickel-iron strip for controlled expansion properties, special Cu-Ni-Sn alloys for electronics, porous nickel strip for alkaline batteries and fuel cell electrodes, composite bearings, etc [2].

1.3.6. Spray Deposition.

Spray deposition is not a powder metallurgical process within the strict definition of that term since metal in actual powder form is not involved. Molten metal is gas atomised in the normal way and the spray is caused to

impinge while still in the liquid or semi-solid state on a solid former where a layer of dense solid metal of a pre-determined shape is produced. The solid thus produced has a structure similar to that of powder-based material with all the attendant advantages of fine grain, freedom from macro-segregation, etc. In common with the PM process, spray deposition facilitates the production of alloy compositions that are difficult if not impossible to produce conventionally, and in certain cases the benefits that rapid solidification offers can be obtained also. Properties even superior to those of powder-based wrought products have been reported; for example superalloy having a much lower inclusion count than that of its powder-based equivalent.

The range of materials that are being processed in this way is extremely wide and includes Al alloys, Cu alloys, stainless steels, high Cr alloy steels, and superalloys. The range of shapes is extensive also; – round billets, tubes, strip and sheet, and near-net shape pre-forms. Clad materials are also being produced, for example low alloy steel rolls clad with high speed steel. The sizes that can be produced are, naturally, a function of the available plant and they are continually rising. A recent installation will produce tube blanks weighing up to 4.5 t. The commercial viability of the process is markedly influenced by the yield of usable product, i.e. the proportion of the metal atomised that is deposited on the substrate. This in turn is dependent on the design of the equipment, the spray pattern, and the co-ordinated movements of the substrate. The amount of "over-spray" has been progressively reduced and yields as high as 90% are being claimed. With conventional products such as, for example, stainless steel tubing, the benefit of spray deposition is mainly cost saving, in other cases there are significant property improvements. Rolls for metal rolling mills spray-deposited and HIPed have been found to have 2 or 3 times the life of cast rolls of similar composition. Among the materials that cannot be made conventionally, but can be made by spray deposition, are rapidly solidified Al-Li alloys, Al-Sn alloys with high Zn content (11%), highly alloyed Cu-Ni-Sn and Cu-Cr, as well as the composites. In this last case, the reinforcing particles are injected into the metal stream during the atomisation process. Spray deposition seems destined to have a very interesting future. In addition to these breakthrough developments, steady progress is being maintained in the traditional areas of powder metallurgy.

1.3.7. Metal injection moulding (MIM) has over the past decade established itself as a competitive manufacturing process for small precision components which would be costly to produce by alternative methods. It is capable of producing in both large and small volumes complex shapes from almost all types of materials including metals, ceramics, intermetallic compounds, and composites. Components made by MIM technology are finding new applications in industry sectors such as automotive, chemical, aerospace, business equipment, computer hardware, biomedical and armaments [2].

1.4. Sintering

As the term "sintered part" implies, sintering is a key part of the operation. It is here that the compact acquires the strength needed to fulfil the intended role as an engineering component. In general, sintering requires heat. The ISO definition of

the term reads: "The thermal treatment of a powder or compact at a temperature below the melting point of the main constituent, for the purpose of increasing its strength by bonding together of the particles". Theories about exactly what happens during sintering have provided the subject matter of innumerable conferences and learned scientific papers, but these need not concern us here. Suffice to say that atomic diffusion takes place and the welded areas formed during compaction grow until eventually they may be lost completely (Fig. 6). Recrystallisation and grain growth may follow, and the pores tend to become rounded and the total porosity, as a percentage of the whole volume tends to decrease. The operation is almost invariably carried out under a protective atmosphere, because of the large surface areas involved, and at temperatures between 60 and 90% of the melting-point of the particular metal or alloys. For powder mixtures, however, the sintering temperature may be above the melting-point of the lower-melting constituent, e.g. copper/tin alloys, iron/copper structural parts, tungsten carbide/cobalt cemented carbides, so that sintering in all these cases takes place in the presence of a liquid phase, hence the term liquid phase sintering. It is, of course, essential to restrict the amount of liquid phase in order to avoid impairing the shape of the part.
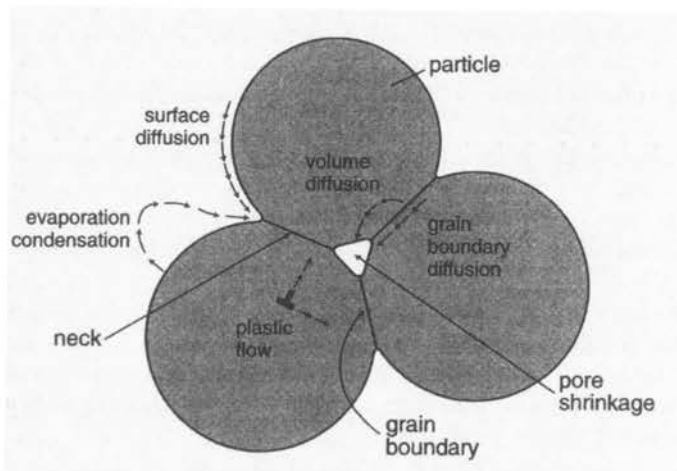

FIGURE 6. A three particle sketch of sintering [3].

Control over heating rate, time, temperature and atmosphere is required for reproducible results. The type of furnace most generally favoured is an electrically heated one through which the compacts are passed on a woven wire mesh belt. The belt and the heating elements are of a modified 80/20 nickel/chromium alloy and give a useful life at temperatures up to 1150°C. For higher temperatures walking beam furnaces are preferred, and these are increasingly being used as the demand for higher strength in sintered parts increases. Silicon carbide heating elements are used and can be operated up to 1350°C. For special purposes at still higher temperature molybdenum heating elements can be used, but special problems are involved, notably the readiness with which molybdenum forms a volatile oxide. Molybdenum furnaces must operate in a pure hydrogen atmosphere [2].

1.4.1. Controlled Atmosphere. These are essential for almost all sintering processes, to prevent oxidation and to promote the reduction of surface oxides. In practice dry hydrogen, cracked ammonia, and partially combusted hydrocarbons are mainly used, although the first named is often precluded because of cost. It is, however, used for sintering carbides and magnetic materials of the Alnico type. Dissociated ammonia containing 75% hydrogen and 25% nitrogen can readily be produced free from oxygen or water vapour, and having a dew point of the order of $-50°C$. It can replace pure hydrogen for many applications at approximately one-third the cost, with the obvious exceptions where reaction with nitrogen cannot be tolerated. It is particularly useful for sintering iron, steel, stainless steel, and copper-base components.

The most widely used atmospheres primarily because of their lower cost, are produced by partial combustion of hydro-carbons. By variation of the air-to-gas ratio, a wide range of compositions is obtained. For practical applications, since the combusted gas contains water vapour it must be dried to a dew point of less than $0°C$ for satisfactory operation with iron components. Hydrocarbon gas, such as methane, butane or propane, reacted with a limited amount of air may contain up to 45% of hydrogen, some carbon monoxide and dioxide with nitrogen as the remainder. Because of the endothermic nature of this reaction, external heat has to be supplied, and for that reason the resulting atmosphere is called endogas. If the hydrocarbon is burnt with just insufficient air for complete combustion, an atmosphere which may contain 5% or less of hydrogen and a very large percentage of nitrogen is produced, and as this reaction is exothermic, the atmosphere is called exogas. It is the cheapest atmosphere available, but its reducing potential is low and thus the removal of oxides from the powder compacts is less efficient and lower sintered strengths may result. For sintering steels, i.e. ferrous alloys containing carbon as an alloying element, the carbon potential of the atmosphere is very important. It should be in equilibrium with the steel.

Finding increasing application are so-called "synthetic" atmospheres, also called nitrogen-based atmospheres, since they are produced by careful mixing of predominantly nitrogen with hydrogen, and, for the sintering of steels, a hydrocarbon gas in predetermined proportions. These, though possibly more expensive than exo or endogas, have the advantage of cleanliness, more reliable adherence to the specified composition, and inherently low water vapour content [2].

1.4.2. Sinter-Hardening. New types of sintering furnaces allow low alloy steel parts to be sintered with neutral carbon potential (without decarburization or carburization) and then to be hardened in a rapid cooling zone. The heat treatment is achieved by high speed circulation of a water cooled protective gas in the rapid cooling zone of the furnace with cooling rates of up to $50°C/sec$ achievable between $900°C$ and $400°C$. This results in a homogeneous martensitic structure in the PM steels. Close dimensional tolerances are maintained in the sinter-hardened parts thus eliminating the need for sizing.

The combination of sintering and hardening in one step has reduced the production costs of low alloy steel parts which need post sintering heat treatment. The sinter-hardening furnace also provides other cost benefits through its ability to gen-

erate the endothermic sintering atmosphere in the furnace itself from a combustion gas and air, and also through the use of the endothermic gas flowing out of the sintering zone to heat the PM parts from ambient temperature to approximately 500-600°C [2].

1.4.3. Vacuum Sintering. Vacuum can be regarded as a special case of a controlled atmosphere, and is probably the best from the scientific point of view. Gas within the compact is readily removed and readily oxidisable metals such as aluminium, beryllium, niobium (columbium) and tantalum, the oxides of which are not reduced even by the best gaseous reducing atmospheres may be sintered. Vacuum sintering, however, is very expensive and for that reason is unlikely to find application in the production of standard, run of the mill mechanical parts where the atmospheres referred to above give quite satisfactory results. Apart from equipment cost and relatively low rates of production, the process is difficult if not impossible to make continuous and to automate. However, for certain special applications, the number and volume of which is increasing, vacuum sintering is becoming the standard. An example is the sintering of high speed steels and similar highly alloyed metals [2].

1.4.4. Dimensional Changes During Sintering. As mentioned above, sintering leads to progressively increased strength by causing the particles to weld together by diffusion. Generally, the part tends to increase in density as sintering proceeds and this still further improves the mechanical properties. Increase in density implies, of course, an overall shrinkage which leads to complications. It is possible, however, to get an increase in size i.e. growth taking place during sintering. This growth can result from a number of factors:

- entrapped gases within the compact;
- water vapour formed within the object by reduction of oxides;
- decomposition products of the lubricant.

Rapid heating and high green density intensify all these effects and may lead not only to overall growth but to blistering and distortion. Clearly such behaviour must be avoided.

Another cause of growth which is quite distinct from the above is the result of having mixed powders of different elements. Conspicuous examples are iron containing copper, and copper containing tin (to form bronze). The exact mechanism whereby this growth occurs has not been established to everyone's satisfaction, but there is general agreement that it is a diffusion effect. The growth is most marked above the melting point of the lower melting constituent. In this case also fast heating rates tend to increase growth. Under controlled plant conditions reproducible size change can be maintained. Figure 7 presents the comparison of the dilatometry changes for two iron powders using a composition of Fe-8Cu. The water atomised iron exhibits a large net expansion, while the sponge iron exhibits a net shrinkage, since there are pores for molten copper absorption in this porous powder.

It is, of course, necessary to allow for this change in the design and manufacture of the tools, but it is possible and increasingly practised so to balance the composition and sintering regime that no dimensional change takes place. It should,
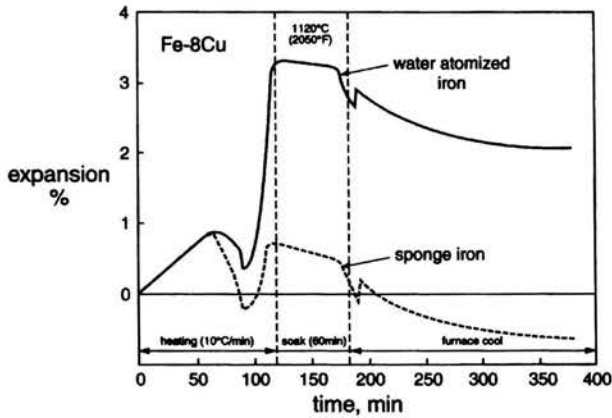
FIGURE 7. Comparison of the dilatometry dimensional changes for two iron powders [3].

however, be noted that dimensional change is influenced also by compact density; the lower this is the greater the tendency to shrink. This is one of the reasons why uniformity of density of the compact is of such importance [2].

1.4.5. Activated Sintering. This is a term used to describe the process in which a purposeful addition is made either to the powder mix or to the atmosphere in order to achieve more rapid sintering, or sintering at a lower temperature. The mode of operation is commonly by promoting more efficient removal of surface oxide on the particles, but anything that leads to an increasing rate of diffusion of the atoms of the metal will be effective as an "activator" [2].

1.4.6. Liquid Phase Sintering. As already mentioned there are a number of commercial processes during which a liquid phase is present at some stage of the sintering operation. Such a phase markedly assists the sintering operation, and can be regarded as a special case of activated sintering. Tin with copper, copper with iron, the binder metal (often cobalt) in cemented carbides, are typical examples [2].

1.4.7. Selective Laser Sintering. Selective laser sintering is where a solid object is formed through the laser sintering of selected areas of thin layers of heat fusible powder. The parts produced are self-supporting and do not require complex support structures. The process begins by depositing a very thin layer of heat fusible powder into a work space container. This layer of powder is heated to just below its melting point.

The first cross section of the component being produced is traced on the layer of powder by a heat-generating CO_2 laser. The temperature of powder impacted by the laser beam is raised to the point of sintering, fusing the powder particles to form a solid mass. The laser beam intensity is modulated to sinter the powder only in the areas defined by the object's design geometry. The process sequence continues

as another layer of powder is deposited into the workspace on top of the previous layer. This sequence is repeated with each sintered layer fusing to the sintered layer below it. Virtually any shape, feature, or geometry can be created by selective laser sintering or rapid prototyping as it is otherwise known.

Whilst this technology is primarily used for the manufacture of rapid prototypes from polymers, it can also be used both directly and indirectly for laser sintering of metallic components. Indirect metal sintering involves sintering polymer coated metal powders to form a fragile green shape which is then post processed in a furnace where the polymer binder evaporates and the powder metal sinters together. The resulting porous skeleton is infiltrated with a lower melting point metal such as copper or bronze. Direct metal sintering involves using laser sintering of uncoated metallic particles in a continuous belt furnace – or vacuum furnace is used [2].

2. Mechanical properties of sintered steels

The properties of materials produced by melting, particularly the physical characteristics, are determined by the chemical composition, the crystal structure, the deformation state (work hardening, anisotropy) and the heat treatment. This also applies to sintered materials which are usually characterized by a fine grain structure and isotropy. Two specific parameters must, however, be considered in the case of sintered materials: the density and/or porosity, and the controlled inhomogeneity. The service properties and the areas of application are decisively influenced from these. The formula used to predict the porosity effects on the properties of PM steels are summarised:

$$\varepsilon = 1 - \frac{\gamma_s}{\gamma_{fd}} = 1 - \rho, \tag{2.1}$$

$$\lambda_s = \lambda_d \left(1 - 2\,\varepsilon\right), \tag{2.2}$$

$$R_m = R_{mo} \left(1 - f_p\,\varepsilon^{2/3}\right), \tag{2.3}$$

$$R_m = R_{mo} \exp(-4.3\,\varepsilon), \tag{2.4}$$

$$R_m = a + b\,(\mathrm{HB}) = b'(\mathrm{HB}), \tag{2.5}$$

$$E_s = E_{fd}\left(1 - \varepsilon\right)^{3.4}, \tag{2.6}$$

$$G_s = G_{fd}\left(1 - \varepsilon\right)^{3}, \tag{2.7}$$

$$\gamma_s = 0.068\,e^{[1.372(1-\varepsilon)]}. \tag{2.8}$$

The meaning of the various symbols is the following:

ε is the porosity of the sintered materials,
ρ is the relative density of the sintered material,
γ_s is the density of the sintered material,
γ_{fd} is the density of the fully dense corresponding material,
λ_s is the thermal (or electrical) conductivity of the sintered material,

λ_{fd} is the conductivity of the fully dense corresponding material,

R_m is the ultimate tensile strength of the sintered material,

R_{mo} is the ultimate tensile strength of the fully dense corresponding material,

f_p is the factor of the pores, depending on raw material, density, sintering conditions,

a, b, b' are proportionality constants,

HB is the Brinell hardness,

E_s is the Young modulus of the sintered material,

E_{fd} is the Young modulus of the fully dense corresponding material,

G_s is the shear modulus of the sintered material,

G_{fd} is the shear modulus of the fully dense corresponding material,

γ_s is the Poisson ratio of the sintered material.

The controlled porosity can, as for instance with filters and bearings, be carrier of important service properties. It can, however, also be used in certain structural parts to reduce the weight of the component. Many sintered materials exhibit sufficient strength and toughness even at 80 to 85% space filling and thus make a marked weight reduction possible which can be advantageous in the case of moving parts.

Controlled inhomogeneity can combine the properties of several metals or of metals and non-metals, as is the case with contact materials and cermets. Consideration must therefore be given to the physical characteristics and the service properties specific for powder metallurgy materials when studying the material properties.

In the case of physical properties such as tensile strength, elongation, yield strength, modulus of elasticity, fatigue strength, coefficient of thermal expansion, electrical conductivity, magnetic permeability and remanence, a fundamental difference must be made between the influence of density and the influence of alloying. The right combination of these two fundamental parameters creates the optimum material specification for each application.

2.1. Density dependence

Usually, performance improves with density. Therefore, full-density processing is coupled with high alloying levels to boost the properties. Both factors (densification and alloying) work together, as illustrated in Fig. 8 for varying carbon levels in a 4% Ni steel. All the mechanical properties improve with density. Further, as the carbon content is adjusted, strength increases, but toughness and ductility decrease. Densification improves all properties, while alloying targets specific properties. For applications involving impact or cyclic loading, alloying and densification are simultaneously applied to maximize properties.

The Brinell hardness, the electrical conductivity and the thermal conductivity follow the same relationship as the tensile strength as a function of density. The dynamic material properties such as impact toughness, reduction of area, and bending fatigue, on the other hand, follow the same relationship as the elongation.

On one hand, full density provides an avenue to improved properties; on the other hand, it represents a greater expense. Specialized equipment is required, and prealloyed powders are necessary to reach highest property levels. The type of powder most responsive to full-density processing is a clean, prealloyed powder, typically formed by gas atomisation.
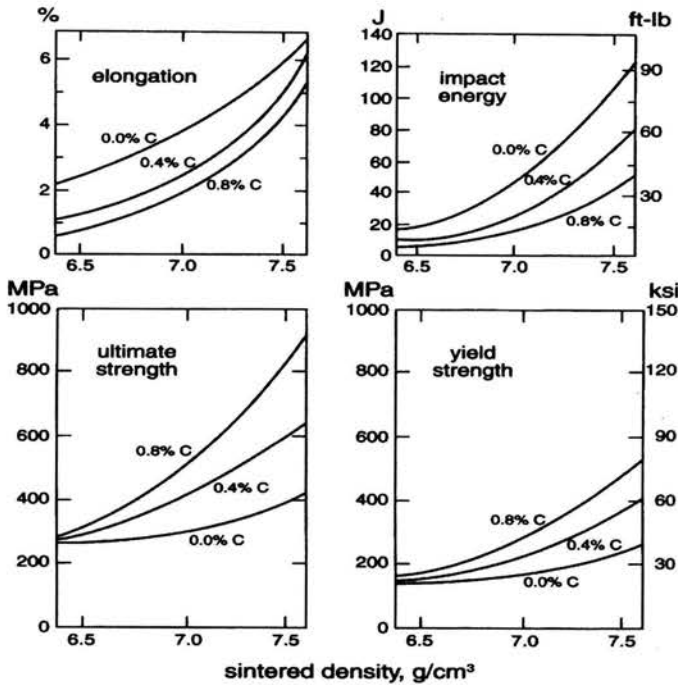
FIGURE 8. Mechanical properties variations with density for Fe-4Ni alloys with varying carbon levels [3].

For certain applications requiring high reliability, the full-density P/M steels are cost-effective when compared with other metalworking technologies. This is especially true in high-alloy steels (such as tool steels), where the raw material is expensive. Microstructure control gives better properties as compared with wrought technology. An example with 4640 steel, all three tensile properties (yield strength, ultimate strength, and elongation) are improved by higher densities. Although strength and ductility exceed wrought values, fatigue properties are sometimes less certain. Again, the difficulty usually traces to contaminants on the particle boundaries. Sufficient deformation during densification eliminates any embrittlement associated with contamination. Therefore, some full-density P/M products are forged after densification [3].

2.2. Strengthening by alloying

The strength of unalloyed metals is relatively low. Even at high density sintered aluminium only reaches a strength of 140 MPa. Sintered copper reaches 210 MPa and sintered iron 300 MPa. Higher strength requirements can be met only by alloying as illustrated in Fig. 9.

When considering the powder metallurgy of iron one can start out from the basic assumption that all the alloying elements that are used for the improvement of wrought steels also can be used for the improvement of the strength of sintered
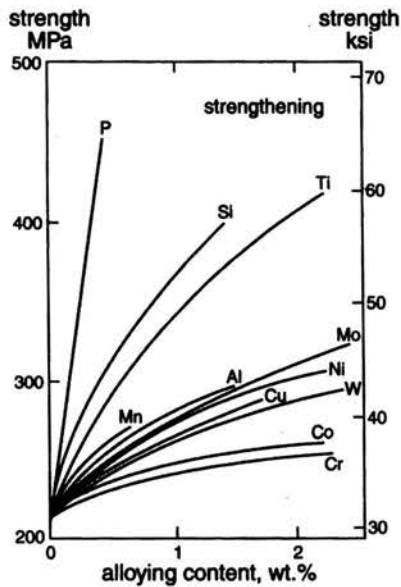
FIGURE 9. Strength versus amount of alloying addition for body centred cubic form of iron [3].

steels. The particular conditions prevailing in the sintering furnace and the compli-cated equilibria developed there between the metal and the protective atmosphere are, however, a formidable obstacle to the use of a few alloying elements which are especially important in wrought steel metallurgy, such as carbon, manganese, and chromium. These elements are oxidized with even a minimal impurity in the sintering atmosphere and can, therefore, with unsuitable processing parameters, in-fluence the properties of the sintered material detrimentally rather than beneficially. Alloying elements which don't react with the sintering atmosphere are, therefore, preferred from the point of view of the fabrication process. For this reason powder metallurgy preferentially makes use of the elements copper, nickel, molybdenum, phosphorus and tin. Of these, copper, phosphorus, and tin by no means have the same significance for wrought steels as in powder metallurgy. Manganese, chromium, and vanadium have only recently become used in the manufacture of sintered parts, the last two of these elements requiring a particular alloying practice.

Three different methods are common in powder metallurgical alloying technique. The most common method is the use of powder mixes. In this case the raw materials are mixes of the basic metal powders with the alloying elements and/or highly concentrated alloy constituents. The formation of the alloy takes place by diffusion during sintering.

In more recent times much progress has been made with a method known as partial prealloying. In this case the powder is mixed with the alloying components and then subjected to a heating process in which only a superficial alloying of the particles takes place at the points of contact. For the same sintering temperature and sintering time there is better homogenizing and better utilization of the alloying

elements. This practice has been well proven, particularly in the iron-copper-nickel-molybdenum system.

The third method is based on the use of completely prealloyed powders. In this case the alloy formation takes place in the melt and the powder is made by atomization. Thus, each powder particle has the composition of the finished sintered material.

In addition to the techniques for improving the strength of wrought metal by alloy formation, powder metallurgy also allows the use of dispersion hardening in which the finely dispersed particles are encased in the base metal matrix thus obstructing dislocation motion and thereby resisting deformation. Solid solution strengthening, transformation strengthening of carbon containing ferrous alloys, as well as precipitation hardening and dispersion hardening of aluminium and aluminium alloys will serve as practical examples for the following more detailed discussion [4].

2.2.1. Solid solution hardening. In the case of aluminium, solid solution hardening is used in the non age-hardenable aluminium-copper-magnesium and aluminium-silicon-magnesium alloys for manufacturing high strength structural parts. Among copper alloys, bronze, brass, and nickel silver obtain their properties by solid solution hardening.

In the case of iron, solid solution strengthening has been the most important alloying principle for many years. The elements copper, nickel, tin, molybdenum, and phosphorus have been investigated in detail in this connection. Sintered iron materials with high strength derived solely from solid solution strengthening have been produced on the basis of copper, nickel, and molybdenum which are all relatively insensitive to the sintering atmosphere. The single phase alloys of this system are characterized by high strength and toughness. In the iron-copper binary system the alloys containing 1.5 to 4.5% copper are of particular importance. Their strengths are shown as a function of density in Fig. 10.
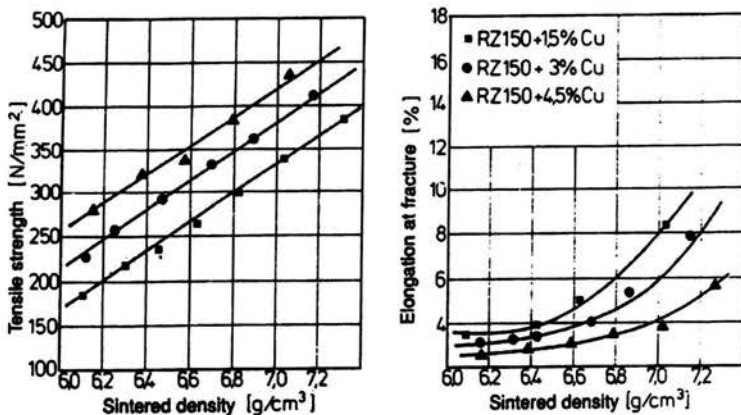

FIGURE 10. Tensile strength and elongation of Fe-Cu sintered alloys as a function of density [4].

The strengthening effect of nickel is somewhat weaker than that of copper. Therefore high nickel contents have to be used in order to achieve the same strength as for the iron-copper alloys. The iron-nickel alloys have a higher toughness than iron-copper alloys of comparable strength. They are also easy to weld and are, therefore, preferred for sintered components which are to be assembled by welding. The strengthening effect of both the above mentioned alloying elements are added in the ternary iron-copper-nickel alloys. These alloys, especially those with 1.0 to 5.0% copper and 1.0 to 6.0% nickel, are distinguished by high strength in combination with relatively good elongation (Fig. 11).
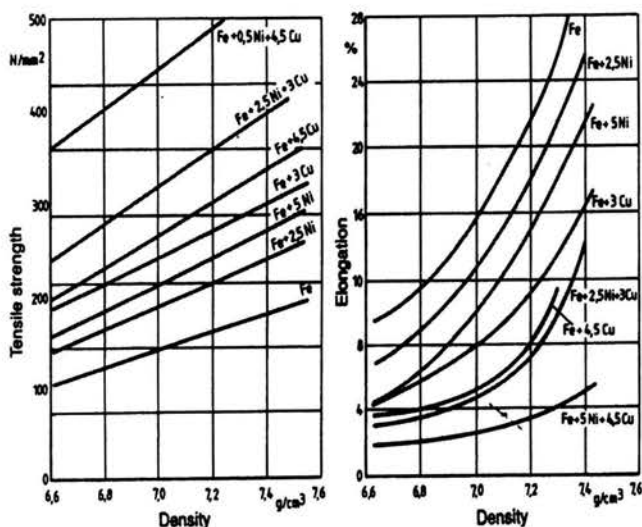
FIGURE 11. Tensile strength and elongation of binary and ternary sintered alloys from the Fe-Ni-Cu system as a function of density [4].

The introduction of partially prealloyed low alloy steel powders of the iron-copper-nickel system which, in addition contain the alloying element molybdenum (Distaloy) have contributed much to progress in the manufacture of solid solution hardened sintered materials. The advantage with these powders is that the diffusion during the sintering process is accelerated. This means that in addition to very good strength, the sintering temperature and the sintering time can be reduced. Table 1 gives a survey of the mechanical properties of this type of material.

Phosphorus-bearing sintered iron alloys have become of particular importance in recent times. They belong to those which derive their strength from solid solution hardening. It is characteristic that these alloys don't suffer a reduction in ductility when the tensile strength is increased as is the case for most alloying elements. The iron-phosphorus system was investigated at an early stage for its applicability in powder metallurgy as, with the addition of phosphorus, sintering takes place in the α-phase. In this case, the diffusivity is two order of magnitude higher than in the lower γ-region. Thus, short sintering times and low sintering temperatures can be

TABLE 1. Mechanical properties of sintered Distaloy alloys (σ 0.1: limit of proportionality, σ_B: ultimate tensile strength. δ: elongation at fracture, $\Delta l/l_0$: mass change [4]).

Designation	Basis-Powder Fe	Composition (% by weight)			Filling Density [g/cm^3]	Sintered Density [g/cm^3]	Mech. Properties (0.5%C) 1120°C gettered, cracked gas			
		Ni	Cu	Mo			σ 0.1 [N/mm^2]	σ_B [N/mm^2]	δ [%]	$\Delta l/l_0$ [%]
Distaloy SA	SC 100.26	1.75	1.5	0.5	2.70	7.05	400	590	2.5	+0.04
Distaloy SE	SC 100.26	4.0	1.5	0.5	2.70	7.05	450	750	3.0	+0.08
Distaloy AB	ASC 100.29	1.75	1.5	0.5	3.00	7.20	410	640	3.5	+0.17
Distaloy AE	ASC 100.29	4.0	1.5	0.5	3.00	7.20	460	800	4.0	+0.18

used. It must be mentioned that due to the fact that sintering takes place in the α-region, sintering is accompanied by considerable shrinkage. It must be taken into account also that sintering is accompanied by the formation of a liquid phase in the iron-phosphorus system, which brings about a high ductility and good magnetic properties.

Whilst red phosphorus as an alloying element has not led to a technically viable solution, two new processes have proven to be very suitable for industrial production. One consists of the use of ferro-phosphorus as a mixed-in alloying component and the other involves the manufacture of a water atomized prealloyed iron powder with a phosphorus content of 0.7%, which is diluted with high compactibility iron powder to a phosphorus content of 0.3-0.4%. Both methods are suitable for the manufacture of iron-phosphorus alloys with very good strength and toughness. The particularly important ternary alloy iron-0.45% phosphorus-0.6% carbon reaches a tensile strength of $550\,N/mm^2$ and an elongation of 5.5% at a density of $7.0\,g/cm^2$.

Other important alloying elements in steel production are chromium, manganese, vanadium, molybdenum and combinations of these. Research carried out on the carbon-free systems iron-chromium-copper and iron-manganese-copper have provided important fundamental knowledge for the alloying technique of systems with elements of high oxygen affinity. A tensile strength of 650 to $700\,N/mm^2$ and an elongation of 2.5 to 3% can be achieved in the systems Fe-Mn and Fe-Mn-Cu in combination with carbon. Very recently a manganese-silicon-carbon alloy was developed the tensile strength of which is 800 to $1000\,N/mm$ with an elongation of 2 to 3%.

These results led to the decision not to use the pure elements as alloy carriers but their carbides. The carbides of the metals chromium, vanadium, and tungsten as alloy carriers are dissolved at 1250°C in the iron matrix, thus facilitating the manufacture of heat-treatable sintered steels of heretofore unknown strength in the as-sintered condition [4].

2.2.2. Precipitation hardening.
Precipitation strengthening is a well known technique in the metallurgy of wrought metals and is used particularly for increasing the strength of aluminium alloys. Aluminium alloys made by powder metallurgy also can undergo additional strengthening by precipitation hardening.

It is also possible to increase the strength of single phase iron-copper alloys by precipitation hardening. A thorough investigation has shown that a solution annealing at 890 to 970°C followed by quenching in water and ageing at 500°C for 2 hours gives a precipitation hardening effect raising the strength from 460 to $670\,N/mm^2$ in a sintered steel with 5% nickel and 4.5% copper [4].

2.2.3. Dispersion hardening.
By a dispersion hardened alloy we understand a multiphase material in which the particles of one or several usually ceramic phases (dispersoids) such as oxides or carbides are embedded in a crystalline usually metallic matrix. Precipitation-hardened alloys also fall under this definition.

The microstructure of dispersion strengthened alloys is characterized by a uniform and discrete distribution of the embedded particles in the matrix. They have an average diameter of 0.05 to 5 microns and are thus considerably larger than

vacancies and dislocations but smaller than the grain size of the matrix. There is usually no thermochemical interaction such as reactions or the formation of solid solution between the matrix and the disparsiod up to the melting point of the matrix (noncoherent phase boundary). The dispersoid is usually considerably more difficult to deform than the matrix material and thus acts as obstacles to deformation of the plastic matrix material. This strengthening effect is greater the more uniform the dispersion of the ceramic particles, and the smaller their average distance from each other. A very good dispersion and thereby small average interparticle distances is technically achieved by precipitation. Strengthening by precipitation is therefore usually superior to other methods of dispersion strengthening.

The powder metallurgy process technique provides a good possibility of introducing such particles. SAP is such a dispersion hardened material based on aluminium. Its strength is derived from finely distributed particles of aluminium oxide (Al_2O_3). Worthy of mention is the well known example of "thoria dispersed nickel", the so-called TD nickel in which the nickel is hardened by 2% ThO_2.

Dispal is a newly developed dispersion hardened material containing insoluble dispersed Al_2O_3. This material is produced by reactive grinding, cold isostatic pressing followed by several powder metallurgy process steps and finally hot extrusion [4].

2.3. Mechanical properties of iron based sintered steels

In this section the mechanical properties of various P/M steels are summarized. Table 2 lists several alloys and typical mechanical properties. When the alloy exhibits less than 1% elongation to failure, the yield and tensile strengths are essentially the same. This is a common feature of porous P/M alloys. Accordingly, the yield strength is not reported. In such cases, it is appropriate to rely on the transverse rupture strength, since this is applicable to brittle alloys. The last entries in Table 2 are various stainless steels, 430L, 304L, 316LSC, and so on. The 400 series are largely iron-chromium, while the 300 series contain nickel (austenitic stainless steels). The designation of L indicates low carbon (below 0.03%), the N designates nitrogen-alloyed, while the SC indicates copper and tin alloying (C for Cu and S for Sn). Although not complete, this tabulation provides some overview on the relative property levels obtainable.

The elastic modulus scales with density and is not significantly different between these alloys. At a density of $6.2\,g/cm^3$ the elastic modulus is about $110\,GPa$ and Poisson's ratio is 0.25 with a transverse rupture strength about 1.5 times the ultimate tensile strength. When the density reaches $7.2\,g/cm^3$, the elastic modulus is $155\,GPa$ and Poisson's ratio is 0.28 with a transverse rupture strength about 2.0 times the ultimate tensile strength. For comparison, full dense steel has an elastic modulus near $200\,GPa$ and Poisson's ratio is near 0.3. Mosca provides the most comprehensive tabulation of mechanical properties for die-compacted steels, and he suggests a monotonic relation between Poisson's ratio and density and elastic modulus and density, independent of the alloy.

Little is known about the mechanical properties of porous P/M steels at elevated temperatures. One study measured the tensile properties after one hour in air at 675°C using two 400 series stainless steels. At densities in the $7.1\,g/cm^3$, the tensile strength was in the 70-80 MPa range, which represented a fivefold reduction from

TABLE 2. Representative mechanical properties of die compacted and sintered steels [3].

Alloy	Condition*	Density [g/cm^3]	Yield Strength [MPa]	Tensile Strength [MPa]	Elongation [%]	Impact** [J]	Hardness
0.3C (1030)	AS	7.4	180	275	15	34	30 HRB
0.8C (1080)	AS	7.0	260	390	3	7	70 HRB
0.8C (1080)	HT	7.1	630	660	Nil	7	35 HRC
lCr-0.7Mn-0.3Mo-0.7C	HT	7.1	–	1200	1	30	42 HRC
2CU-0.8C (FC-0208)	AS	7.0	410	610	2	8	77 HRB
2Cu-0.8C (FC-020g)	HT	7.1	490	720	Nil	7	43 HRC
3.5Mo	HT	7.6	230	310	25	–	105 HRB
2Ni-0.5C (FN-0205)	AS	6.9	210	350	3	16	59 HRB
2Ni-0.5C (FN-0205)	HT	6.9	650	830	Nil	6	29 HRC
2Ni-0.9Mo-0.5C (4650)	AS	7.3	460	750	4	8	93 HRB
2Ni-0.9Mo-0.5C (4650)	HT	7.2	–	1070	Nil	9	39 HRC
2Ni-1.5Cu-0.5Mo-0.6C	AS	7.2	530	700	3	–	95 HRB
0.45P (45P)	AS	7.4	245	370	14	45	60 HRB
12Cr (410L)	AS	6.9	190	340	20	80	50 HRB
16Cr (430L)	AS	7.2	240	380	22	145	62 HRB
17Cr-lMo (434L)	AS	7.1	250	375	18	100	57 HRB
18Cr-8Ni (304L)	AS	6.5	280	390	10	34	62 HRB
19Cr-llNi (304L)	AS	6.8	315	480	15	66	67 HRB
17Cr-12Ni-2Mo(316L)	AS	6.6	140	280	19	47	20 HRB
17Cr-13Ni-2Mo-0.3N (316LN)	AS	7.2	240	380	22	145	62 HRB
17Cr-12Ni-2Mo-2Sn-lCu (316LSC)	AS	6.9	170	345	22	95	39 HRB

* AS = as-sintered; HT = heat-treated.   ** Unnotched impact energy per square centimeter.

the room-temperature tensile strength. It is suspected that longer exposure times will greatly degrade strength.

The properties of die-compacted steels are highly variable, with many processing factors affecting behavior. Thus, the tabulated data show only general trends. Even the lubricant can change sintered strength by 20%, the graphite source can change strength by 8%, and the iron powder source will change strength by 30%. Thus, depending on such factors, a twofold shift in properties occurs between manufacturing operations [3].

3. Surface engineering of sintered steels

Choosing a surface treatment for powder metallurgy (PM) components can be a difficult task. Not only are there many options to choose from, but the characteristics of PM parts can further complicate the selection. Dawid Whittaker of David Whittaker & Associates surveys the contenders [5].

"Surface Engineering is the design of surface and substrate together as a system, to give a cost-effective performance enhancement of which neither is capable on its own". In reality, whether considering powder metallurgy parts or fully dense engineering materials surface treatment is more often seen as: "an additional final treatment to enhance an otherwise adequate product", the so called "sticking plaster" approach.

In principle, all of the surface treatments applied to fully dense steel products are available for the treatment of ferrous PM materials, but there are two important provisos. Firstly, the ability to hold close dimensional tolerance is one of PM's critical competitive advantages, so any treatment which loses this advantage can not be considered. Secondly, where PM parts contain porosity, this can exert a significant influence on the response to several of the available treatments.

The major reasons for surface engineering of PM parts are to enhance:

- Wear resistance or other tribological properties;
- Corrosion resistance;
- Fatigue strength.

The treatments, applied to PM parts, essentially divide into five categories, see Table 3:

- Coatings: a deposition of a layer of a separate material onto the surface of the substrate, without any chemical reaction;
- Chemical conversion treatments: a chemical reaction between the surface layers of the original substrate and an external reactant;
- Thermochemical treatments: diffusion of other species, such as C or N, into the surface layers of the original substrate;
- Thermal treatments: change in microstructure of the surface layers of the original substrate by thermally cycling through a phase transformation;
- Mechanical deformation methods: mechanical deformation of the surface layers of the original substrate, mainly to induce compressive residual stresses but also to provide densification of the surface layers.

TABLE 3. Surface treatments for PM parts [5].

Treatment	Examples	Performance characteristic influenced
Coating	Electroplating Electroless (autocatalytic) plating Zinc coating methods Painting Metallizing Plastic coating Enamelling	Corrosion resistance Wear resistance Tribological properties Aesthetic properties Heat resistance
Chemical conversion treatments	Steam treatment Phosphating Nitracolor Blueing Anodising Passivation	Corrosion resistance Wear resistance Porosity sealing Tribological properties Aesthetic appearance
Thermochemical treatments	Carburizing Carbonitriding Nitrocarburizing Nitrotec Nitriding Plasma thermochemical treatments Chromizing Suplphurizing Manganizing	Wear resistance Fatigue strength Surface hardness (Corrosion resistance)
Thermal treatments	Induction hardening Laser hardening Laser surface melting	Surface hardness Wear resistance Fatigue strength
Mechanical deformation methods	Shot peening Repressing Balizing Surface cold rolling Laser shock processing	Fatigue strength Surface contact Wear resistance

3.1. Coatings

Electroplating can be used to apply coatings to PM parts, but only after a pre-treatment (e.g. infiltration with copper or impregnation with resin) to seal the porosity and prevent entrapment of the electrolyte. Electroplated finishes are usually to improve corrosion resistance. The most common examples are zinc plating (usually followed by bichromate passivation to give a black or military green finish), nickel plating and a glossy or matt chromium flash plating on top of nickel.

Electroless nickel-phosphorus has advantages over electroplated nickel in terms of control over coating thickness and of throwing power. Layers of regular thickness between 0.002 mm and 0.006 mm are generated. As deposited hardness of 500 Hv can be raised to around 1000 $Hv_{0.1}$ after heat treatment, because of precipitation hardening created by the phosphorus addition. Hard chromium plating gives a thick layer (0.07 mm minimum) with a hardness of Rockwell C 40 or above. Nickel or chromium plating give adequate corrosion protection for indoor environments, but

poor performance in salt spray tests. Zinc plating, however, gives very good salt spray corrosion resistance, with red corrosion strength of 200 hours minimum.

"Dry" zinc coating methods remove the need for pore sealing.

Sheradizing, involving tumbling components in zinc powder and fine sand in a sealed drum at about 375°C, creates zinc diffusion into the substrate and hence a fine-grained zinc coating.

Mechanical plating involves tumbling parts in a drum with zinc dust, tiny glass balls and an activating solution. The balls hammer the zinc onto the substrate surfaces, creating cold welding. No heat is involved in this process

Of growing interest are the organometallic zinc coating processed, such as "Dacromet" or "Deltatone". The coatings consist of bichromated zinc-aluminium flakes in an epoxy resin and are applied by a dip-spin method to thickness of 0.008-0.010 mm. They generally give 400-500 hours salt spray resistance, although more recent developments have shown that the protection standard can be extended to 2000 hours.

Painting is applied to PM parts when rust prevention, corrosion resistance, good appearance for an exterior part or electrical insulation is required. There is no restriction on paint material, but modification to viscosity is needed to prevent impregnation of porosity.

Plastic coatings consisting of a solid lubricant (e.g. a fluorocarbon polymer) and an epoxy paint binder improve wear resistance by use of low friction coefficient solid lubricants. They are applied, after surface preparation by zinc phosphating, by dipping at room temperature and subsequently drying at 160°C to give a layer of 0.01-0.15 mm.

Enamelling applies various silicates to which colouring agents may be added and that are vitrified in air at around 800°C. Enamelled parts are used in for a combination of corrosion and heat resistance.

Metallizing of PM parts can be carried out by oxyacetylene flame, electric arc or plasma. The flame method is the most often used, with the commonly deposited metals including carbon steel (0.1-0.8%C), stainless steels, Al, Al-Si, aluminium bronze, manganese bronzes, phosphor bronzes, Mo, Zn and a range of Ni and Co based alloys for items subject to wear. The work piece can be at room temperature or hot, in which case the deposited layer is more compact. Deposited layers are generally a few tenths of a millimeter thick and not particularly even, so, for precision applications, subsequent grinding is required.

3.2. Chemical conversion

Steam treatment is the most commonly applied of all surface treatments to PM parts. The treatment involves heating parts to 530-550°C in a steam atmosphere to create a surface layer of magnetite Fe_3O_4, by oxidation of the ferrous substrate, to improve wear and frictional properties and to provide some rust protection (further enhanced by impregnation with oil). The oxide layer (0.001-0.005 mm thick) covers the whole of the outer surface but also penetrates through interconnected porosity to the center of the part. This filling of pores increases apparent hardness and hence wear resistance, as well as conferring a moderate degree of pressure tightness.

Phosphating involves the formation of complex surface phosphates (commonly zinc or manganese), around 0.0005-0.001 mm thick, by chemical attack in baths. Zinc phosphating is used as a pre-treatment for paint or plastic coatings. Manganese phosphating is used in frictional applications.

Blueing involves chemical attack in a potassium chlorate bath at 150°C providing a dark blue surface color, around (0.001 mm thick), which is aesthetically pleasing arid confers some rust protection.

Nitracolor involves the formation of an oxide coating at a temperature in the range 200-550°C in-line during the cooling cycle after sintering, using wet nitrogen as the oxidant. The color formed varies with treatment temperature (from straw to dark gray).

Anodizing is applied to aluminium parts to improve appearance and corrosion resistance. A spongy aluminium oxide surface layer is formed electrolytically and may be subsequently colored by pigments. Anodised parts cannot withstand temperatures above 60-70°C because of degradation by evaporation of water retained in the oxide layer.

Passivation is applied to stainless steel parts and involves the formation of protective surface oxides. These oxides can be generated thermally (hold at 350-550°C in air for 15 minutes) or chemically (in a bath of nitric acid or sodium chromate solution). To avoid retention of the solution in porosity, the chemical method requires prior resin impregnation [5].

3.3. Thermochemical treatments

These treatments also involve diffusion of a different chemical species into the substrate, but, unlike chemical conversion, rely largely on retaining the diffusing species in solid solution rather than formation of a new compound. As for fully dense ferrous materials, the most common diffusing species are carbon and nitrogen.

Gaseous carburizing can be applied to PM parts to raise apparent hardness to 800 HV or above, giving improved abrasive wear resistance. The ingress of carburizing atmosphere through interconnected porosity, however, makes the achievement of a distinct case/core interface difficult. So, performance parameters like fatigue strength, which rely on the generation of surface compressive residual stresses, are not as significantly improved as in carburizing wrought steels.

Carbonitriding can give better control over case depths because of its lower treatment temperatures (790-845°C compared with 920-950°C for carburizing). Carbonitriding of Fe-1.5%Cu PM material at 7.1 g/cm^3 density can, for instance, improve bend fatigue endurance limit to levels comparable with nitrided wrought steel. Because of the shallower case depths but higher surface hardnesses, carbonitriding is also a useful treatment for applications requiring abrasive wear resistance and retention of some core toughness.

Plasma-based thermochemical treatments also overcome problems associated with ingress of C- or N- combining atmospheres through interconnected porosity. Despite its high cost compared with the gaseous process, plasma nitriding has established a niche in surface treatment of PM parts. In recent years, new iron powder grades, fully pre-alloyed with around 1.5%Mo, have been developed to give good response to case hardening treatments. These materials respond well to both carbur-

izing and plasma nitriding, at density levels around $7.1\,g/cm^3$ and core carbon levels of 0.2% and 0.5% respectively. Interstitial elements (like boron) or substitutional elements (such as chromium, sulphur or manganese) can be used. In manganizing, the austenite stabilization by manganese is followed by subsequent deformation-induced transformation to martensite, giving a high surface work hardening rate.

Steam treatment is a process peculiar to PM parts which involves exposing the part at a temperature around 500°C to high pressure steam. This leads to the formation of a layer of magnetite (iron oxide) on all accessible surfaces and a number of desirable property changes result (Fig. 12). Firstly the corrosion resistance is increased by the filling of some of the porosity, and secondly, this reduction in porosity of the surface layer leads also to improved compressive strength. Thirdly, the oxide layer significantly increases the surface hardness and more importantly the wear resistance. Steam-treatment is often followed by dipping in oil which enhances the blue/black appearance and still further increases the corrosion resistance. The treatment is not generally applicable to hardened and tempered parts because the exposure to the high temperature would undergo the hardening [5].
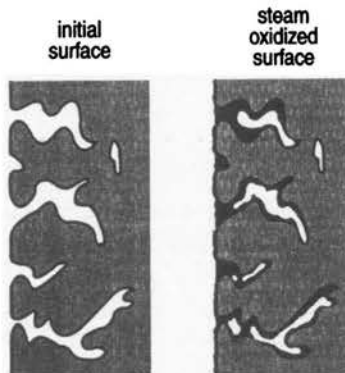
FIGURE 12. Steam sealing of the pores [3].

3.4. Thermal treatments

As with fully dense steels, thermal treatments require the presence of carbon, to contribute to the hardness of the martensitic surface layer generated.

Induction hardening is used as a local surface hardening method and gives a hardened layer considerably deeper (a few millimeters) than with case hardening. The treatment is appropriate for parts carrying high loads locally but requiring toughness. For instance, some PM gearbox synchronizer hubs have an induction hardened thrust face.

Compared with induction hardening, the benefits are the more precise selection of location to be hardened and the low distortion levels generated.

Similarly, laser surface melting to eliminate surface microstructure has found selected applications with specialized PM materials, such as high speed steels [5].

3.5. Mechanical deformation

Shot peening is a controlled blasting of a part's surface with shot. It does not produce significant plastic deformation, but does impart compressive residual stresses. It is a low cost process, routinely applied to forged or cast components to improve fatigue strength. Its ability to produce similar benefits in PM materials is well documented with improvements in fatigue strength of up to 40% having been reported.

Heavy coining or repressing can generate densification particularly in the surface layers. As discussed earlier, repressing can be effectively combined with a manganizing treatment.

Ballizing involves passing a cemented carbide ball through the bore of a part after sintering to improve tolerances, surface finish and roundness, but also to give surface densification and work hardening.

Surface cold rolling to create plastic deformation and densification in the surface layers of a sintered part has been used, often in combination with subsequent carburizing, to improve rolling contact fatigue strength and bend fatigue strength. Considerable improvements of both of these parameters can be generated enabling the parts to compete closely with the equivalent levels for carburized wrought steels. This process has been used for local densification on thrust faces of a range of PM parts and its use has been reported in North America for treatment of bearing races. In Japan, its use has been identified in gear applications in oil pumps, helical camshaft and crankshaft timing gears and agricultural machinery and motorcycle transmissions.

Laser shock processing has potential advantages over surface rolling where very precise location of surface densification is sought, particularly where such locations are relatively inaccessible (the laser beam can be transported by optical fibre). It can also be used to treat a wide range of substrate materials. Where surface rolling can be readily used, the laser shock process will have significant disadvantages in cycle times and, hence, cost [5].

4. Nitriding of sintered steels

Nitriding is a thermochemical treatment widely used to improve the wear and fatigue resistance of wrought steels. This treatment modifies the microstructure of surface layer by inducing the formation of [6]:

- a thin (5-15μm) compound layer, consisting of γ'-Fe_4N and ε-$Fe_{2-3}N$ nitrides on the external surface;
- a thick (200-$400\,\mu$m) diffusion layer, consisting of a dispersion of submicroscopic nitrides or carbonitrides in a nitrogen enriched solid solution; the subsurface layers are both solution and precipitation – hardened and in addition, compressive residual stresses are accumulated, which contribute to the increase in mechanical resistance.

A microhardness profile such as the one exemplified in Fig. 13 is induced: both the compound and the diffusion layer are indicated and the parameter $d_{550\,HV}$ is defined to represent the penetration depth. This is an important parameter for two reasons:

- the diffusion layer mechanically supports the compound layer; in other words it provides the load bearing capacity to the treated surface;
- in many tribological conditions the diffusion layer must resist to a distribution of Hertzian stresses characterized by high values even at some depth from the external surface [7].

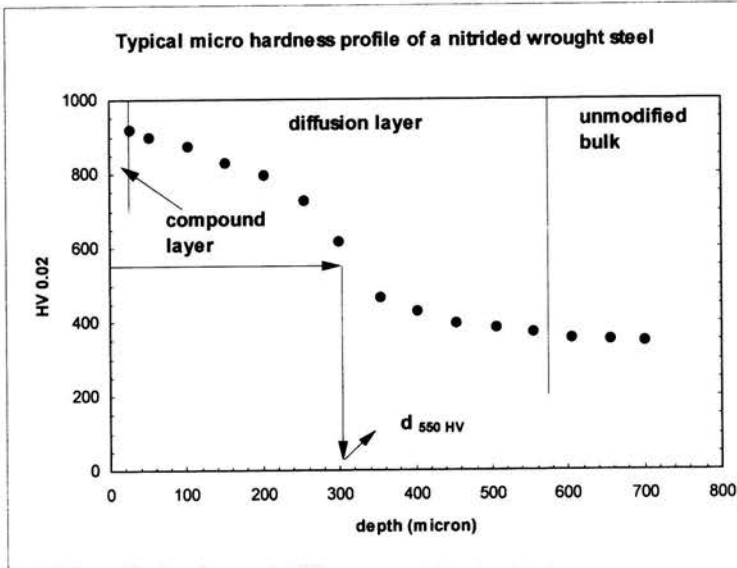In addition the diffusion layer must be sufficiently hard to provide fatigue resistance.

FIGURE 13. Typical microhardness profile of a nitrided wrought steel [6].

4.1. Plasma nitriding

The main problem in nitriding PM steels is porosity. It increases the surface area (i.e. the path for rapid diffusion of interstitial nitrogen) and favours the penetration of nitriding medium into the bulk of the material. Therefore, both gas and liquid nitriding tend to induce an excessive hardening penetration and, as a consequence, an unacceptable embrittlement of pieces. The above treatments are strongly affected by porosity and this can constitute a serious problem for complex pieces, which frequently present an irregular distribution of porosity in the surface layers, due to the effect of friction against die walls and punches during compaction. The problem can be overcome by closing the open porosity by means of:

- the activation of the sintering process, which enhances densification and closes pores [8];
- sealing pre-treatments by stem, sulphur dioxide [9], glass resin, which impede the penetration of the atmosphere into the interconnected porosity but which do not eliminate the pore surface.

The first solution seems the more practicable, even though the excessive densification of pieces during sintering can sometime damage the geometrical precision of complex structural parts, such as gear, for instance.

In many applications plasma nitriding [10] can be a valid alternative. In this surface-hardening process, ionized nitrogen reacts with metal surface in a vacuum vessel. Nitrogen and controlled amounts of other defined gases may be present. Operating conditions are low pressure, between 1 and 10 torr, and high direct current (DC) voltage, from about 200-1000 V, while the current density is normally below $10\,\mathrm{mA/cm^2}$. The vessel is the anode, while the heartplate and the parts are the cathode. With this arrangement, electrical current will flow, around the cathode, similar to a glow discharge tube. During the process, the current density is uniform around the cathode surface, while the local effects can be controlled by adjusting room pressure. Extremely reduced pressure and high voltage generate gaseous ions, which are attracted by the cathode, while the electrons released from the cathode migrate toward the anode; these movements establish a current flow. The electrically charged particles form a nearly neutral mix, also called plasma. For this reason, the process is also known as plasma-nitriding [11].

As a comparison, ion implantation is different. In this case, in fact, hydrogen ions are physically driven inside a metal, where they remain in the lattice, as discrete atoms, without forming metallic nitrides. Operating conditions differ substantially: voltage may reach 100 KeV; $\mu\mathrm{A/cm^2}$ is the order of magnitude of current density; and pressures are from 100 to 1000 times lower. Ion-nitriding is a chemical process, where surface reactions occur. Before ion-nitriding, the surfaces to be treated must be cleaned from any contaminant. Cleaning is performed by sputtering with hydrogen or argon; in this phase voltage is at a peak. After cleaning, when ion-nitriding starts, energy is transferred to the surfaces of the component in the form of heat. Nitrogen gas is ionized and the N ions (or "combined" ions, such as $NxHy+$) bombard the cathode and the iron present reacts with nitrogen, forming a surface layer of iron nitride. In a subsequent stage, the diffusion of nitrogen will promote nitride precipitations with some alloying elements present, (3) such as Al, Cr, Mo, V, Ti. In order to reduce cycle times, the charge is preheated, electrically, to about 573 K. The parts to be treated must be carefully cleaned, before the process, in a vapour degreaser if necessary. It must be stressed that in ion-nitriding the surface area of the parts, rather that the weight, is the controlling parameter of the process.

Due to the particular mechanism of nitrogen enrichment of the surface, the effect of porosity is poorer than for the other treatments mentioned above and therefore plasma nitriding does not need for preliminary pores closure. Moreover, greater control of penetration can be achieved and both the embrittlement and dimensional variations of pieces can be more easily avoided [12]. On the other hand plasma nitriding is more expensive than gas nitriding and does not appear to be suitable for the treatment of small pieces or of pieces of different geometry (i.e. surface/mass ratio) within the same batch.

In association with producers of both powders and sintered components a wide research program was carried out to study the application of plasma nitriding to sintered parts. Particular attention was paid to the investigation of the effect of the composition and of the microstructure of the base material rather than to the treatment parameters. In this chapter the main results of this study are summarised

along with other indications from the literature, in order to give some guidelines for correct design of a plasma nitrided component.

4.2. Material requirements in nitriding a sintered component

It is well known that nitriding steels contain percentage of elements such as Cr, V and Al, which have a high affinity for nitrogen, in order to favour the formation of a well defined, thick and hard diffusion layer. Otherwise, after treatment nitrogen is highly diluted in the matrix, without producing the correct hardness profile. In addition, these steels are hardened and tempered at the same temperature as nitriding before thermochemical treatment. The addition of these elements to the sintered steels requires the use of sintering atmospheres consisting of pure hydrogen with a very low dew point or of vacuum, and of high sintering temperatures, in order to reduce the very stable oxides which cover the surface of powder grains [13]. All these requirements increase the technical complexity of the sintering process and, in turn, the production cost: as a consequence the economical convenience of powder metallurgy may be reduced, in comparison to alternative technologies. For this reason, the efforts of the researchers were at first devoted to the treatment of conventional PM structural steels and to the proposal of new materials having both good sinterability and good nitridability.

4.3. Nitriding of Fe-Ni-Cu-Mo-C and Fe-Mo-C steels

The most common PM structural steels are based on the Fe-Ni-Cu-Mo-C system; their microstructure is made up of martensite, bainite, perlite, Fe-Ni martensite and low percentage of ferrite; the amount of the different microstructural constituent depends on the chemical composition. Some of them were plasma nitrided at 550°C while a thick and compact layer can be easily obtained, the hardness profile in the diffusion layer is not suitable for those applications characterised by high Hertzian stresses; this result confirms the findings of [14]. The interpretation is based on two factors:

- copper opposes the volume diffusion of nitrogen, which tends to diffuse into the bulk of the material along the pores surface and grain boundary [15];
- the Fe-Ni constituent which can predominate in the microstructure, cannot be solution and precipitation-hardened, as demonstrated by specific study on an Fe-Ni alloy [16].

Therefore, this kind of material has proved to be suitable for nitriding only for the production of components subjected to sliding with very low Hertzian stresses during application.

The above results confirm that both Ni and Cu have to be avoided in most nitrided components. As a consequence, the research was oriented to other materials based on a prealloyed Fe-1.5% Mo powder produced by Höganäs [17].

5. Wear mechanisms of ferrous PM sintered steels

In order to favour the use of ferrous sintered materials in new applications, their performance under different loading conditions have to be carefully established. In

this context, a complete understanding of their sliding behaviour has to be achieved, since many applications require a sliding contact between mechanical components. In the case of wrought steels great progress in this context has been made by Lim and Ashby, who produced their well known wear map for steels [18]. Since the two controlling tribological parameters are normalised pressure (i.e. the ratio between the nominal applied pressure and the hardness of the softer mating material) and sliding velocity, they built up a map which gives, as a function of these two parameters, the regions where the different wear mechanisms prevail, the transition boundaries between such regions, and also information on the wear rates.

A schematic drawing of the wear map for wrought steels is shown in Fig. 14. In the x axis and in the y axis the sliding velocity v (m/s) and the normalised pressure are set (in logarithmic scales). The normalised pressure p is defined by

$$ p = \frac{F}{AH} $$

where F is the normal load, A the nominal area of contact, and H is the hardness (in MPa) of the softer material.
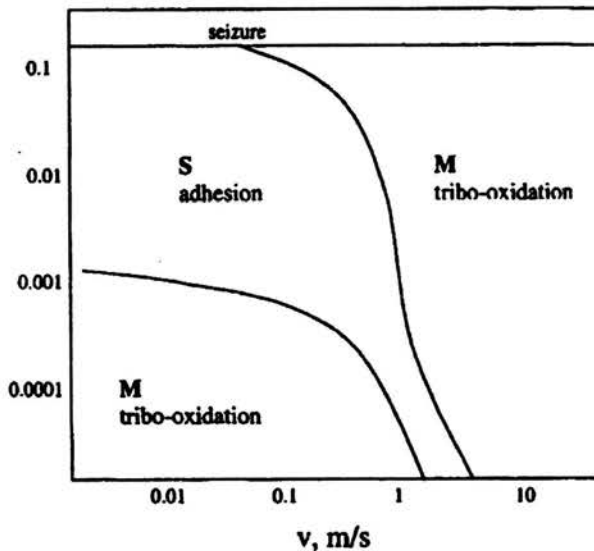
FIGURE 14. Schematic of wear map for wrought steels. M indicates mild wear and S indicates severe wear [18].

It can be observed that at high normalised pressures ($p > 0$-2) seizure occurs, independently of the sliding velocity. If sliding velocity is lower than about 1 m/s (which is the most common situation in practice), two regions are present depending on the normalised pressure. If p is greater than about 5×10^{-4}–10^{-3}, wear by adhesion takes place. Wear is a result of the plastic deformations at the metallic contacts between the materials asperites. If on the other hand, p is lower than about 5×10^{-4}–10^{-3}, wear is by tribo-oxidation. This wear mechanism is also known as

oxidative wear at low sliding speeds. This mechanism considers that wear fragments are initially formed by adhesion and remain trapped in the contact region. Here they oxidise, even if the contact temperature is low, because of the high reactivity of their surfaces towards atmospheric oxygen. Successively the oxidised debris agglomerate and also sinter together forming surface glazes which impede the metallic contacts between the mating materials. At high sliding velocities (typically $v > 1 \, \text{m/s}$) the surface flash temperature becomes so high as to induce a direct oxidation of the asperities. Wear, also in this region, is by tribo-oxidation but the oxidation mechanisms are different from that described previously. Also in this case, however, surface glazes are formed and they protect the contacting materials.

In general the wear by adhesion is severe and that by tribo-oxidation (at low as well as high sliding velocities) is mild, because of the protective action exerted by the oxidised glazes. In order to quantify the intensity of wear it is useful to make reference to the "specific wear rate" concept. The specific wear rate is denned as the ratio between the wear volume and the product between the sliding distance and the applied load. In general, wear can be considered mild if the specific wear rate is lower than $10^{-8} \, \text{mm}^2 \, \text{N}^{-1}$. Otherwise it can be regarded as severe. A schematic sketch of wear mechanisms and wear processes is shown below.

In general the wear by adhesion is severe and that by tribo-oxidation (at low as well as high sliding velocities) is mild, because of the protective action exerted by the oxidised glazes. In order to quantify the intensity of wear it is useful to make reference to the "specific wear rate" concept. The specific wear rate is denned as the ratio between the wear volume and the product between the sliding distance and the applied load. In general, wear can be considered mild if the specific wear rate is lower than $10^{-8} \, \text{mm}^2 \, \text{N}^{-1}$. Otherwise it can be regarded as severe. A schematic sketch of wear mechanisms and wear processes is shown below.

WEAR MECHANISMS	WEAR PROCESSES
ADHESION	SLIDING
TRIBO-OXIDATION	FRETTING
CONTACT FATIGUE	ROLLING-SLIDING
ABRASION	ABRASION
	EROSION
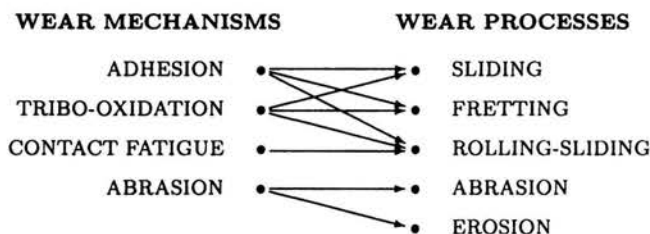
6. Rolling-sliding wear of ion nitrided Fe-Mo sintered steels

Sintered parts are frequently subjected to rolling-sliding in service, hence Straffelini and al. [19] studied the suitability of plasma nitriding on rolling-sliding wear of Fe-Mo sintered steels. The selected materials were two Fe-Mo-C alloys, based on a prealloyed Fe-Mo powder which has been developed specifically for applications in which thermochemical treatments are necessary. These materials are listed in Table 4.

Ion nitriding was compared with conventional heat treatment (quenching and stress relieving), since the latter constitutes a reliable alternative from both the

Table 4. Nominal composition of materials used and treatment cycles.

Material	Base material	Treatment cycle
A	Fe – 1.5 Mo – 0.5 C	Ion nitriding
B	Fe – 1.5 Mo – 0.3 C	Quenching/stress relieving, followed by ion nitridnig
C	Fe – 1.5 Mo – 0.5 C	Quenching/stress relieving

technological and economic points of view. Plasma nitriding was carried out at 550°C; the other treatments parameters are described elsewhere [20].

Wear tests were carried out in dry conditions for two main reasons, namely, to simulate the heaviest usage conditions of pieces and to study the response of the microstructure to the severe and complex wear conditions produced by rolling-sliding. Attention was paid to the phenomena occurring on the surface and in the subsurface layers of the running materials to highlight the wear mechanisms. A careful microstructural and morphological characterization of the worn specimens was carried out in addition to analysis of the wear debris and the results were correlated with the microstructural characteristics of the treated materials.

Dry rolling-sliding wear tests were carried out on an Amsler type tribotester, using discs 40 mm in diameter and 10 mm in thickness. Heat treated specimens required careful ultrasonic cleaning to remove quenching oil from the interconnected porosity.

Specimens of identical material and treatment ran against each other, with a 10% difference between rotation speeds (400 and 360 rev min^{-1}). The normal load ranged from 100 to 2000 N, and tests were carried out at room temperature and normal humidity. Weight changes were measured after each 5000-10 000 revolutions on both discs.

6.1. Tests at 100 N

Figure 15 shows the results of wear tests carried out at 100 N. The cumulative weight loss as a function of the distance rolled by the driver disc is reported for the materials under study and for the untreated Fe-l-5Mo-0-5C steel for comparison. It can be seen that every treatment cycle increases the wear resistance of the base material, and that significant differences between each treatment can be highlighted. Both materials (A and B) submitted to ion nitriding show two clear wear stages. In the first stage, wear rate is very low (less than 10^{-6} g/m) and of the same order of magnitude; in the second stage, wear rate increases and, in particular, the wear rate of material A becomes greater than that of material B (6.2×10^{-6} and 2.8×10^{-6} g/m, respectively). In the heat treated material the first stage is absent and a steady state is soon reached, corresponding to a wear rate of 3.2×10^{-6} g/m, which is similar to that shown by material B.

The wear mechanisms of the as sintered and heat treated materials at 100 N have been discussed previously [21]. While both oxidative and plastic shearing wear phenomena are observed in the as sintered material, the strengthening produced by heat treatment inhibits plastic flow and only oxidative wear was found on the martensitic material.
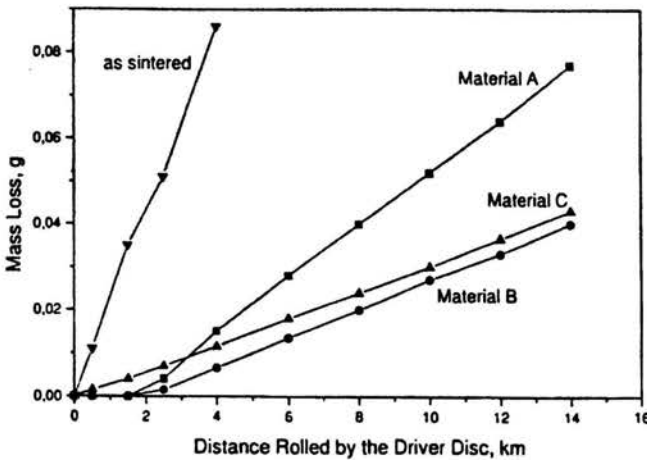
FIGURE 15. Wear curves for present materials and Fe-1-5Mo-0-5C alloy in as sintered state tested at 100 N: mass loss of driven disc shown as function of distance rolled by driver disc [19].

In the first stage of wear of both ion nitrided materials, there is a lapping of the contact surfaces with the formation of a transfer layer, as shown by a small weight increase of the driver disc at the expense of the driven disc, the loss of material from the tribosystem being negligible. After this initial period, the increased number of junctions and in particular the increased local temperature induce a wear transition with the appearance of new wear mechanisms. A micrograph observation, together with the analysis of the XRD spectrum of the wear debris which shows the presence of hematite peaks and the absence of α-Fe peaks, clearly demonstrates the occurrence of oxidative wear of the white layer, in agreement with the results reported by Sun and Bell [22] for the rolling-sliding wear of an ion nitrided wrought steel [19].

6.2. Tests at 500 N

Figure 16 shows the results of wear tests at 500 N. Tests were carried out on the treated materials only, the comparison with the as sintered materials having little significance in the light of the results shown in Fig. 15.

The increased load enhances wear rate and, for the nitrided materials, induces the disappearance of the first stage of wear present in the tests at 100 N. Wear is still oxidative for material C: no metallic fragments are detected by XRD and no plastic flow is shown by the microstructural characterization of worn specimens. For material B, oxidative wear of the white layer is still present but now some contribution of metallic wear to the global process is highlighted by debris analysis. Furthermore, the normal cross-section of the worn specimen shows a partially destroyed white layer and the longitudinal section clearly indicates the occurrence of plastic flow in the diffusion zone, no longer protected by the hard surface layer. In addition, in the same subsurface layer some cracks are clearly observed in correspondence to the sharper pores. Pores act as stress enhancers in the loaded section and may favour
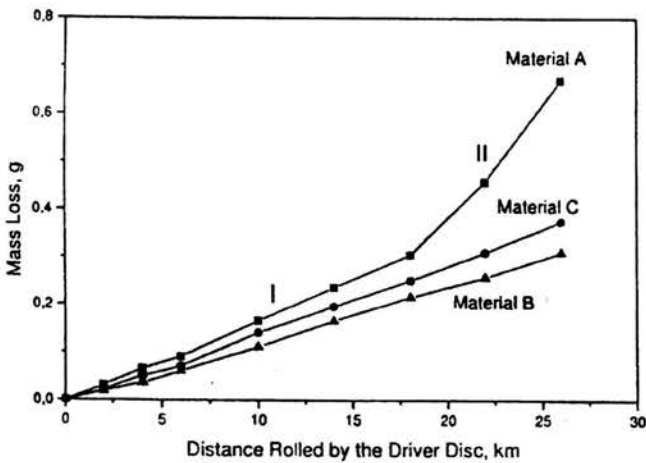
FIGURE 16. Wear curves of materials tested at 500 N [19].

the nucleation of fatigue cracks when the number of cycles is sufficiently high. However, no wear fragments were produced by fatigue for the whole duration of the test. Also at this load level, the wear rates of materials B and C are reasonably similar ($1 \times 4 \times 10^{-5}$ and 10^{-5} g/m, respectively).

In contrast to materials B and C, in material A two wear stages can be observed. In the first stage, wear is due to oxidative and plastic shearing mechanisms and this wear stage is similar to that shown by materials B and C. However, the contribution of plastic shearing to the wear process is greater than for the other two materials, which accounts for the greater wear rate (2×10^{-5} g/m). The surface layer also undergoes considerable wear damage and once a critical level is reached there is a transition to wear completely controlled by plastic shearing and, at the end of the test, by some oxidation of zones of the diffusion layer. This transition is clearly due to the inability of the matrix to sustain the nitrided layer, which is continuously damaged by the acting surface traction forces. In contrast with material B, the hardness of the matrix below the nitrided layer (i.e. of the diffusion layer) rapidly decreases to low levels and the work hardening of the matrix in the subsurface zones is not sufficient to provide the necessary load bearing capacity [19].

6.3. Tests at 2000 N

Figure 17 shows wear curves at 2000 N. The curve for martensitic steel maintains a constant slope, as in the previous experiments. The wear curve for material A is not reported because the material experienced a rapid removal of the nitrided layer, leading to severe metallic wear, so the test was stopped early. For this load, the wear curve of material B can again be subdivided into two stages. Microstructural characterisation indicates the complete destruction of the white layer during the first stage. This occurs by oxidative wear with a similar rate to that for the heat
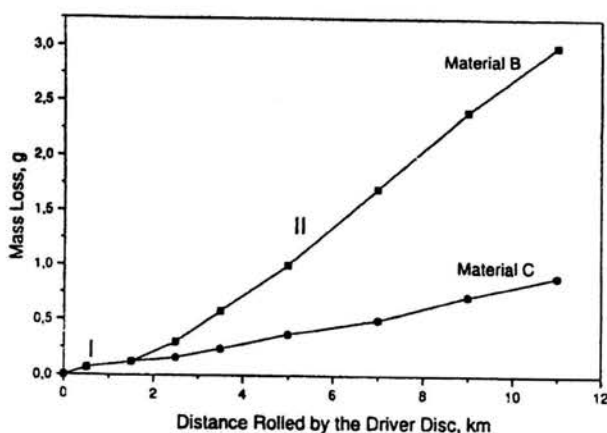
FIGURE 17. Wear curves for materials tested at 2000 N [19].

treated material, as confirmed by the initial equal slope of the wear curves. After the complete removal of the white layer, a wear transition occurs. The evolution of the wear mechanisms during this second stage was investigated carefully by XRD of the wear debris collected at three different steps of the wear curve. The increase of the α–Fe contribution with respect to hematite demonstrates the occurrence of a continuous decrease of the contribution of oxidative wear with respect to metallic wear, despite both mechanisms being active throughout the duration of the test [19].

6.4. Discussion

The wear mechanisms and the corresponding wear rates for the three materials studied and for each applied load are summarised in Table 5. For material C, which in the present study constitutes a reference material for the nitrided materials, the controlling wear mechanism under every load is oxidation. Mechanical strength produced by heat treatment provides the load bearing capacity necessary to avoid extensive plastic deformation in the subsurface layers and consequent shearing wear phenomena; some subsurface densification and the presence of fatigue cracks are observed at the higher applied load (2000 N) only. It is suggested that a more pro-longed test will reveal fatigue wear originating in correspondence with the pores, which arc well known to raise local stresses. With increasing load there is, as ex-pected, an increase of the wear rate because of the increased local temperature, which in turn increases the oxidation rate.

For ion nitrided materials, the presence of the white layer protects them com-pletely only in the first stages of the tests carried out at 100 N (the lowest load investigated) when a material transfer only is observed. As the test proceeds, the local temperature continuously increases until it reaches an equilibrium value and at a certain temperature suitable conditions to promote oxidation of the nitride layer with sufficiently rapid kinetics are reached. It should be noted that both iron and iron nitrides oxidise readily, as predicted by their standard free energy values

TABLE 5. Wear mechanisms and wear rates of materials at different applied loads [19].

Material	100 N load		500 N load		2000 N load	
	Wear mechanism	Wear rate $[\text{g m}^{-1}]$	Wear mechanism	Wear rate $[\text{g m}^{-1}]$	Wear mechanism	Wear rate $[\text{g m}^{-1}]$
A	1. Lapping 2. Oxidation	$< 10^{-6}$ $6 \cdot 2 \times 10^{-6}$	1. Oxidation/plastic shearing 2. Plastic shearing	2×10^{-5} 4×10^{-5}	...	...
B	1. Lapping 2. Oxidation	$< 10^{-6}$ $2 \cdot 8 \times 10^{-6}$	Oxidation/plastic shearing	$1 \cdot 4 \times 10^{-5}$	1. Oxidation/plastic shearing 2. Plastic shearing	9×10^{-5} $3 \cdot 3 \times 10^{-4}$
C	Oxidation	$3 \cdot 2 \times 10^{-6}$	Oxidation	1×10^{-5}	Oxidation	9×10^{-5}

compared with those of hematite. Thus a wear transition occurs and the wear rate increases considerably. Whereas the wear rate of material A is greater than that of material B owing to the contribution of some brittle cracking of the white layer, material B shows a wear rate similar to that of material C which is connected to the similar oxidation kinetics of iron and iron nitrides.

At the end of the tests carried out at 100 N the while layer was still present, although with reduced thickness, on the surface of the nitrided specimen. However, when normal force is increased, the higher contact stresses produce both plastic shearing and nucleation and propagation of fatigue cracks in the diffusion layer. These phenomena are favoured by the more rapid destruction of the white layer. Only material B is able to resist wear (at least in the first stages of the test) at the highest load investigated (2000 N). In particular, it can be observed that the wear mechanisms which occur at 2000 N are similar to those occurring at 500 N. The wear test at 500 N was interrupted when the white layer was still present on the wear surface and therefore no contribution of metallic wear to the wear rate is observable.

Under the conditions studied, the wear behaviour of the nitrided steels is clearly influenced by the local temperature increase and by the microstructure of the hardened layers. At low applied loads, the white layer has a positive effect on wear resistance, leading to better wear behaviour for these materials compared with that shown by the martensitic reference material as long as local temperature is low and is not able to induce the oxidation of the iron nitrides at a significant rate. When the local temperature rises sufficiently to promote oxidation of the white layer, the wear rate of the nitrided materials becomes analogous to that shown by material C and hence the use of plasma nitriding is no more beneficial than conventional heat treatment. When the white layer is finally removed, the wear resistance of the nitrided materials is determined mainly by the mechanical properties of the diffusion layer. The wear resistance of the nitrided materials then becomes inferior to that shown by material C. The reason for the poorer behaviour compared with a martensitic micro-structure may be clearly explained by analysing the microhardness profile of the ion nitrided material B is superimposed on that of the heat treated material. It is clearly evident that ion nitriding provides hardening comparable to heat treatment in the external layers only, microhardness reaches the bulk values rapidly, and an increase of treatment time does not substantially modify the microhardness profile [19].

6.4.1. Conclusion. The alloy Fe-1-5Mo-0-5C in the as sintered state and the alloy Fe-1-5Mo-0-3C in the as treated state were submitted to ion nitriding to investigate the influence of this surface treatment on dry rolling-sliding behaviour. As a comparison, Fe~1-5Mo-0-5C in the as treated state was submitted to the same tests. For the material in the as treated state only, the controlling wear mechanism is oxidation, independent of the load condition and duration of the test. However, for the nitrided materials, different wear stages are observed during the tests and different wear mechanisms are active, depending on the applied load.

When the applied load is low (e.g. 100 N) the white layer is able to resist wear at the beginning of the test, leading to an initial stage characterised by a very low wear

rate. As the test proceeds the increased local temperature induces oxidation of the white layer which in turn increases the wear rate. On increasing the applied load, the first stage of wear disappears and some metallic wear occurs, in particular in the material nitrided in the as sintered state. The material which was heat treated before ion nitriding possesses a greater ability to sustain the white layer. In all cases the wear resistance of the nitrided materials becomes inferior to that of the heat treated material.

On the basis of these results, it may be concluded that plasma nitriding (and of course nitriding in general) can improve the technological properties of these conventional structural PM materials only when Hertzian stresses are low, i.e. when the mechanical properties of the subsurface layers are not the main requirement. In all the other applications (fatigue, rolling-sliding, pure rolling) conventional heat treatment seems more suitable than nitriding for improving technological behaviour, since these materials do not have a chemical composition suited to fully exploiting the positive effects of nitriding.

To exploit the benefits of ion nitriding on wear resistance of the materials studied, the survival of the white layer during the wear process is essential. This conclusion suggests that further investigation would be useful, with two main purposes: first, to experiment with other alloying elements able to increase oxidative wear resistance of the white layer and to induce the formation of a diffusion zone with greater hardness; and second, to test the materials under lubricated conditions to highlight the wear resistance of the white layer, as determined by the reduced metal to metal contact and by the controlled local temperature, and to compare the behaviour of the fatigue cracks which propagate from the pores in the diffusion layer in the nitrided materials, and in the martensitic microstructure in the heat treated material [19].

7. Wear resistance of gas nitriding sintered steels

A particular treatment was studied and patented by some of the authors [23], which combines nitrogen, oxygen and sulphur in one batch only. Thus it is very important to study the applicability of the gaseous thermochemical treatment to suitable PM material and to be hardened by means of nitrogen surface enrichment, at the same time. From the different P/M structural steels, the prealloyed Fe-Mo1.5% Mo and AISI 316L austenitic stainless steels were selected. The chemical composition of the base material was modified by boron for two main reasons: from the theoretical point of view, boron influences the hardenability of steel and its high affinity for nitrogen allows to form boron nitrides which may increase the hardness of the diffusion layer, and furthermore, boron being α-stabilising element and activates the sintering process of iron alloys by the formation of liquid phase and in consequence the near full density may be obtained [24]. This last effect is very important, because it may strongly reduce the nitrogen penetration during nitriding, which is one of the biggest problems in gas nitriding of porous sintered steels [25].

The specimens were produced by blending a prealloyed Fe-1.5% Mo powder and separately water atomised AISI 316L austenitic stainless steel powder and elemental

boron powder of 2.4 µm of average grain size in two different percentages: 0.2 wt.%B, 0.4 wt.%B. Boron-free specimens were also produced for comparison. The chemical composition of the commercial powders used in this study are shown in Table 6.

TABLE 6. Chemical composition of powders.

Powder	Nominal chemical composition [%]						
	Cr	Ni	Mo	Si	Mn	C	Fe
Astaloy Mo	–	–	1.5	–	–	–	balance
AISI 316L	16.3	12.75	2.28	0.87	0.17	0.019	balance

The specimens $\phi\, 20 \times 5$ mm were compacted at 600 MPa with die wall lubrication in an uniaxial press. Sintering was carried out at 1200°C (Astaloy Mo) or at 1240°C (AISI 316L) in laboratory furnace under pure dry hydrogen. The time of isothermal sintering for both sintered alloys was 30 minutes. The density, total porosity and interconnected open porosity was measured by the usual water displacement method. The sintered density depends on the chemical composition of specimens and on the boron concentration.

The gaseous thermochemical treatment of sintered materials comprises three steps, each related to one specific chemical element used to modify the surface of the pieces; nitrogen, sulphur and oxygen. It should be noted that austenitic stainless steels contain elements with high affinity for nitrogen to favour the formation of hard and stable nitrides in the surface layer. These elements, however, also form stable oxides and for this reason they are not particularly suitable for nitriding since transport phenomena responsible in inducing the formation of the external compound layer and diffusion layer require destabilisation of oxide covering the surface of powder grains. To overcome these drawbacks depassivation of sintered specimens have been performed. In order to protect against repassivation the austenitic stainless steels have to be coated by the iron galvanic layer which simultaneously enhanced nitriding process. The surface treatment is carried out in an industrial furnace. The detailed description of the treatment parameters is protected by the patent and is not available. The treatment temperature ranges between 400°C and 560°C and the complete treatment time is about 15 hours. Different treatments procedures were

TABLE 7. Material and surface treatments.

Material	No treatment	Nitriding	Nitriding and Oxidation	Nitriding and Sulphurizing	Nitriding Oxidation and Sulphurizing
Astaloy Mo	A	AN	ANO	ANS	ANSO
Astaloy Mo + 0.2% B	A2	A2N	A2NO	A2NS	A4NSO
Astaloy Mo + 0.4% B	A4	A4N	A4NO	A4NS	A4NSO
AISI 316L	L	LN	LNO	LNS	LNSO
AISI 316L + 0.2% B	L2	L2N	L2NO	L2NS	L2NSO
AISI 316L + 0.4%B	L4	L4N	L4NO	L4NA	L4NSO

experimented on the sintered materials, as summarised in Table 7, where the codes used for their identification are also reported.

The treated specimens have been characterised by means of light and scanning electron microscopy, microhardness measurements, the X-ray diffraction analysis of surface layers and the concentration depth profile of oxygen and nitrogen by using a LECO GDS 750 instrument. Furthermore, in order to confirm the constitution of the surface layers, some specimens were characterised by means of the Wavelength Dispersion X-ray Spectroscopy (WDXS) and the Energy Dispersion X-ray Spectroscopy (EDXS). In order to determine the surface roughness Hommelwerke Profilometer T1000 was used. Wear tests were carried out on an Amsler tribotester with a block on disk configuration, in dry sliding condition, by using 100Cr6 steel as the counterface material (63HRC). The wear tests were performed under a load of 20 N and with surface sliding speed of 0.8 m/sec.

7.1. Microstructural characterization

The values of density ρ_s (g/cm^3), total porosity ε (%) and interconnected open porosity ε_i (%) are reported in Table 8.

TABLE 8. Density ρ_s [g/cm^3], total porosity ε [%] and open porosity ε_i [%] of sintered materials.

Material	ρ_s [g/cm^3]	ε [%]	ε_i [%]
Astaloy Mo	7.1	10	9
Astaloy Mo + 0.2%B	7.1	10	7
Astaloy Mo + 0.4%B	7.3	7.4	1
AISI 316L	6.6	16.2	13
AISI 316L + 0.2%B	7.1	8.5	1.5
AISI 316L + 0.4%B	7.8	1.0	0

For Astaloy Mo powders boron tends to increase the sintered density and to close the residual porosity; however while density starts to increase in correspondence with 0.4% B, just at 0.2% B an effect on the closure of pores is observed. On the contrary, for AISI 316L powders, boron increases the sintered density and close the interconnected pores just at 0.2% B.

The unalloyed sintered Astaloy Mo has homogeneous ferritic microstructure. The boron alloyed materials have a heterogeneous microstructure consisting of an almost continuous eutectic constituent surrounding the hard matrix grains in the bulk and near-full dense ferritic surface layer [26]. The microstructure of sintered boron alloyed AISI 316L is similar to that obtained to the Astaloy Mo alloy powder. Whereas the unalloyed AISI 316L presents the usual austenitic microstructure with the irregular and interconnected porosity, the alloyed specimens are characterised by the presence of the second constituent, which surrounds austenite grains as a discontinuous for 0.2% B or continuous network for higher boron content. In addition, a near full-dense surface layer was found on the alloyed specimens. Such surface layer is characterised by the absence of boron. The microstructural characteristics of the specimens were interpreted on the basis of the sintering mechanisms and discussed in other paper [27]. Figures 18 and 19 show the bulk microstructure of the sintered Astaloy Mo and AISI 316L, respectively.
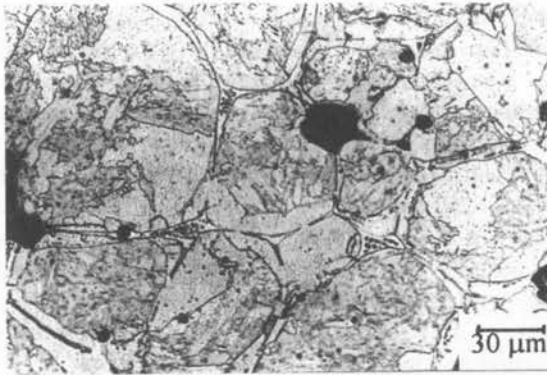
FIGURE 18. Microstructure of material A4 [28].
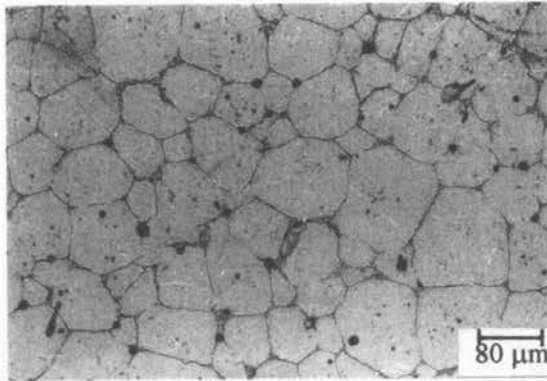
FIGURE 19. Microstructure of material L4 [28].

The thermochemical treatment of P/M based iron steel, first has been pointed out on nitriding, because it is the base treatment of all specimens. Figures 20 and 21 show the representative microstructure of specimens AN and A4N. The microstructure of material AN shown in Fig. 20 suggests that bulk nitriding occurred, which was caused by the interconnected porosity. A distinct compound layer was not observed, even if the presence of ferritic grains in the external layers is insignificant. The microstructure of the bulk material AN shows ferritic grains with some needle-like γ'-Fe_4N precipitates and an average microhardness of $480\,HV_{0.05}$, surrounded by a white network whose microhardness ranges between $350\,HV_{0.05}$ and $500\,HV_{0.05}$. The white network consists of a mixture of the γ' and ε-$Fe_{2-3}N$ nitrides, as confirmed by XRD analysis as shown for instance in Fig. 24 for a graph showing the results from Table 9. The low hardness of this constituent is due to the presence of micropores. Concerning the other boron free materials, the microstructure and the microhardness are the same as for AN material. Only a very thin external surface

TABLE 9. Major crystallographic phases detected by XRD analyses of samples after various treatments.

Treatment	Material					
	A	A2	A4	L	L2	L4
N	$Fe_4N/Fe_{2-3}N$	$Fe_4N/Fe_{2-3}N$	$Fe_4N/Fe_{2-3}N$	CrN/Fe_4N	CrN/Fe_4N γ-Fe	CrN/Fe_4N γ-Fe
NO	Fe_3O_4/Fe_2O_3 $Fe_4N/Fe_{2-3}N$	Fe_3O_4/Fe_2O_3 $Fe_4N/Fe_{2-3}N$	Fe_3O_4/Fe_2O_3 $Fe_4N/Fe_{2-3}N$	CrN/Fe_4N Fe_3O_4/Fe_2O_3	CrN/Fe_4N γ-Fe Fe_3O_4/Fe_2O_3	CrN/Fe_4N γ-Fe Fe_3O_4/Fe_2O_3
NS	FeS Fe_3O_4 $Fe_4N/Fe_{2-3}N$	FeS Fe_3O_4 $Fe_4N/Fe_{2-3}N$	FeS Fe_3O_4 $Fe_4N/Fe_{2-3}N$	FeS Fe_3O_4/Fe_2O_3 Fe_4N/CrN	FeS Fe_3O_4/Fe_2O_3 Fe_4N/CrN	FeS Fe_3O_4/Fe_2O_3 Fe_4N/CrN
NSO	FeS Fe_3O_4/Fe_2O_3	FeS Fe_3O_4/Fe_2O_3	FeS Fe_3O_4/Fe_2O_3	FeS Fe_3O_4/Fe_2O_3	FeS Fe_3O_4/Fe_2O_3	FeS Fe_3O_4/Fe_2O_3

FIGURE 20. Microstructure of material AN [28].
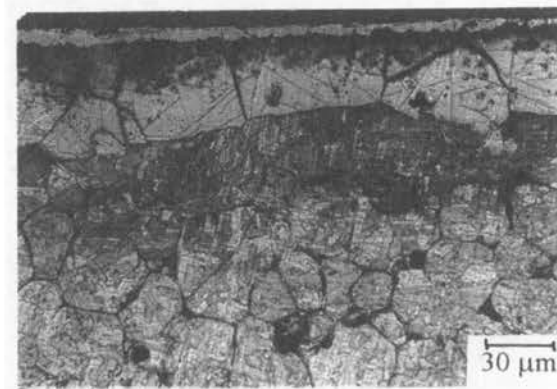
FIGURE 21. Microstructure of material A4N [28].

layer of about 1-4 μm in thickness of FeS in material ANS can be observed. Similar thin oxide layer in material ANO and a very thin oxide layer with a thin sulphide layer in material ANSO can be noticed.

On the contrary, the microstructure of the A4N material shows a typical thick compound layer which consists of both the nitrides γ' and ε-$Fe_{2-3}N$, as shown in Fig. 25. The microhardness of this compound layer is about 800 $HV_{0.01}$. The near full-dense subsurface boron-free layer shows large needles like γ' nitrides in the ferritic grains. By moving towards the bulk the microhardness decreases from 550 $HV_{0.05}$ to about 420 $HV_{0.05}$. The microhardness of the matrix where the eutectic constituent is present is about 280 $HV_{0.05}$. The other boron alloyed materials show similar thick compound layer, and the same diffusion layer and bulk microstructure as the A4N material. The sintered austenitic stainless AISI 316L steel shows the CrN nitride in addition to γ' and γ-phases. The characteristic microstructures of material LNSO and L4NSO are shown in Figs. 22 and 23, respectively.
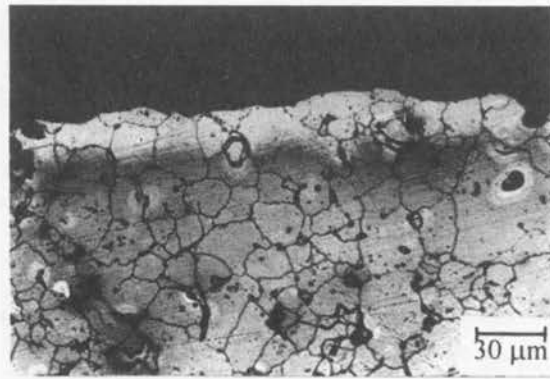
FIGURE 22. Microstructure of material LNSO [28].
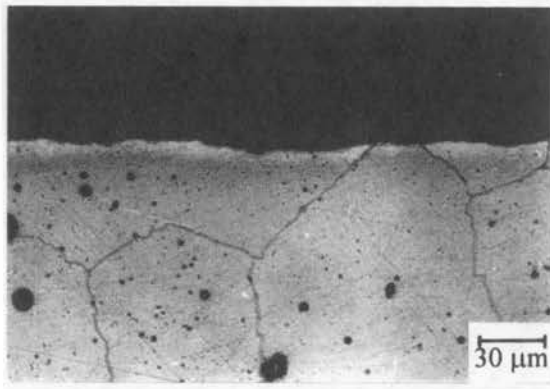
FIGURE 23. Microstructure of material L4NSO [28].
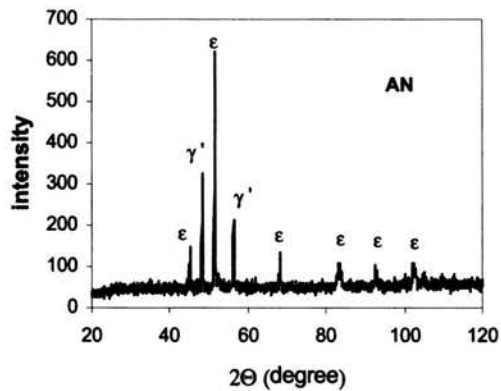
FIGURE 24. Typical XRD pattern of material AN [28].
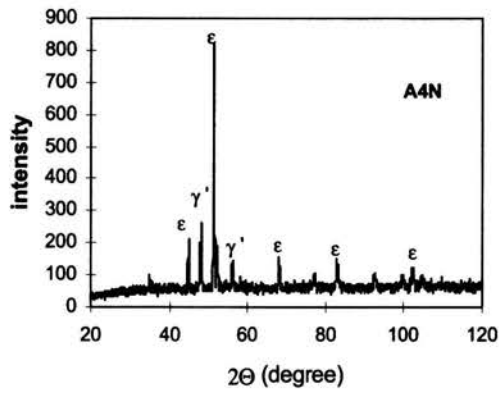
FIGURE 25. Typical XRD pattern of material A4N [28].
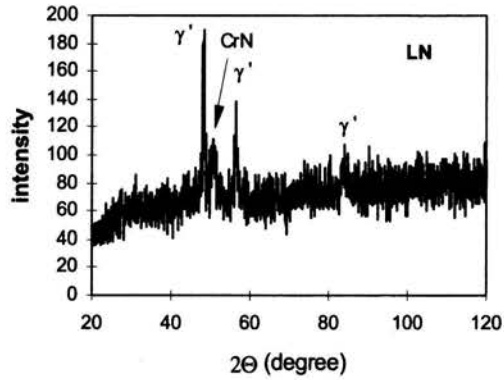
FIGURE 26. Typical XRD pattern of material LN [28].
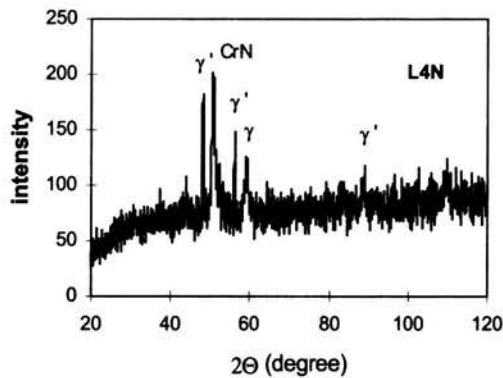
FIGURE 27. Typical XRD pattern of material L4N [28].

From these results it is clearly evident that boron, present in the iron base alloys, modifies the nitrogen diffusion, decreasing the penetration depth of nitrogen and increasing the average surface hardness. Finally, the thermochemically nitrided boron alloyed specimens demonstrated typical characteristics of a nitrided case depth: a distinct compound layer and a well defined diffusion layer, consisting of a dispersion of submicroscopic nitrides in a nitrogen enriched solid solution. However, the BN precipitation is not confirmed, because the microhardness values measured in the diffusion layer of A4N and in the ferritic grains of AN are very similar.

The results of XRD analyses of specimens A, L and A4, L4 treated in all the experimental conditions can be concluded as follows:

- oxidation of the previously nitrided surface forms magnetite, but is not able to transform the whole compound layer in material A4, L4, as demonstrated by the diffraction peaks of nitrides in XRD patterns of samples A4NO or L4NO,
- sulphuration of the nitrided surface is able to modify the compound layer and forms FeS and Fe_3O_4,
- the nitriding, sulphuration and oxidation form a mixture of FeS and iron oxides in the compound layer; these last dominate in comparison with the NS treatment, as expected.

The above results find confirmation in the concentration depth profiles. Figures 28 and 29 show, the depth profile of oxygen and nitrogen in specimens ANO and ANS respectively. While oxidation produces a sharp oxygen segregation on the surface as a consequence of a very thin oxide layer on the external surface, sulphuration induces the interdiffusion of sulphur, nitrogen and oxygen, from which a mixture of sulphides, oxides and nitrides is formed. The semiquantitative concentration depth profile in Fig. 29 is representative of specimens ANSO too and the depth profiles in the specimens with the other base composition are quite similar to those reported in the above figures.
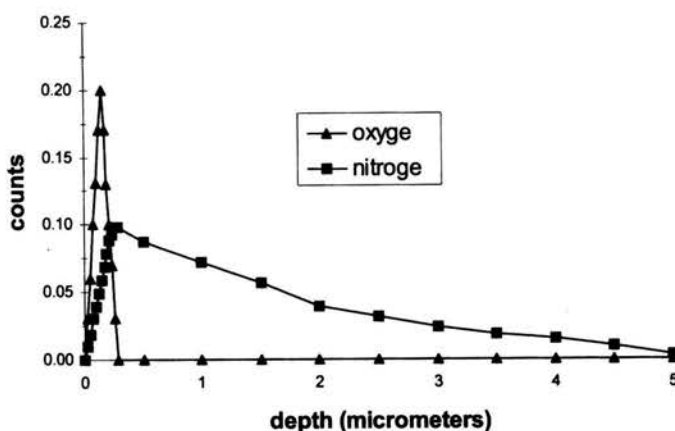
FIGURE 28. Semiquantitative concentration depth profile of oxygen and nitrogen in material ANO [28].
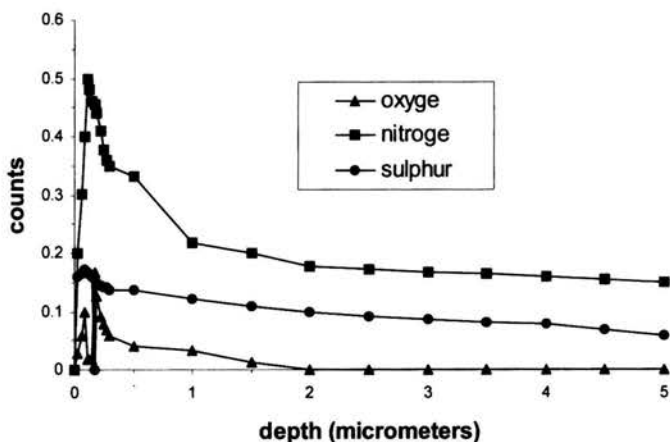
FIGURE 29. Semiquantitative concentration depth profile of oxygen, nitrogen and sulphur in material ANSO [28].

In order to confirm the constitution of the surface layers, a detailed characterisation by the WDXS spectroscopy and EDXS analysis are carried out on A4NSO specimens. From these results (Figs. 30 and 31) one can conclude that FeS is formed in the compound layer.
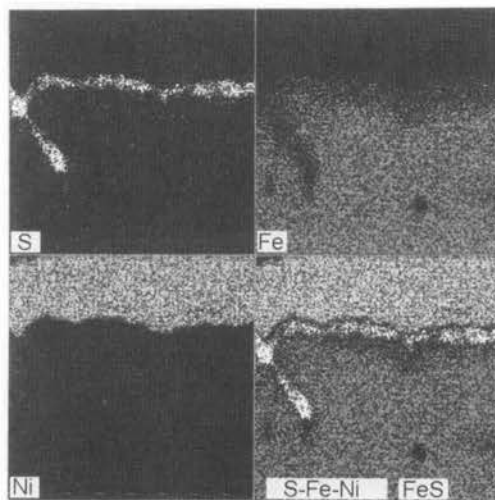
FIGURE 30. WDXS analysis of material A4NSO [28].

Figures from 32 to 35 show the surface morphology of the materials A, A4N, A4NSO, L4NSO, respectively. It is clear that only after nitriding, sulphuration and oxidation a noticeable modification of the surface morphology is obtained. This
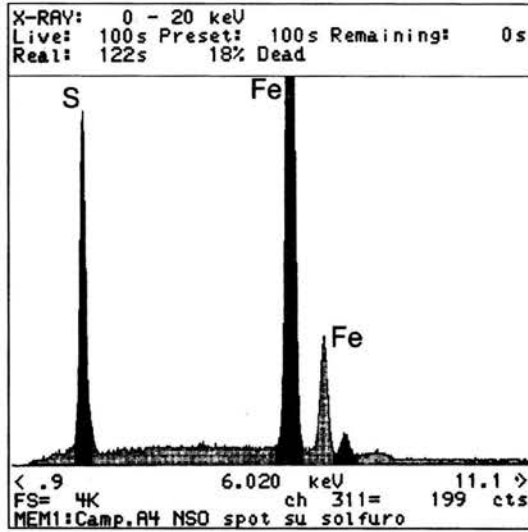
FIGURE 31. EDXS characterisation of material A4NSO [28].

observation agrees with the XRD analyses. As predicted, nitriding does not change the surface morphology, which is maintained after oxidation, too, because of the very low thickness of the oxide layer. In contrast, sulphuration tends to eliminate all the surface irregularities of the nitrided pieces. The specimen A4NS has the same surface morphology as A4NSO, and the above figures are representative of the other base materials, too. The roughness of a sintered part is highly dependent on the surface porosity (open porosity). Due to these pores the classical parameters R_a and R_z and so on, measured with a normal roughness meter appear to be much larger for sintered surface than for that of wrought part with identical functional properties.
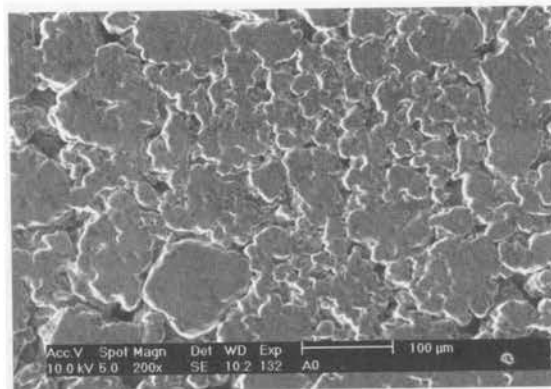
FIGURE 32. Surface morphology of material A [28].
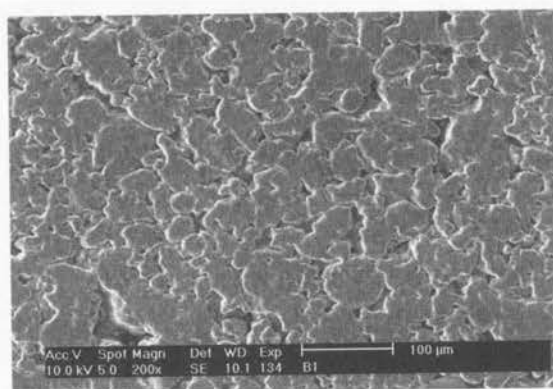
FIGURE 33. Surface morphology of material A4N [28].
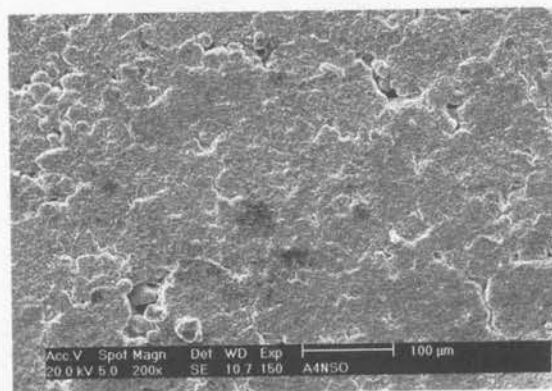
FIGURE 34. Surface morphology of material A4NSO [28].
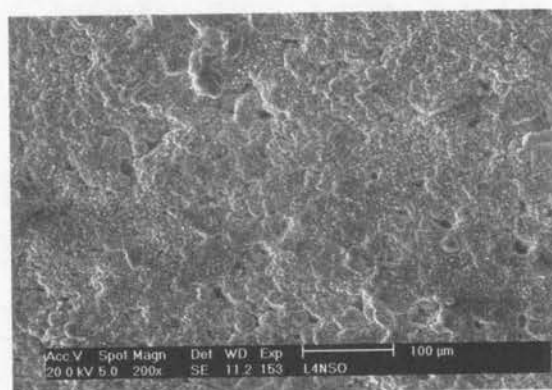
FIGURE 35. Surface morphology of material L4NSO [28].

With sintered or sized surface excellent friction behaviour can be obtained even at high R_a and R_z values (Table 10).

TABLE 10. Roughness – R_a [μm] of surface treated sintered materials.

A	AN	ANO	ANS	ANSO	A4N	A4NO	A4NS	A4NSO
3.42	3.11	2.81	2.37	1.94	2.27	1.96	1.68	1.53
L	LN	LNO	LNS	LNSO	L4N	L4NO	L4NS	L4NSO
2.89	2.26	1.91	1.61	1.22	2.76	2.1	2.03	1.63

Finally, Fig. 36 shows the results of the preliminary dry sliding wear test of five different samples: untreated, A4N, A4NO, A4NS, A4NSO. The weight loss in Fig. 36 is the average value obtained from three successive and similar wear tests of a given sample. It is clear from this results that all the treatment are able to increase the wear resistance of the base material; moreover, sulphuration is more effective than oxidation. This is due to the combined contribution of the well known influence of FeS on the sliding behaviour and the very low thickness of the magnetite layer formed by oxidation. However, when oxidation is carried out after sulphuration, a further increase in the wear resistance is attained. The results of the wear test are only indicative.
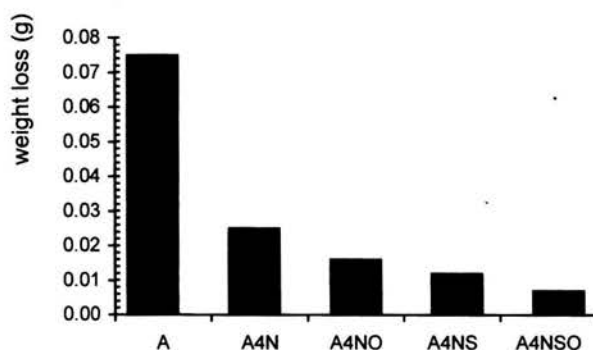
FIGURE 36. Results of the wear test [28].

7.2. Conclusion

It has been shown that with pores closure caused by the boron addition the disadvantage of deep gas nitriding can be eliminated. Furthermore, boron is able to reduce the nitrogen penetration, because it activates the sintering process and closes the residual porosity. However during sintering a depletion from external layers of the base material occurs, and the added element cannot be exploited to form a fine precipitation of hard and stable nitrides in the diffusion layer. Therefore, the microhardness of this layer is not high, because the needle-like γ' nitrides don't harden the matrix. The effect of boron is then limited to the control of the nitrogen

penetration. The combined treatment induces the formation of a surface layer consisting of FeS, magnetite and iron nitrides. In particular sulphuration significantly changes the surface morphology of the treated specimens. As a consequence, the dry sliding wear resistance of the material increased.

7.3. Surface durability of gas nitriding Fe-Mo alloys

The base material was a sintered B alloyed Fe-1.5%Mo alloy produced by compaction at 600 MPa and sintering at 1200°C in pure hydrogen. Boron was added as elemental powder in a low percentage (0.4%) in order to induce liquid phase sintering which closes the porosity and allows a better control of the nitriding depth to be achieved.

The nitrided specimens were characterised at the optical microscope and the Scanning Electron Microscope (SEM) and the constitution of the compound layer was investigated by X-Ray Diffractometry (XRD). Dry sliding wear tests were carried out in a pin-on-disc apparatus (the nitrided specimen was the pin), by using a X210Cr13 tool steel as the counteracting disk. The cylindrical pins have a 6 mm diameter and, after several preliminary tests, the load was set up at 15 N, with the purpose to induce a progressive and measurable wear of the compound layer. The sliding speed was 0.47 m/sec. The experimental apparatus measures the displacement of the pin support, so that the wear curve can be recorded continuously. The tests were carried out for a total sliding distance of 15 000 meters, long enough to differentiate the behaviour of the materials investigated.

The main microstructural characteristics are summarised in Table 11, where the constitution of the compound layer, its thickness and the microhardness are reported. In Figs. 37 to 40 the SEM micrographs of the four compound layers are shown, as well.

TABLE 11. Constitution, thickness (s) and microhardness of the compound layers.

Material	Constitution of the compound layer	s [μm]	$HV_{0.01}$
N	γ'-Fe_4N / ε-$Fe_{2-3}N$	12	600-1070
NO	γ'-Fe_4N / ε-$Fe_{2-3}N$ / Fe_3O_4 / Fe_2O_3 / α	17	960
NS	γ'-Fe_4N / ε-$Fe_{2-3}N$ / Fe_3O_4 / FeS	12	960
NSO	γ'-Fe_4N / ε-$Fe_{2-3}N$ / Fe_3O_4 / Fe_2O_3 / FeS	11	1000

Figure 37 shows the microstructure of the compound layer of material N. The outer layer, where the ε nitride predominates, is rather porous and this results in a lower microhardness (600 $HV_{0.01}$) than in the inner compact part (1070 $HV_{0.01}$). Figure 38 shows the compound layer of NO where the biphased oxide layer in the outer part cannot be distinguished. Table 11 indicates the presence of some α ferrite in the compound layer, which is produced by the oxidation of the nitrides, as reported by Somers et al. [30]. Figure 39 shows the compound layer of NS. Sulphuration has almost completely cancelled the porosity of the layer and caused some oxidation, as Table 11 indicates. Oxide and sulphide particles are finely intermixed, as the O and S concentration profiles show [28]. Finally NSO compound layer is shown in Fig. 40. The layer is well compact again and the thickness of the
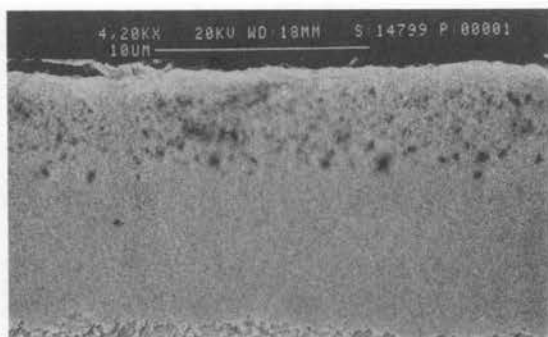
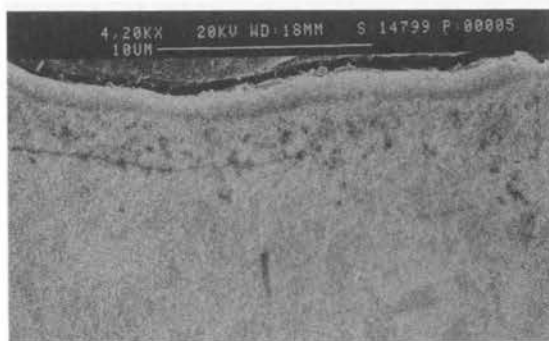FIGURE 37. Compound layer of material N [29].

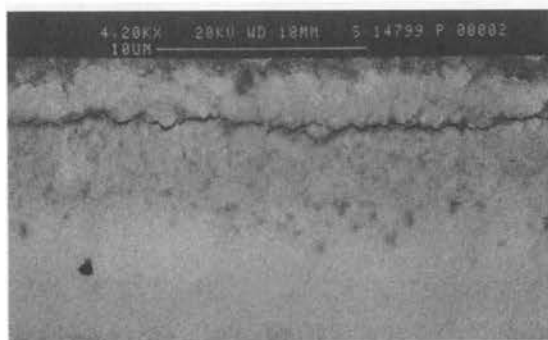FIGURE 38. Compound layer of material NO [29].

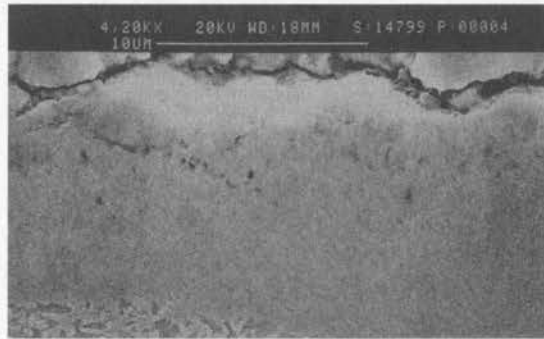FIGURE 39. Compound layer of material NS [29].

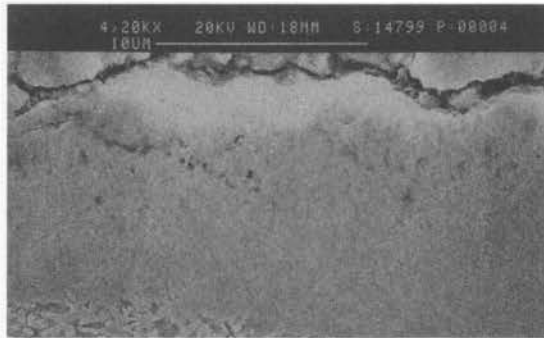FIGURE 40. Compound layer of material NSO [29].

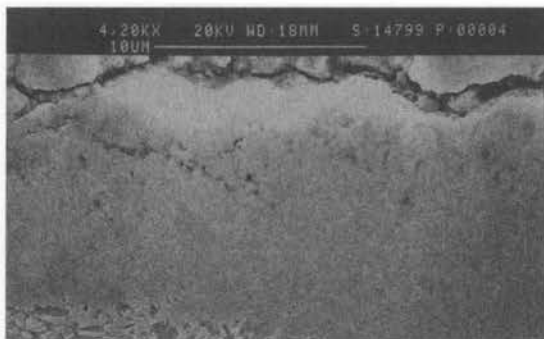FIGURE 41. Surface morphology of untreated material [29].

FIGURE 42. Surface morphology of material NS [29].

oxide/sulphide layer is greater than the penetration depth of X-rays (a Cu tube was used for XRD) so that the inner γ' layer was not detected by XRD.

The treatments modify the surface morphology in a different way. The best surface topography is shown by NS and NSO, where the irregularities due to the surface porosity of the sintered substrate (Fig. 41). are almost completely cancelled (Fig. 42 relevant to NS). Nitriding and oxynitriding causes only small changes in the surface topography.

Figures 43 and 44 show the wear curve of the untreated material and of NO, respectively. The wear curve of the untreated material shows a constant linear behaviour after a short running-in, which indicates the fast attainment of a steady state condition. Contrary, Figure 44 shows a prolonged period with an absolutely very low wear, after that a transition to a second step occurs, where wear rate (computed by the slope of the curve) is about one order of magnitude lower than that displayed by the untreated material (3×10^{-6} mm/m versus 2×10^{-5} mm/m).

All the treated materials have similar wear curves but while the wear rate in the second step is almost the same (2 to 5×10^{-6} mm/m), the sliding distance at which the transition occurs is very different. Table 12 reports the transition distance of all the materials.

TABLE 12. Wear transition distance of the compound layers.

Material	Transition distance [m]
N	2 290
NO	6 940
NS	> 15 000
NSO	3 440

The characterisation of the specimens worn up to different intermediate sliding distances and of the wear debris indicates that the first step corresponds to the wear of the compound layer and the second to the wear of the diffusion layer. Both the process occur by an oxidative wear mechanisms, as demonstrated by the analysis of the wear debris.

Figure 45 shows an example of the XRD spectrum of the debris which is constituted by hematite only. The lower wear rate with respect to that of the untreated material can be attributed to the higher hardness (the harder the substrate, the higher the mechanical support to the oxidised surface and, in turn, the lower the oxidative wear rate). The transition distance can be taken as representative of the wear resistance of the compound layer or, in other words, of its durability: the greater the distance, the greater the durability.

All the surface treatments here considered increase the wear resistance of the base material, mainly thanks to the properties of the compound layers. In particular the layer produced by NS has the highest durability. At the end of the test (15000 meters sliding) the compound layer was still present on the wear surface, as Fig. 46, which is a cross section of the worn pin, shows.

The very high durability results from the contribution of different factors: (a) the high hardness, (b) the low porosity, (c) the better surface topography which increases the load bearing surface area, (d) the presence of FeS which, as well known,
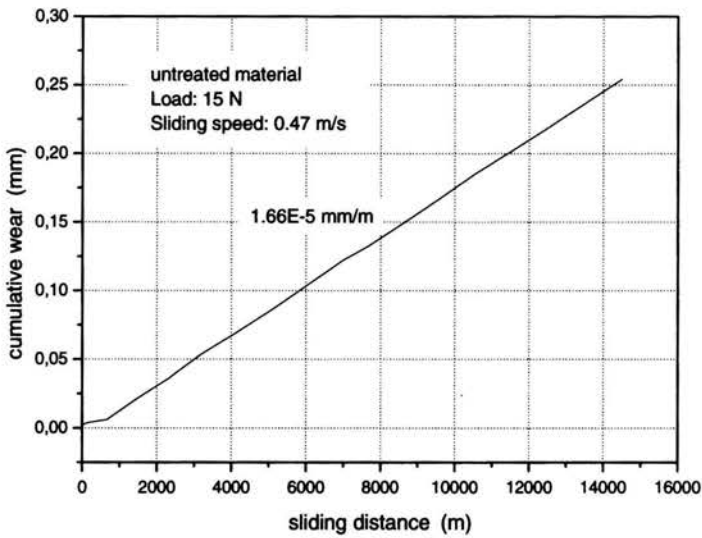
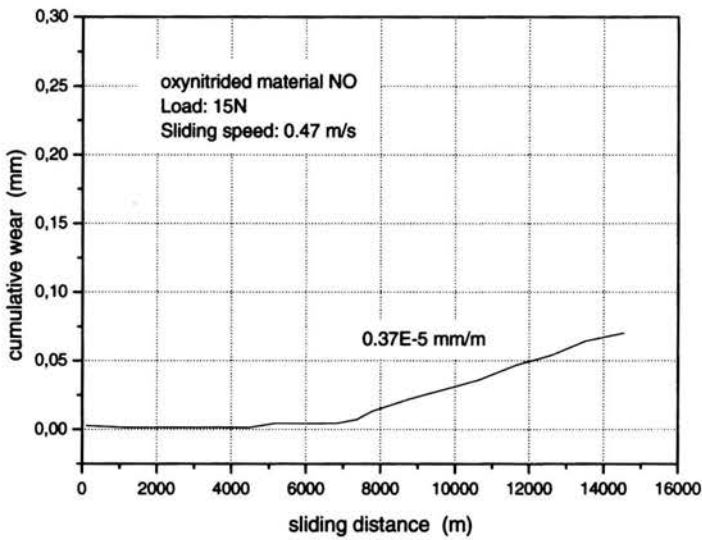FIGURE 43. Cumulative wear curve of untreated material [29].

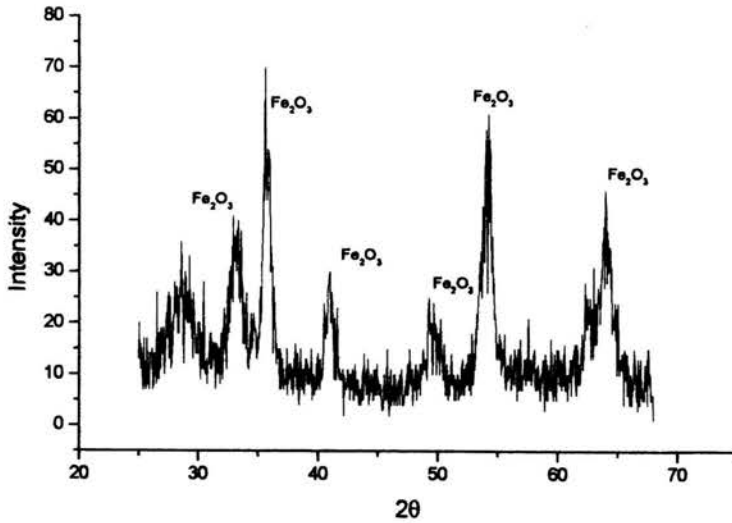FIGURE 44. Cumulative wear curve of material NO [29].

FIGURE 45. X-ray diffraction pattern of wear debris collected during the test [29].
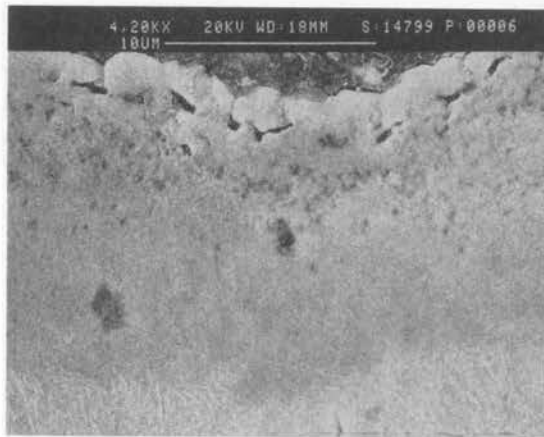

FIGURE 46. Surface morphology of material NS after wear test [29].

has very good friction properties against steel. Even an outer oxide layer improves the surface durability of a nitrided surface, as the transition distance of NO demonstrates if compared to that of N, but the effect is not so strong as for NS. The combination of oxidation and sulphuration does not give significant advantages.

7.4. Final remarks

A sintered Fe-1.5%Mo-0.4%B material was subjected to different gas nitriding treatments in order to study the effect on the dry sliding wear resistance. In addition to nitriding, oxynitriding, sulphonitriding and oxysulphonitriding were investigated. These combined treatments produce compound layers formed by iron oxide and/or iron sulphide in addition to the usual γ'-Fe$_4$N and ε-Fe$_{2-3}$N nitrides produced by nitriding. The wear experiments show that all the treatments greatly improve the wear resistance of the base material, and in particular sulphonitriding which forms a compound layer with a durability well higher than that of the layers formed by the other treatments. This result is due to the improved surface topography, layer compactness and to the presence of iron sulphide which posses excellent friction properties against steel.

8. Wear behaviour of steam treated sintered alloys

Steam treatment is the most widely used surface treatment for iron base sintered components. Its effect on the technological properties of P/M parts is well known. Among these properties, wear resistance is improved because of the reduction in friction coefficient and increase in the load bearing capacity [31].

In association with an industrial partner/a five-year research project has been carried out in the Department of Materials Engineering, University of Trento, aimed at optimization of the process parameters for the production of steam treated P/M parts having high dry wear resistance. The process was carried out both in a batch mode and in continuous furnaces [32]. Alloys with different chemical compositions were included and specific wear experiments were carried out on laboratory-scale equipment.

Specific attention was given to metallurgical interpretation of the wear mechanisms. Here is the review of these findings in order to discuss the tribological behaviour of steam treated P/M materials and to delineate the effect of base material composition on wear behavior.

The study was carried out on the alloys summarized in Table 13.

TABLE 13. Nominal composition and sintered density of the alloys [31].

Alloy	Nominal chemical composition					Density [g/cm^3]
	Fe	C	Cu	Mo	Ni	
1	100					6.6
2	99.7	0.3				6.6
3	98		2			6.6
4	98	0.5		1.5		6.8
5	93.4	0.6	1.5	0.5	4	6.8

Specimens for the wear experiments (disks: 40 mm diameter × 10 mm height, with an internal hole 16 mm diameter) were produced in industrial plants under representative industrial conditions (sinter at 1120°C for 30min in endogas). Steam treatment was carried out both in batch and continuous furnaces. The steam treatment temperature was fixed at 550°C, and the other process parameters (atmosphere composition, treatment time and belt speed in the continuous furnace) were optimized [32]. Some specimens were heat treated to provide a base reference. Heat treatment consisted of austenitizing at 860°C for 10 min, quenching in oil at 65°C and stress-relieving for 2h at 150°C. The density of the sintered and heat treated specimens was in the range 6.6-6.8 g/cm^3. After steam treatment, porosity is closed (less than 1% open porosity, as determined by water displacement [32]) and an oxide layer 8-10 μm thick cover the external surface.

The wear tests were carried out using an Amsler disk-on-disk tribometer with test loads in the range 25-100 N, without a lubricant. Table 14 summarizes the experimental conditions adopted for the wear tests: the alloys used for the specimen disk and for the counterface disk, rotation speeds (n_1 and n_2) and the total sliding distance. In dry sliding, only the steam treated disk rotates and a different counterface material is used to reduce the effects of adhesion. In rolling-sliding the same materials were used for both the specimen and the counterface disk. Both disks rotate, but at different speeds, in order to induce different tangential speeds to produce a 10% slippage. These test conditions are normal for this form of wear testing [34].

TABLE 14. Details of wear experiment [31].

	Sliding	Rolling-Sliding
Specimen Disk	Steam Treated Material $n_1 = 100$-200-400 rev/min	Steam Treated Material $n_1 = 400$ rev/min
Counterface Disk	AISI 4340 (33 HRC) $n_2 = 0$	Steam Treated Material $n_2 = 300$ rev/min
Sliding Distance	1 420 m	10 000 m

Wear was determined by weighing the specimens at regular intervals after careful cleaning. No weight gain was observed. In all the cases, at least three experiments were carried out for each condition, and the results are average values. In addition, the friction coefficient was monitored continuously during the test.

Figure 47 gives a qualitative representation of the results of preliminary experiments carried out under dry sliding conditions. The results refer to alloy no. 4 tested at a sliding speed of 0.4 m/s with different loads. The data indicate that:

- steam treatment reduces the wear volume of the sintered material;
- the steam treated material exhibits a sharp increase in wear volume between 50 N and 100 N load;
- in the low load region, the steam treated material exhibits a similar (30 N) and a lower (50 N) wear volume than the heat treated material;
- at 100 N load the wear volume of the steam treated material is higher than that of the heat treated material.

1=no wear; 2=wear volume<0.1%;
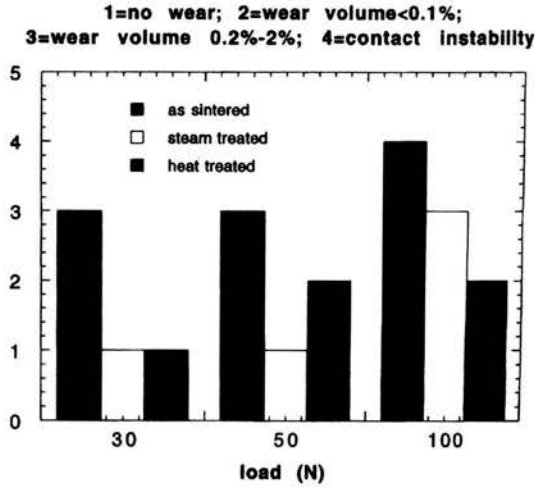**3=wear volume 0.2%-2%; 4=contact instability**

FIGURE 47. Dry sliding wear response of alloy no. 4 as a function of processing history [31].

The beneficial effect of steam treatment on the wear resistance of the sintered alloy steel is thus confirmed for the load range examined. Moreover, the results indicate that steam treatment may be preferred to conventional heat treatment.

Figure 48 shows the wear data for steam treated alloy no. 4 tested at 100 N. Three steps, each with a different wear rate, can be distinguished from the examination of the wear debris and the worn surfaces:

Step A: The surface oxide layer is essentially undamaged on the surface of the specimen and the wear rate is negligible;

Step B: Adhesive wear of the surface oxide layer occurs, causing a measurable weight loss of the steam treated alloy;

Step C: Wear of the subsurface material by delamination or oxidation occurs, depending on the sliding speed, after complete removal of the surface layer. Here the wear rate is constant and significantly higher than that in step B.

Thus, the two initial steps are linked to the wear process of the surface oxide layer. As long as the layer remains on the surface, the wear rate is low and for this reason the wear behaviour of the steam treated alloy was found to be better than that of the heat treated material, Fig. 47. At 30 N and 50 N the transition distance between steps B and C is close to the total sliding distance of the test reported in Fig. 48 and the total wear volume of the steam treated alloy is lower than that of the heat treated one. In contrast, at 100 N the transition distance is low due to the effect of the load and the wear of the bulk material predominates during the test.

The hardening effect of the oxide that is formed in the interconnected pores during steam treatment is lower than that of the stress-relieved martensite produced by heat treatment; thus, the wear volume of the steam treated alloy is higher than that of the heat treated one. This trend was maintained over the entire sliding speed range experimented as shown, for example, in Fig. 49; this figure compares the wear
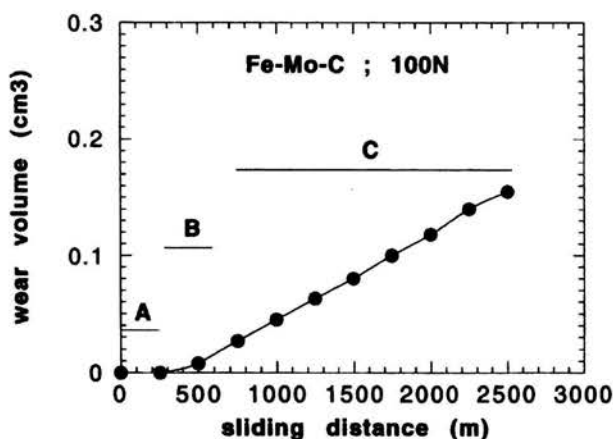
FIGURE 48. Wear volume as a function of sliding distance for steam treated alloy no. 4 [31].
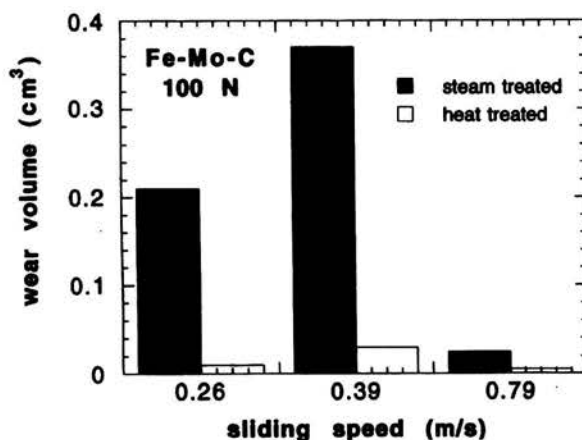

FIGURE 49. Effect of heat treatment on the sliding wear behaviour of alloy no. 4 at three sliding speeds [31].

volumes of alloy no. 4 subjected to the two treatments and tested at 100 N. It is seen that wear increases with sliding speed from 0.26 m/s to 0.39 m/s, and then decreases. This trend is explained in terms of the increase in frictional heat as the sliding speed increases. The wear behavior derives from a combination of two phenomena: thermal softening of the base material which reduces wear resistance, and the occurrence of surface oxidation which induces mild oxidative wear. The former effect prevails at intermediate speeds and the latter prevails at the highest speed, reducing significantly the wear volume [31].

Analogous results have been obtained for unalloyed Fe-C steel. In comparison with the untreated base material, the steam treated alloy maintains a higher wear resistance, even after complete removal of the surface oxide, as shown in Fig. 50, which compares the wear rate during stage C (Fig. 48) of alloys no. 1, 2 and 3. Similar results were obtained under dry rolling-sliding conditions. For example, Fig. 51 shows the wear rate of alloys no. 4 and 5 in the as-sintered, steam treated and heat treated conditions; the test load was 100 N. The figure confirms that the wear resistance of the steam treated alloys is higher than that of the as sintered alloys, but lower than that of the heat treated alloys. In terms of the wear mechanisms the damage process of the external oxide layer starts at the beginning of the test so that the protective action described previously cannot intervene [31]. The rolling-sliding condition is more severe than pure sliding, as confirmed by other experiments on both sintered and wrought alloys. Under these conditions the improvement of wear resistance by steam treatment is due mainly to the hardening effect of the oxide layer in the interconnected pores. The wear resistance is lower than that of the martensite.
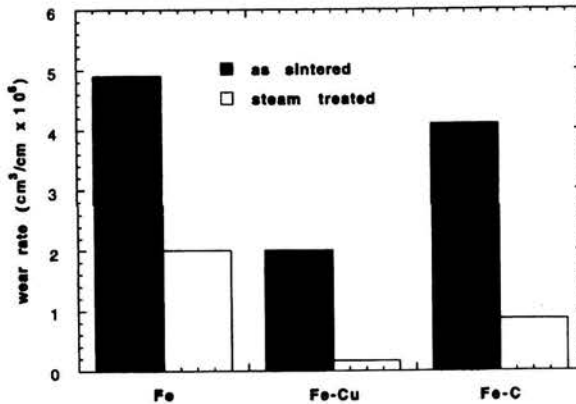

FIGURE 50. Effect of steam treatment on the sliding wear behaviour of alloys no. 1, 2 and 3 [31].

Figure 51 shows that the Fe-Mo-C alloy has a higher wear resistance than the Fe-Ni-Cu-Mo-C alloy. The difference between the two alloys decreases after steam treatment (though still appreciable) and is almost negligible after heat treatment. The mechanisms are both oxidative wear and delamination, the former prevailing when the mechanical properties of the alloy are increased by the two treatments. In this case the microstructural homogeneity of the Fe-Mo-C (fully bainitic) is responsible for the higher wear resistance, since the presence of softer phases in the other alloy (produced by a partially prealloyed powder) favours the nucleation of cracks by delamination. This effect tends to be offset by heat treatment which increases the mechanical properties of the alloy, thereby reducing the role of delamination during wear. Steam treatment does not provide sufficient hardening to prevent delamination, and the negative effect of the microstructure is maintained [31].
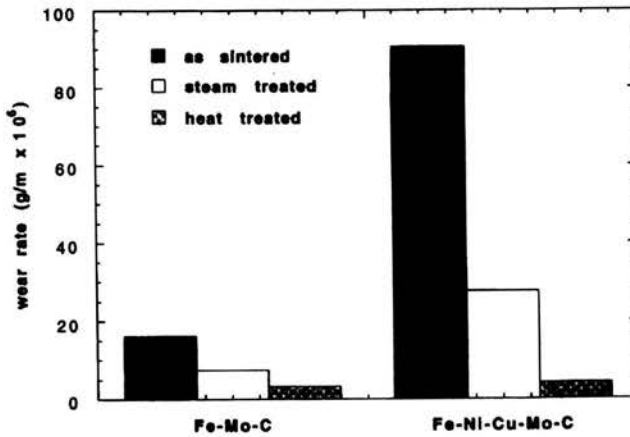
FIGURE 51. Effect of steam treatment and heat treatment on the rolling-sliding wear response of alloys no. 4 and 5 [30].

8.1. Surface durability of steam treated PM steels

The sliding experiments show that under low to medium load, the surface oxide formed during steam treatment can be more effective in reducing wear than the stress-relieved martensite produced by heat treatment or case hardening. It is therefore important to study the wear process in this layer, in order to identify the tribological conditions under which the steam treated alloy is able to resist wear. For this reason it is possible to introduce the concept of "surface durability".

From previous work [31] it has been demonstrated that the wear process in the surface oxide under dry sliding conditions can be studied by monitoring the magnitude of the friction coefficient during the wear test. For example, Fig. 52 shows μ as a function of sliding distance for steam treated steel alloy no. 2 sliding against AISI 4340 steel under the following conditions: 50 N load, 0.314 m/s sliding speed. Three steps can be identified on the diagram, each of which corresponds to a specific phenomenon, as demonstrated by characterization of the worn surfaces [31].

Step 1: The surface layer does not undergo wear and the level of friction is very low due to the solid lubricating effect exerted by the undamaged oxide layer;

Step 2: A transfer layer is formed on the oxidized surface, because the hardness of the oxide is higher than that of the counterface steel; friction increases but no wear debris is produced;

Step 3: The friction coefficient is stabilized at a constant value with fluctuations due to the production of oxide debris; the first fluctuation is related to initiation of the wear process of the surface oxide. The entire wear process of the alloy comprises two other steps which occur at a larger sliding distance (> 300 m) and are not included in the figure;

Step 4: The oxide layer undergoes extensive wear and friction increases because of the metallic joints that form between the counteracting surfaces;

Step 5: The surface oxide is destroyed completely and metallic wear of the sub-
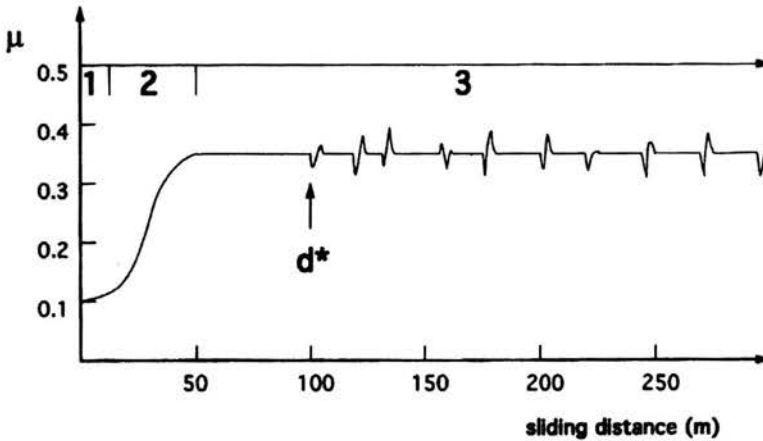surface material occurs.

FIGURE 52. Relation between friction coefficient and sliding distance at 50 N load for steam
treated alloy no. 2 [31].

The parameter d^* shown in Fig. 52 is taken to be representative of the "surface
durability" of the alloy. Its dependence on test load is shown in Fig. 53; for a test
load of 30 N no wear of the surface oxide was detected, even for sliding distances
> 1420 m. Therefore this load is considered to be analogous to the "endurance limit"
of the alloy under these specific test conditions; it represents the load at which the
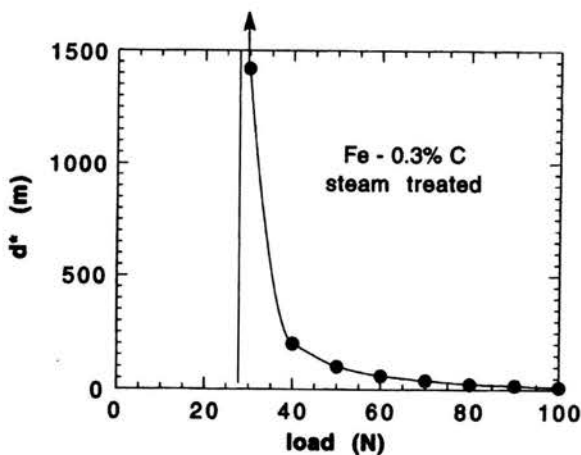surface oxide is able to protect the subsurface material against wear.

FIGURE 53. Effect of test load on d^* for steam treated alloy no. 2 [31].

Under dry rolling-sliding conditions the wear process is more complex. It has been shown that the formation of the transfer layer occurs at the beginning of the test, even at low loads, and that wear of the surface layer and of the subsurface alloy occurs almost simultaneously [31]. Thus, it is not possible to define a sliding distance with the same significance as d^*.

The wear curve for alloy number 1 (pure iron) tested under rolling-sliding conditions at 75 N is shown in Fig. 54. Two steps can be defined from a characterization of the worn specimens [31]:

Step 1: Formation of the transfer layer without wear in the steam treated alloy;

Step 2: Wear of the surface layer by adhesion and of the subsurface alloy by delamination. Under these conditions a theoretical approach was used to determine
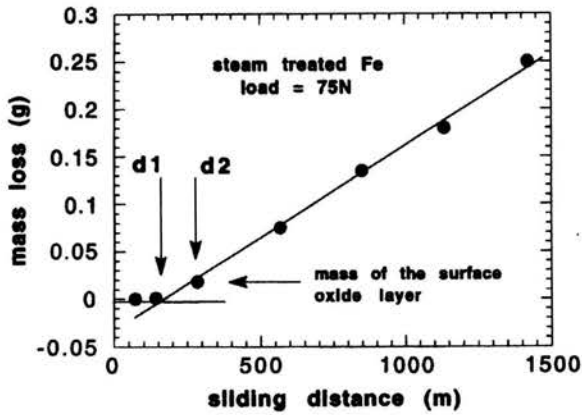

FIGURE 54. Mass loss as a function of sliding distance in rolling-sliding wear of steam treated alloy no. 1 at 75 N load [31].
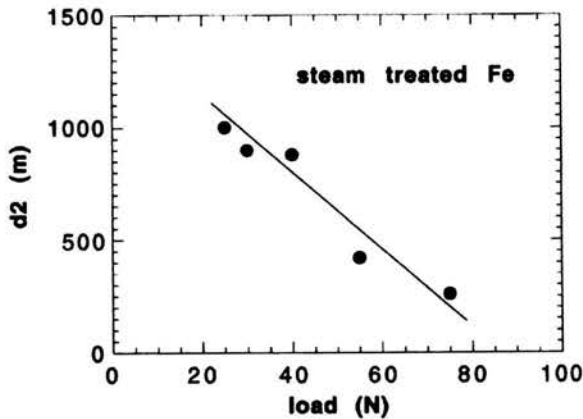

FIGURE 55. Effect of test load on d_2 for steam treated alloy no. 2 [31].

two distances: d_1 at which step 2 initiates, defined by the intersection of the two parts of the wear curve; d_2, at which the surface oxide is completely destroyed, and is defined as the distance at which mass loss corresponds to the mass attributable to the surface oxide (computed from the known thickness and density of magnetite). Both parameters are approximate; because of excessive scatter in d_1, d_2 was selected as representative of the "surface durability". Figure 55 shows the dependence of d_2, on test load.

A comparison between pure sliding and rolling-sliding cannot be made based on the parameters d_1, and d_2 due to their different physical meaning. Instead these parameters can be used to compare different alloys under the same contact conditions, as discussed in the following section [31].

8.2. Effect of base material composition on surface durability

A comparative study was carried out under pure sliding [35] and rolling-sliding [33] conditions on alloys 1, 2 and 3. These alloys are used widely in the production of steam treated P/M parts. Figure 56 shows the wear results for pure sliding; it is clear that the "surface durability" increases in the order: Fe-C > Fe > Fe-Cu. This trend was also confirmed under rolling-sliding, as shown in Fig. 56. These results suggest that the composition of the base alloy is important and must be considered when designing a steam treated component.
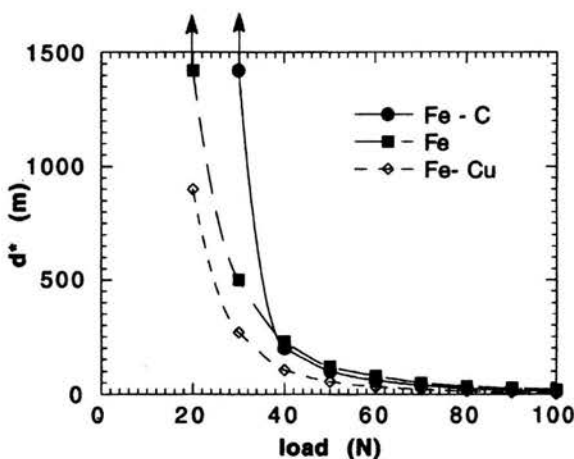

FIGURE 56. Effect of test load on d^* for steam treated alloys no. 1, 2 and 3 in sliding wear [31].

The effect of chemical composition is attributed to two main factors:
1. The influence of the alloying element on the mechanical properties of the base material;
2. The influence of the alloying element on the oxidation of iron. Both carbon and copper increase the hardness of iron and, therefore, the load bearing capacity of the alloy. This is an important factor in wear, even when the damage process
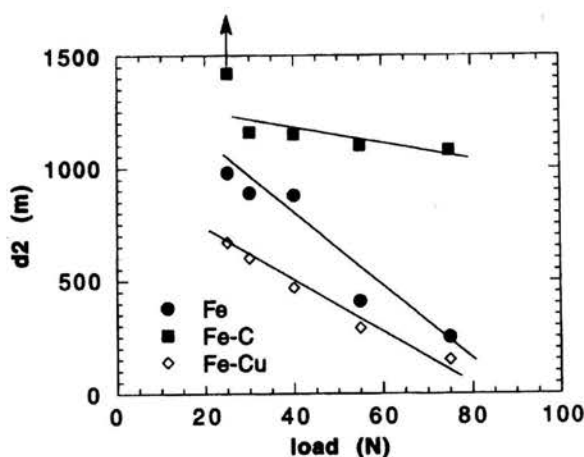
FIGURE 57. Effect of test load on d_2 for steam treated alloys 1, 2 and 3 in rolling-sliding wear [31].

is confined to the surface layer [31]. This effect is confirmed for carbon, but the effect of copper is negative. It is well known from thermodynamics that copper has a lower affinity for oxygen than iron. Also the low activity of copper in solid solution in iron further decreases its reactivity in an oxidizing atmosphere. For this reason, only iron is oxidized during steam treatment, as confirmed by the accumulation of copper at the metal-oxide interface [31]. In consequence, the microstructural quality of the surface oxide in the Fe-Cu alloy is not conducive to wear resistance. Primary factors are:

(a) Microdefects and residual stresses because of selective oxidation at the surface [31];

(b) The formation of an external layer of hematite, caused by the presence of copper at the metal-oxide interface and which inhibits the normal cut-diffusion of iron necessary to sustain the formation of magnetite; consequently oxidation of magnetite to hematite occurs at the surface, sustained by the in-diffusion of oxygen [31].

Since carbon does not affect the oxidation of iron significantly since it is present in the microstructure in the form of pearlite nodules, its presence is beneficial. This positive effect is maintained when carbon is added to a Fe-Mo base powder to produce alloy no. 4. In contrast, the negative effect of copper prevails with an attendant negative effect on "surface durability" [31].

8.3. Final remarks

The results of research project on the wear resistance of steam treated sintered ferrous alloys have been reviewed. Data confirm the positive effect of steam treatment on the tribological behaviour of sintered iron base alloys. The following conclusions are drawn:

1. The oxide that grows in the interconnected pores enhances mechanical properties, in particular the load-bearing capacity of the steam treated alloys.

2. The oxide that grows on the external surface of P/'M parts reduces the friction coefficient and protects the subsurface layers against metallic wear.

3. This second effect depends strongly on the resistance of the surface oxide; as long as it remains undamaged the improvement in wear resistance can be higher than that provided by conventional hardening treatments, particularly at low to medium load levels.

4. The concept of "surface durability" is proposed in order to quantify the wear resistance of a surface layer.

5. "Surface durability" can be determined by means of dry sliding experiments; under dry rolling-sliding conditions the wear process is complex and only an approximate (although significant) assessment can be made.

6. For both tribological conditions considered, the chemical composition of the base material influences significantly the wear behaviour; in particular copper reduces "surface durability" whereas carbon increases, this parameter relative to pure iron.

7. Chemical composition is an important process parameter in designing a steam treated sintered component.

8. Copper should be avoided, whereas the addition of carbon is beneficial.

9. When delamination wear occurs, the microstructural homogeneity of the base alloy has a strong influence on wear [30].

9. Developments of new material

For many applications (high Hertzian contact stresses, fatigue), the mechanical properties of the diffusion layer are much more important than those of the compound layer and nitriding has to produce a strength profile higher than the stress profile (Fig. 58). In order to obtain such a strength profile, specific elements (chromium, aluminium, molybdenum, and vanadium) are added to wrought steel. These elements have a greater affinity for nitrogen than iron, and form submicroscopic precipitates in the diffusion layer. Only in these conditions is nitriding able to significantly improve the mechanical properties of the diffusion layer.

For example, chromium was added as a prealloyed powder to atomised iron to obtain a 4 % Cr alloy by sintering in dissociated ammonia at 1250°C. [10]. Because of the microstructural heterogeneity after sintering, due to the inhomogeneous Cr distribution, the microhardness in the diffusion layer varies between 200 $HV_{0.05}$ in the Cr-free grains and 780 $HV_{0.05}$ in the Cr rich grains. The result can be improved by nitriding a homogeneous prealloyed material based on the above powder or on ferritic stainless steel [36]. A positive effect of chromium on plasma nitriding was demostratyed by Roso et al [37]. Promising results were also obtained by Maliska et al. [16] by nitriding a homogeneous Fe-4 % Mn alloy; a further improvement of these results can be reasonably attained by optimising the treatment parameters and/or by adding some carbon to the base material.
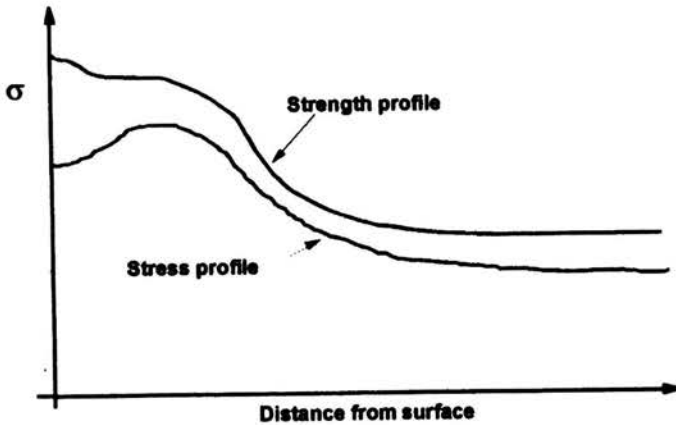
FIGURE 58. Strength profile of nitrided material capable of resisting Hertzian stress profile [35].

Prealloyed Fe-0.5Mo-xCr with two different chromium contents was tested by A. Molinari and al. [35]. By adding graphite, a material similar to the conventional wrought nitriding steel can be obtained. Plasma nitriding was carried out both on the as sintered material and after heat treatment, in order to investigate the effect of microstructure on nitriding. and microstructure of materials [35].

Plasma nitriding has been applied to sintered materials produced using a newly developed Fe-Cr-Mo prealloyed powder. Graphite was added to produce a 0.4% C steel. Nitriding was carried out on the carbon free material and on the steel, the latter in the as sintered condition as well as after heat treatment. The results demonstrate the liability of the material to develop a hard and defined diffusion layer on all the materials investigated owing to CrN precipitation. Carbon improves the mechanical properties of the diffusion layer. The best results in terms of maximum hardness and thickness of the diffusion layer were obtained on an Fe-3Cr-0.5Mo-0-4C material, sintered after quenching and stress relieving. However, wear experiments demonstrate that heat treatment is not necessary for wear resistance, the lowest wear rate being measured on the material nitrided in the as sintered condition.

The results of wear tests and impact tests indicate that plasma nitriding is an alternative to conventional quenching and stress relieving for material Fe-3Cr-l-5Mo-0-4C. The two treatments constitute alternative solutions to resist Hertzian contact stresses. In order to choose the optimum solution, both economic and technical aspects have to be considered. Apart from economic aspects (the cost of the two treatments depends on many factors, but they should be comparable), some technical limitations have to be taken into account. In principle the main limitations of heat treatment are the necessity to rinse the treated pieces to remove quenching oil, to control the effects of dimensional variations caused by martensitic transformation, and to control surface carbon content in order to avoid decarburisation. This last aspect is very important because the wear resistance and fatigue resistance of a quenched component depend very much on surface hardness and, in turn, on surface carbon content. On the other hand, the main technical limitation of plasma nitrid-

ing is the so called edge effect: overnitriding may occur as a result of the discharge concentration on the sharp edges. Overnitriding causes the formation of asperities in the compound layer and of grain boundary carbonitrides in the diffusion layer. Both effects are deleterious for wear resistance. Another limitation is that plasma nitriding cannot be carried out simultaneously on pieces with surface/mass ratios which are too different when heating is achieved by sputtering, since they do not reach the same temperature or, at least, do not warm up with the same heating rate because of the particular heat exchange mechanism. This could produce different results on the different pieces. This problem can be solved by using the hot wall furnaces, where heating is independent of sputtering. From the above considerations, plasma nitriding can constitute a valid and reliable alternative to heat treatment.

Plasma nitriding and conventional heat treatment provide the same wear resistance and impact resistance to the base material. Therefore, they are alternative technological solutions for components which have to resist Hertzian contact stresses and fatigue; however, plasma nitriding may be preferred to conventional heat treatment for some technical reasons [35].

To conclude this paper, the author want to begs pardon to all scientists that contributed to widen the knowledge of surface properties of PM sintered materials, but to avoid any omission, the list of reference should be increased considerably.

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