CHAPTER 1

REVIEW OF LITERATURE

1.1 INTRODUCTION

Steam oxidation as a surface finishing technique has been in use for many years to improve the appearance of small mechanical components produced from steel or cast iron and to improve their resistance to wear and corrosion. Examples of components which are steam treated are gears, cams, chains, pinions, compressor parts, bearings, pulleys, sprockets etc. Typically, all exterior surfaces react to form a very thin skin (2.5 to 5 μm) of oxide.

These days, there is considerable interest in Powder Metallurgy (PM) as a manufacturing technique for fabrication of small structural components. The technology has shown the highest rate of growth during the last three decades, i.e. 6-7 % on an average in the world. This is mainly due to (i) saving in material and machining cost, (ii) high productivity method yielding products exactly or very close to final dimensions requiring very little or no machining afterwards, (iii) simple and automated method of manufacture and (iv) its being energetically favourable process.
However, conventional PM products are less hard and strong as compared to their wrought or cast counterparts having identical chemistry. This is due to inherent porosity (10-25 %) present in them which may be isolated or interconnected. The interconnected porosity in PM parts may constitute up to 97 % of the pores or voids in the part. Thus, PM parts require some type of treatment to seal, at least the surface pores particularly for corrosion resistance. Various methods of closing the pores are as follow:

1.1.1 Alloy Infiltration

In this method, a low melting alloy slug is placed on the part which is then put through the sintering furnace at a temperature which is above the melting point of the alloy. The molten alloy then wicks through the part, effectively sealing off the porosity. This process greatly increases the strength of the part and improves machinability.

1.1.2 Wax Impregnation

This is a less common method of sealing, primarily because it is difficult to get rid of surplus wax on the surface and because use of the part at elevated temperatures can cause the wax to melt.
1.1.3 **Plastic impregnation**

This is presently the most prevalent method used for sealing PM parts. It is usually applied under vacuum and uses relatively fast curing resins. Unless there are unusual cracks or very large voids in the part, resin impregnation will seal against high pressure of hydrogen as well as hydraulic pressure.

1.1.4 **Steam treatment**

This is possibly the least expensive method of sealing pores. When sintered ferrous components are exposed to steam at elevated temperature, a layer of oxide upto 5 µm thick forms on all exterior surfaces and also within the interconnected pore network to an extent which is dependent on the steam treatment conditions (1). Following advantages have been claimed for steam treatment of sintered ferrous parts:

(i) Magnetic iron oxide formed improves wear resistance of the surface to abrasive wear during service. The oxide formed within the pore network provides wear resistance (2,3) after surface layer is wornout.

(ii) The oxide layer formed is extremely adherent (4,5)
and is less prone to defects such as cracks and blisters than oxide coating formed in air.

(iii) Compressive strength of the part increases (3).

(iv) The oxide layer becomes impermeable at thickness of about 5 µm (6) and resistance to rusting of treated component is improved. The danger of local corrosion cells being created within pores is reduced.

(v) In case of high density sintered parts, surface pores can be completely closed. Impregnation and consequent entrapment of electrolyte during subsequent electroplating operations is prevented but conductivity remains sufficiently high for direct plating to be carried out. When surface pores are completely closed the parts can withstand high gas pressures (7).

(vi) The small dimensional increase (about 10 µm), after treatment does not create problems (4).

(vii) The treatment is economic (8) and it has been claimed that the cost of pore sealing by steam treatment is about 15% of that arising during infiltration with copper and about 30% of that
incurred during plastic impregnation (5).

(viii) The blue-black colour developed during treatment is pleasant in appearance especially after subsequent oil dipping.

Additional reported works (9-20) on the effects of steam oxidation on porosity and properties of sintered iron also claim one or more of the above benefits.

1.2 STEAM TREATMENT OF Fe–Cu SINTERED ALLOYS

Effect of copper on steam treatment of sintered iron has also been studied quite extensively (17, 21-31).

Sunter and Cosh (17) after studying steam treatment of sintered iron and iron 1.1 wt % Cu alloy found that corrosion rates were considerably reduced. They have claimed superior surface finish and corrosion resistance to that of a similarly shaped wrought and machined part.

Hammer and Vannerberg (21) found that small additions of copper had little effect on the oxidation of solid iron at 500°C in oxygen or oxygen-argon atmosphere.

Phadke and Davies (25) carried out ageing treatment at 500°C in nitrogen or vacuum of Fe–2 to 6 wt. % Cu powder compacts sintered at 1150°C for 1 hr. and found
significant increase in hardness of quenched as well as furnace cooled (25°C/min) specimens after precipitation hardening treatment. Massive martensite was found in some regions of 4 and 6 wt % Cu alloy after water quenching but it was absent from the 2 wt % Cu alloy. Solution treated peak hardness values increased with copper percentages. However, the 2 wt. % Cu alloy showed maximum percentage increase in hardness although the magnitude of hardness increase over the solution treated values was nearly the same in the three alloys.

The above observations led to the authors (26) to prepare Fe-2 % Cu compact from elemental powders and sinter for 1 hr. at 1150°C and cool at an average rate of 75°C/min in an industrial sintering furnace. The resulting alloy was aged at 500°C in an inert atmosphere and also in steam. The hardness increase during ageing in an inert atmosphere was about 22 %. However, ageing in steam resulted in an additional gain in hardness due to simultaneous precipitation of copper and also formation of Fe₃O₄ by void filling. The hardness values obtained during ageing in steam were compared with the values calculated from data obtained on steam oxidized pure iron compacts and results of ageing in inert atmosphere. The
result showed that degree of hardness increase due to steam oxidation was found to be nearly the same in pure iron and in the Fe-Cu alloy studied. This preliminary study appeared attractive from the point of eliminating separate solution and ageing treatments in Fe-Cu sintered alloys. Later on Phadke (27) carried out ageing of iron-copper compacts containing 2, 4, 6 and 8 wt% Cu at 500°C and observed that hardness increased after furnace cooling but the response to subsequent ageing decreased as the copper content increased. The magnitude of increase in peak hardness was detected in Fe-8 Cu alloy. The size of the precipitates which could be resolved at a magnification of 20000 X was above about 25 nm in all the alloys. Similar results were found in a further study (28) by simultaneous ageing and steam oxidation. The results indicate that the oxidation rate decreases with copper addition.

The response to simultaneous ageing and steam oxidation decreases with increasing copper content. For maximum benefit, it is necessary that maximum mass gain due to formation of Fe$_3$O$_4$ should occur before or concurrently with peak hardness due to precipitation of copper. This condition was fulfilled only in the case of Fe-2 % Cu alloy.
Razavizadeh and Davies (29) selected sponge and atomized - two types of iron powders and after compaction to densities of 6.0, 6.4 and 6.8 Mg/m$^3$ and after sintering under standard conditions subjected sintered compacts to steam oxidation at 450, 525 and 600°C. Kinetics of oxidation were always faster for sponge iron than for atomized iron and there was a corresponding increase in the rate of pore closure and in surface hardness. It was concluded that for effective sealing of surface pores components should be of high density and be steam treated at 600°C but for attainment of maximum hardness components should be of high density and be steam treated at 525°C. After certain time, dependent on initial density and steam treatment temperature, surface pores became sealed and steam could no longer permeate through the internal pore net-work. Open porosity decreased to an apparently low level.

Razavizadeh and Davies (29), have summarized the previous work on theoretical and kinetic aspects of steam oxidation. It has been shown (6) that Fe$_3$O$_4$ is the only oxide formed when the ratio $P_{H_2O}/P_{H_2}$ lies between 0.1 and 1 when the temperature of reaction falls between 400–600°C. At low temperatures, (25°C), the only product formed when iron reacts with water vapour free from oxygen
is Fe(OH)$_2$. However, if air is present, some Fe$_3$O$_4$ also forms (32). At temperatures above 60°C Fe$_3$O$_4$ is formed. FeO does not form at temperatures less than 570°C but within the range 570–700°C both FeO and Fe$_3$O$_4$ form and the proportion of FeO produced increases with temperature. The phase diagram for the Fe/O$_2$ system shows that at 570°C, FeO decomposes eutectoidally to α-Fe and Fe$_3$O$_4$.

The initial rate of steam oxidation, as measured by weight gain, is very rapid and more than 50% of the total weight gain occurs within 10 min. (30 and 32). The reaction rate decreases markedly after about 1 hr. Franklin and Davies (1) examined the influence of treatment at 520 and 650°C and demonstrated that at 650°C very rapid oxidation occurred, but because of surface sealing, a lower total oxide content is achieved after long treatment times than is normal at the lower temperature. It was suggested that treatment at the higher temperature might be appropriate as a preliminary to electroplating. In a further study (30) of Fe–2 to 8 wt % in alloy compacted to a density of 6.8 Mg/m$^3$ and sintered for 1 hr. at 1120°C and steam treated at 525°C, it was observed that wear resistance of sintered iron were improved by steam treatment and by addition of copper in amounts up to 8 wt %. However, steam treatment of sintered Fe–Cu alloys has
adverse effects on wear resistance. An increase in hardness was associated with an increase in wear resistance. They used atomized iron powders grade ASC with admixed copper as well as pre-alloyed iron powder which were compacted to 6.8 Mg/m$^3$ density and sintered at 1120°C for 1 hr. in dissociated ammonia atmosphere and half of the specimens were steam treated at 525°C for 100 minutes. By X-ray examination of Fe-2 to 8 wt. % Cu powder compacts sintered at 1120°C for 1 hr. at 6.4 to 6.8 Mg/m$^3$ and steam treated at 525°C, it was confirmed (31) that the principal product formed during steam treatment was Fe$_3$O$_4$ and that copper was not oxidized by steam. It has been concluded (33) that, precipitation treatment in a steam atmosphere, as opposed to in an inert atmosphere, increases the hardness of the sintered Fe-2Cu alloy.

In alloys containing more than 2 % Cu, precipitation treatment in an inert atmosphere promotes greater hardening than that in a steam atmosphere.

Steam treatment increases the radial crushing stress (RCS) of sintered iron but decreases the RCS of all iron copper alloys.

In a recent work (33) effects of steam treatment and time were studied on the air tightness and oxide formation
characteristics of sintered Fe-0.5 % graphite steels of different densities. Results showed that surface oxidation rate increased above treatment temperature of 600°C and that there was a maximum in the total amount of oxide produced at temperature between 500 and 550°C. The amount of total oxide decreased with an increase in density of the specimen. Metallographic observations showed that different oxide layers predominated over the range of steam treatment temperature used. The effects of the different oxide formation on air tightness were discussed. It was shown that the air tightness of the steam treated steels was closely related to the total amount of oxide produced, regardless of specimen density.

Steam oxidation in a fluidized bed (34) were studied for Fe- based PM parts containing 1.1 % carbon, 2.7 % Cu, 0.32 % Mn, 0.09 % Si, 0.01 % P, 0.001 % S, 0.08 % Nitrogen, 0.025 % Al, 0.015 % Mg, oxidized in fluidized bed of 120 µm white corundum floated with saturated steam at 2000 mm Hg and 550-600°C. The use of this method significantly increased the oxidation rate and results in strength and corrosion characteristics exceeding those obtained by conventional oxidation techniques. In fluidized bed oxidation micro-voids characteristics of PM products become completely sealed by dense oxide layer.
In a recent study (35), thermochemical equilibria that governs the oxidation of Fe in steam are examined, with particular reference to the treatment of sintered steel parts, in which open or interconnected porosity plays a role. The parameters required to regulate the amount of steam in accordance with the surface to be oxidized and the characteristics of furnace are shown in simple graphic form. The range of operating temperature is defined by the properties of water and the equilibrium diagram of Fe-O. The thermal balance resulting from the dissociation of H₂O and the formation of Fe₃O₄ is calculated and the possible influence of these phenomena on control of the furnace temperature is taken into consideration. The formation of very hard layers on the surface of porous parts communicating with the external atmosphere induces a considerable increase in apparent surface hardness. If the evaluation is not hampered by microstructural transformation, it is possible to establish a relation between increase in weight and increase in hardness (HV-30 scale) which is consistent with the experimental results. Since steam treatment of sintered steel parts is often used to make them impermeable, a method of calculation suitable for estimating the changes in porosity and permeability in treated material is shown. This
method can be applied as a theoretical basis for an easily used experimental methodology.

The oxidation kinetic study of iron was carried out (36) at 773 K under the total pressure of $10^5$ Pa with the precise control of oxygen partial pressure from $\log \left( \frac{P_{O_2}}{P_a} \right) = -0.7$ to 5.0. The kinetics nearly obeyed the parabolic rate law except between $\log \left( \frac{P_{O_2}}{P_a} \right) = 0.0$ and 0.5. The oxidation kinetics at 773 K were studied by many investigators (32, 37-41) only in air or oxygen atmosphere and most of their results fairly agreed with the results of Sakai et al (36) in air and oxygen. However, Hussey et al (42, 43) who only studied on the oxidation under reduced pressures at 773 K, indicated that the oxidation kinetics did not obey the simple rate law in the range from $\log \left( \frac{P_{O_2}}{P_a} \right) = -1.88$ to 5.0. The enhanced blistering of the oxide film under the reduced pressure may be one of the main reasons for the disagreement between their results and Sakai et al (36).

Below $\log \left( \frac{P_{O_2}}{P_a} \right) = 0.0$ the oxidation provided was parabolic mainly by the growth of magnetite.

The deviation from the parabolic rate law was related to the decrease of the oxidation rate with increasing oxygen partial pressure in the range $\log \left( \frac{P_{O_2}}{P_a} \right) = 0.0$
to 0.5. This may be explained by the formation of dense hematite on the surface of magnetite which occurred more quickly at higher oxygen partial pressures. The similar tendency was also reported by Hussey et al (42, 43) at a little lower oxygen partial pressures.

The oxidation rate increased with increasing oxygen partial pressure from $\log (P_{O_2} / \text{Pa}) = 0.5$ to 1.8 due to the formation of crack in the oxide film which allowed the growth of magnetite.

Above $\log (P_{O_2} / \text{Pa}) = 1.8$, the parabolic rate constants were almost constant independent of the oxygen partial pressure, although the increase of the oxidation rate with increasing oxygen partial pressure in this range was reported previously (14,19), which may be explained by the effect of blistering introduced by the use of the reduced pressure technique.

1.3 SCOPE OF THE PRESENT WORK

The existing literature contains little reference to the influence of alloying additions (except copper) on the response of sintered ferrous alloys to steam oxidation and this was the principal subject of the present investigation. Further, some of the alloying elements, e.g.
phosphorus and molybdenum are capable of causing appreciable age-hardening in ferrite (44). Hörnbögen (45) showed that phosphorus could produce appreciable age-hardening in Fe-P alloys containing 0.15 % C and 1.5 % Mn. Age-hardening occurred in temperature range 400-550°C, but the maximum effect was observed at 450°C. The intensity of age-hardening increased with increasing phosphorus content. At phosphorus content above 0.5 wt. %, increasing amount of ferrite were observed at the solution treatment temperature with increasing phosphorus contents. At 2 % P, the steel was virtually ferrite at room temperature. The precipitating phase was Fe₃P but the details of age-hardening process have not been investigated. Also, phosphorus because of liquid phase sintering and ferrite stabilization, spheroidizes the pores and reduces the amount of interconnected porosity (46) yielding Fe-P sintered compacts at a density of more than 7.2 Mg/m³ a potential alloy for making gas tight components.

The most commonly used alloying additions in sintered ferrous alloys are Cu, Ni and/or Mo in the decreasing order due to their low affinity to oxygen and/or cost.

The difficulty of adding high hardenability but easily oxidizable alloying elements, Mn, Cr and V have been
overcome (47, 48) by adding these elements in the form of master alloy carbides MCM and MVM (containing approximately 20-23 % each of Mn, Cr or V, Mo, 6-7 % C and balance Fe). These additions result into better mechanical properties and make sintered steels amenable to transformation hardening after addition of carbon. Apart from this, literature contains little reference regarding the effect of Ni, and Mo on the sintering behaviour of iron with or without phosphorus (32, 46, 49-54).

Thus the present work is a preliminary but systematic investigation of the effect of alloying elements Cu, Ni, Mo, MCM and MVM - 1 or 2 wt. % with 0.3 and 0.6 wt. % C on the steam treatment of P-containing atomized iron powders. Mechanical properties of sintered compacts of Atomized iron powders have also been determined since with the exception of copper mechanical properties of Ni, Mo and MCM containing iron compacts with phosphorus and carbon are hardly reported in literature (50-54).

Apart from this effect of 1-4 wt. % Cu or MCM on steam oxidation of sintered sponge iron powder containing 0 to 0.6 wt. % P sintered compacts have been studied.

Other premixes which have been used for the present investigation are as follows: