

Chapter I

INTRODUCTION

Powder metallurgical technique has been adopted by man to shape different metals. Strangely enough, the history of powder metallurgy dates back to thousands of years, when many metallic articles (precious metal articles made by the Incas and later the Iron Pillar of Delhi) were believed to be powder metallurgy products.

This art was somehow lost but was again revived only as late as 1826 when platinum ingots were compacted from platinum powder. The major breakthrough was made in the early 1900's when Coolidge and others made ingots of tungsten powder, which were made into the filaments of incandescent light bulbs. The actual march of this newly revived technology began inbetween the two world wars and after that it has never looked back. Today powder metallurgy parts range from light metals to heavy metals, low melting materials to refractory materials and from highly porous parts to dense structural parts.

An unique attribute of powder metallurgy is the ability to produce porous products with interconnected porosity. This attribute, according to the Source Book on Copper and Copper Alloys¹, made possible the development of the self-lubricating bronze bearings, an early P/M product, the first having been used in a Buik automobile in the 1920's. Depending on the sintered density these bearings can absorb from 10 to 30% by volume of oil and can supply a continuous lubricating film even

at low speeds. Porous bronze bearings also have the advantage that they are sufficiently ductile to permit assembly by ring staking.

Self-lubricating bronze bearings depend on conduction and convection for heat dissipation during service. According to Morgan² the idea of self-lubricating bearings probably originated from the attempts to overcome the heat conductivity limitation of oil soaked wooden bearings. The frictional heat developed is proportional to $PV\mu$ where P is the pressure on the bearing, V is the surface velocity and μ is the coefficient of friction.

Although the automobile industry, which was responsible for the development of these bearings, still uses them extensively their applications have now spread over to many other industries. Development of these bearings revolutionized the home appliance industry. By eliminating the requirement of periodic lubrication, the self-lubricating bearing assured many years of trouble-free operation of home appliances and led to a great expansion of the industry. New applications continue to be found and the self-lubricating bronze bearing industry consumes a major portion of the copper powder produced each year. According to a review by Taubenblat³ the manufacture of porous self-lubricating bronze bearings accounts for about 75% of the granular copper powder consumed by the industries.

Self-lubricating porous bronze bearings are used in large numbers in fractional horsepower electric motors.

Applications in which such small motors are used has been given by Victor⁴. Some of them are as follows : electric fans and blowers, sewing machines, food mixers, refrigerators, air-conditioning units, textile equipments, automobile heaters and defrosters, windshield wipers, e.t.c. The list is unending and is well summarized by Tait⁵ in a broad review of non-ferrous powder metallurgy applications in automobile industries.

Although bronze is found to be an excellent bearing material and is extensively used in industries, iron bearings are finding wide applications recently. To a large extent, the world wide copper shortage has contributed to this development. Iron bearings have other advantages in lower material cost and higher strength but rust very quickly. So nearly in all cases where long, trouble-free bearing life is required, bronze bearings are the best.

A small group of special types of bearings, suited for very special applications have been outlined by various authors⁶⁻¹¹. Some of them are high temperature bearings, gas-bearings, aluminium bearings, steel backed bearings, copper-lead bearings, lead-infiltrated bearings, dry bearings e.t.c. It must be remembered that these bearings are in no way an alternative to the normal bronze bearings. These special bearings are used only in places where the normal self-lubricating bronze bearings cannot be used owing to certain service conditions. As a matter of fact, with each passing year the demand for self lubricating bronze bearings is continually

increasing, the annual world production being estimated to be about eight million per day in the year 1964, and is still expanding.

Though the self-lubricating bronze bearings are being manufactured from a very long time back, many of its manufacturing parameters are very vaguely given in the literature. The correlation of manufacturing parameters with the bearing properties are not very clear from the available literature, and as for the physics of sintering is concerned there are two distinctly contradicting theories.

The general outline of the manufacturing process of self-lubricating bronze bearings has been described by a number of authors¹²⁻²⁰. A good comparison between an old method of bearing production with the powder metallurgy route is given by Borden²⁰. According to his article: 'Previously bushings had to be turned and bored from brass bar stocks on automatic screw machines. Production averaged about 230 pieces per hour by this method with rejects often as high as 50% due to dimensional inaccuracies. The same bushing, of sintered bronze, is now being turned out at a rate of 4000 per hour by the briquetting press and 12,000 per hour by the furnace under full production, with practically no rejects'.

The whole process can be broken up into a number of steps like mixing, compacting, pre-sintering and sintering, repressing, oil impregnation and packing. These steps has been outlined in short by Morgan²;

"Metal powders are mixed to give the desired alloy composition, for example, 89% of copper powder, 10% tin powder and 1% of powdered graphite are mixed to produce a graphited bronze.

The mixed powders are compacted to the desired shape in precision tools on automatic presses at pressures between 10 and 35 tons/inch². The compacted briquettes are sufficiently strong to permit handling.

The green compacts are sintered in a reducing atmosphere. Before sintering it is generally pre-sintered at lower temperatures of about 400°C in order to drive out the lubricants and oils. For 90/10 bronze a sintering temperature of about 800°C is used.

The sintered compacts are repressed to remove distortion and to impart dimensional accuracy and a smooth surface finish.

The pores of the coined components are filled with lubricating oil by vacuum impregnation.

The finished bearings are packed in a non-absorbent wrapping, to protect them from dust and avoid loss of oil."

The steps briefly elucidated above may be considered to be the process variables in the manufacture of self-lubricating bronze bearings. Another important variable which influences the properties of self-lubricating bronze bearings

is the material variable. Amongst the material variables one can consider the characteristics of copper, tin and graphite powders, their amounts, and also the amount and type of lubricants used. The type of material and process variable used will determine the final properties of the self-lubricating bronze bearings. So it would be best to discuss the properties of self-lubricating bronze bearings under the two broad heads of material and process variables.

1.1 MATERIAL VARIABLES

The main material variables which affects the final properties of self-lubricating bronze bearings has been outlined below.

1.1.1 Copper

Copper, which happens to be the major elemental constituent of the sintered self-lubricating bronze bearings can be manufactured by a number of ways. The production and properties of copper powders have been discussed by a number of authors^{11,21-27}. In general the routes of manufacturing which are followed includes electrolysis, hydrometallurgy, gaseous reduction and atomization.

The properties of the electrolytic copper powder deposited from sulphate bath depends on the variables that effects the electrolytic process. The oxygen content of electrolytic copper powder is higher when compared with other

methods. This oxygen content is generally seen as a thin surface film of cupric oxide giving a dark brown to black colour to the powders even when the oxygen content is less than 0.5%. Occasionally, the oxide film is either cuprous oxide or a mixture of cuprous and cupric oxides. Rarely particles having a surface of Cu_4O have also been found²⁸.

This type of powder is still used to some extent in the manufacture of porous bronze bearings. Its high cost of production, however, makes it a less attractive proposal for manufacture of porous bearings and is presently being replaced by reduced powders and when possible by atomized powders.

The method of gaseous reduction generally relies on copper mill scales as the starting material. Also copper oxides obtained by the oxidation of chemical precipitates, or finely divided electrolytic copper powders may sometimes serve as the feed material. The oxides are comminuted and reduced to the metal by using carbon monoxide or hydrogen.

Mahindra Sintered Products, one of the largest manufacturers of self-lubricating bronze bearings in this country, uses reduced copper powder. The powders produced by the reduction of mill scales, generally exhibits good green strengths and high apparent densities. It is generally spongy in nature. Also its manufacturing cost is not as high as that of electrolytic copper powder.

As a method of comminution, probably the cheapest possible process is that of atomization. The final properties

of the powders is greatly influenced by the raw material used, the atomizing medium and the final processing of the powders. The over-all oxygen content is not excessive, since the particles are substantially solid and spherical or tear drop shaped, and the films are generally so thin that they are literally transparent. Though this powder has excellent flowability and cheap manufacturing cost, owing to its extremely bad pressing properties, it was for long not used by the bearing industries.

In recent years, considerable flexibility and control has been achieved in metal atomization processes and it is now possible to make copper powders having highly irregular particle shapes with apparent densities as low as 2.1 g/c.c. Though these powders are in the simple atomised condition, their physical appearance is remarkably similar to that of reduced copper powders.

1.1.2 Tin

Tin is the next important metal required in the manufacture of self-lubricating bronze bearings. A great deal of literature and patent survey of this metal was done by Watkins²⁹. Tin is generally produced by a number of methods like shotting, graining, atomization, electrolysis and chemical precipitation. Generally for the powder metallurgy purpose the last three is of use as it yields tin fine enough to be used for mixing and molding work.



The most commonly used powder for the manufacture of self-lubricating bronze bearings is atomised tin. According to Goetzel³⁰ atomization results in a fine product whose particle size distribution can be regulated over a wide range. The oxygen content of the atomized tin is normally below 0.2% . By varying the atomizing parameters the particle sizes can also be varied.

According to Elliot³¹ previously self-lubricating bronze bearings were made with a wide range of compositions, the tin content varying between 5 to 15% by weight. Recently however, there is a tendency to standardise around 10% tin compositions. Standards like ASTM, SAE, MPIF also stipulate a composition of around 10% tin . Tin generally strengthens the copper¹ by solid solution hardening. So with increasing tin percentages the strength of the bearings will increase.

1.1.3 Lubricants

Generally non-metallic additions are done for many reasons. They may be classified as follows Transitory additions which disappear during the sintering cycle or permanent additions which are incorporated in the final product. This latter mentioned category may fulfill any of the following purposes

- a) form an alloy composition
- b) act as free ingrediants
- c) promote controlled porosity
- d) act as binders
- e) act as lubricant.

In self-lubricating bronze bearing production, generally both types of additions are made. One of the

lubricant which is transitory in nature is added to reduce the friction between powder and die wall and the other is a permanent addition which is to provide lubrication during operation of the bearing.

In order to decrease the frictional forces between the powder and die wall, lubricants are either applied to the die wall or admixed with the metal powder. Though lubrication plays an important role in the production of parts by powder metallurgy, very little is known about the best way to apply lubrication³². A number of authors have expressed various views as to the type and amount of lubrication to be used³³⁻³⁹. Generally in industries only upto 1% by weight of these transitory lubricants are added.

Admixed lubrication is suitable for automatic presses. Since there is high speed movement the compound preferred should have high melting point and a long chain. These lubricants are driven out during the sintering cycle.

The other type of non-metallic addition that is used in the manufacturing process of self-lubricating bronze bearings is a permanent addition. This is added to help in the lubrication of the bearing during its operation. Generally graphite is added for this purpose, though presently some special bearings for use in space vehicles has added to it, Molybdenum disulphide as the solid lubricant. These graphite or molybdenum disulphide which are added do not basically affect relations between the metallic components, acting as an

interfering phase in the boundary region, similar to a pore.

According to Elliot³¹ previously self-lubricating bronze bearings contained graphite of upto even 6% by weight, but recently graphite content is being limited to a maximum of 2%. More recently Berry³⁸ has stipulated that specifications for bronze bearings permits a graphite addition upto a maximum of 1.5%. Low graphite contents are naturally preferred as graphite generally reduces the strength of the bearings. Bronze bearings are also made without the additions of any graphite.

Another addition that is generally made before the mixing stage is the light oil. This oil is generally used to help and prevent the finer tin powders from segregating. However, addition of excess light oil to the powder decreases the flowability. Kosho⁴⁰ in his work on bronze bearings used light oil upto 0.2% (weight ratio). This is removed by heating before the sintering cycle for 60 minutes at 150^oC in hydrogen.

1.1.4 Particle sizes

The powder particle size distribution plays an important role in influencing the final properties of self-lubricating bronze bearings. In reality there is no fixed size distribution specified for manufacture. It varies from user to user and is determined by considering the buyers demand and compromising between conflicting requirements. According to Kieffer and Hotop⁴¹ the powder grades may vary from minus 50 mesh to minus 325 mesh. According to Jones the tin powder size

is of less importance. Hall⁴² indicates that tin powders of considerable fineness are extensively used by bearing manufacturers. Some size distribution of commonly used copper, tin and graphite powders used for the manufacture of self-lubricating bronze bearings are given by Goetzel¹³. Jones¹², in the manufacturing process of porous bronze bearings, said that copper powder used is finer than 100 mesh out of which around 50-60% passes through 325 mesh and the tin powder used is generally finer than the copper powder.

Hayashi and Watanabe⁴³ in their works, used two types of tin powders. One contains 60% by weight of 100-150 mesh powder and 40% by weight of minus 270 mesh powder, and the other is totally minus 270 mesh. Their work shows that as the temperature increases beyond the melting point of tin, the tin melts and gets absorbed between the copper particles. The voids left by the tin particles become pores. The tin gradually diffused into copper. After pre-sintering at 400°C, when the temperature is being raised to 800°C, the diffusion becomes active. When the temperature reaches 750°C alpha phase begins to appear. When samples are held for 20 minutes at 750°C new crack like pores appear in addition to the earlier ones. These capillary type of pores are formed due to the sticking together of the particles and their resulting movement. However, when the samples are maintained for 60 to 180 minutes at 750°C the pores become spherical and with longer holding times the samples shrink and pores become smaller. However

when sintering fine tin powder, above the melting point of tin, tin undergoes only diffusion and does not ooze out into the space between the copper particles and hence new pores are not formed. However, as temperature reaches 600°C and alpha phase begins to form, pores are also formed. In samples maintained at 750°C for 60 minutes pores have also increased and they are crack like ones. The authors believe that such pores are formed as follows as sintering progresses the alloy phase tends towards the copper side of the equilibrium diagram. The copper-tin alloys other than the alpha phase are fragile and have lower melting points. So a part of the sintered body is in the molten state at 750°C . Now the sample is undergoing shrinkage due to the sticking together of the particles. The shrunken regions, as a result of formation of alpha phase, becomes separated from the non-alpha region and the space between the two regions becomes crack like pores. Usually when a porous substance shrinks the pores are decreased⁴⁴ but here the pores increase due to the above mentioned reason. Eventually, however, overall shrinkage occurs reducing the porosity.

Kosho⁴⁰ studied the importance of tin particle size in controlling the final properties of self-lubricating bronze bearings. According to him the pores develop due to a "skin shedding" phenomenon of tin powder, and concludes that pores can be controlled with the help of tin powders. He studied the effect of the difference in granularity of tin powder on size and number of oil holes. In case of a sintered body, contraction becomes more intense as the tin powder becomes finer. The

tin size becoming finer means the surface area of the powder increases and its distribution in copper powder becomes finer. So the alloying of copper with tin becomes faster and a strong tendency of densification is observed. Also the pores become finer during the sintering process and they contract and become isolated. With increasing fineness of tin the hardness and density of the compacts also increase. As far as the grain size of the sintered specimens are concerned, they become finer with increasing fineness of the tin powders. Another observation is that keeping the amount of tin same (10% by weight) and varying the granularity of the tin powder, the number of pores in a particular place increases geometrically. Hence the conclusion is drawn that by varying the granularity of the tin powder, control can be exercised over the size and number of pores.

The reason for the grain size becoming finer with finer tin powders has been explained by Kosho⁴⁵ in a later article. According to him if fine grained tin powder is used, hole formed by the "skin-shedding" of the tin powders are finely distributed and as a result growth of crystal grains are hampered.

Kosho⁴⁶ in another work studied the effect of varying tin size on the oil permeability and oil retention capacity. In samples with coarse tin powders which gives coarse oil holes the oil permeability is very good but in contrast to this, since the capillary force is weak, the oil retention

capacity is very weak. The opposite effect is seen in case of samples with fine oil holes.

The effect of close porosity control and proper selection of the lubricating oil to be used is stressed by Geotzel⁴⁷. The pore size can be regulated readily by the grain size of powders used, which can range between 0.0015 inch (0.0038 cm) to 0.006 inch (0.015 cm). Bearings to be subjected to heavy loads at high temperatures require a heavy oil (SAE 60). In its manufacture a comparatively coarse powder must be used with smallest particle size not below 0.004 inch (0.01 cm) in diameter. For bearing to be used for high speeds, low loads and low temperatures, a light oil with low viscosity (SAE 20) is required. Its manufacture should be from fine powders, 0.002 inch (0.005 cm) being the smallest particle diameter. Also according to Pratt⁴⁸ close control of the powder size fraction and degree of compaction gives the required level of porosity. Jones⁴⁹ has reported a Graphite free porous bronze material containing 90.5% copper and 9.5% tin as having very large pores (0.75 mm) which is claimed to be suitable for high load applications requiring external oil supply, without reducing the capillarity of the material required for the reabsorption of the oil. The large pore size acts as a factor which aids in the distribution of oil, which would have been normally impeded by opposing suction forces.

Mazzarella⁵⁰ in his work used nine types of copper sizes and he observed that the porosity decreased with the

powder fineness, which is to be expected.

Lennox and Brewer⁵¹ in their article on porous bronze bearings have said that powder used must be rigidly held to the specification agreed upon by powder manufacturer and user. In the production of porous bronze bearings it is usual to have an electrolytic copper powder and atomized tin powder. Considerable care must be taken to prevent oxidation before use and this necessitates transport in hermetically sealed containers.

In general it can be concluded that increasing the fineness of both copper and tin powders, the rate of homogenization becomes faster. So densification, hardness and radial crushing strength increases with the increase in fineness of both the powders. Also with increasing fineness of the powders the total porosity and also the interconnected porosity drops. The lubricants that are added to the powders generally decreases the strength of the bearings. The graphite amongst the lubricants is known to cause growth of the compacts during sintering.

1.2 PROCESS VARIABLES

1.2.1 Mixing

The elemental powders are blended in ball mills or tumbler mills. The mixing is to be regulated carefully as excess time of mixing will result in the breaking of the

larger powder particles thus giving a overall change in the particle size distribution. On the other hand if the mixing is carried out for too short a time than the tin, not being uniformly distributed in the copper will give irregular properties. It was observed by Kosho⁴⁰ that the addition of light oil is a must in order to maintain a homogeneous distribution of tin in copper.

1.2.2 Compacting

According to Goetzel¹³ the compacting is generally carried out in quick acting mechanical presses. Hydraulic presses may also be used for compaction. The pressures of briquetting varies considerably with the individual manufacturer and also the type of bearing that is to be made. Generally the pressures used are within the range of 15 to 35 tsi (235 to 550 MPa), but it may also be as low as 5 tsi (78.5 MPa) or as high as 50 tsi (785 MPa) when an ultimate sizing operation is to be eliminated. Depending on the size and shape of the bearings the compaction rate may vary from six to several hundred compacts per minute.

Kosho⁴⁰ used moulding pressures from 0.6 to 1.6 T/cm² (59.7 to 159.3 MPa) and also varied the particle size of tin in his mixes. He found that the green density increases almost linearly with the increase in pressure. The sintered density of the compacts increased with the green

density. High sintered density compacts exhibit more closed porosity. An increase in the compacting pressures also results in the increase of the mechanical properties like the hardness and the radial crushing strength.

Berry³⁸ in his works on factors affecting the growth of 90% copper and 10% tin mixes pointed out that the growth increases as green density increases (i.e. compacting pressure increases). His reasons are that with increasing green density the available surface area of copper for alloying with tin will decrease and so an increase in growth can be expected. Also at high green densities the swelling can be more owing to pressure build up during delubrication or the escape of other gases from the compact.

1.2.3 Sintering

The whole process of sintering can be broken up into a number of separate sub-heads and then treated. The main sintering variables are the sintering temperature, sintering time, the rate of heating up to the sintering temperature and the sintering atmosphere.

1.2.3.a Sintering temperature: In this step the pre-sintering may also be considered. The general pre-sintering treatment is carried out in the temperature range of 400 to 500^oC. According to Goetzel¹³ this pre-sintering serves the twin purpose of expelling the volatile lubricants at a low

rate, and also permits sufficient time for the liquification of the tin and its diffusion into copper.

Most of the authors refer to the sintering temperature, loosely, as around 800°C . According to Jones¹² the sintering temperature is between 800 to 850°C . Amongst the early workers, Koehring⁵² observed that a sudden swelling occurred on sintering at 800°C . Similar increase in growth is also observed by Mitani⁵³ at 798°C in his dilatometric work, and the temperature coincided with the first peritectic reaction temperature. Esper and Zeller⁵⁴ in their dilatometric works found breaks in the expansion curves at 230 , 450 , 640 , 750°C which is said to correspond to new liquid phases formed. Elliot³¹ in studying the influence of sintering temperature on growth in the radial direction observed that from 700°C the radial growth continually increases till a temperature of about 825°C is reached and then it drops. He however did not find any significant growth increase as soon as the first peritectic reaction temperature at 799°C is crossed. He attributed the growth factor with temperature to be associated with the progressive fusion of the various intermediate solid solutions.

However Kosho⁴⁵ in his works on influence of sintering temperature on some properties of sintered bronze bearings found that there is not much change (even when the sintering temperature crosses 798°C) observed in the linear contraction and sintered density for mixes having coarser tin powder.

With the increase in the fineness of the tin powder the linear contraction and the sintered density increase with increasing sintering temperature. This is however contradictory to the findings of most of the other workers. Also according to his work the interconnected porosity when expressed as a percent of total porosity decreases when the sintering temperature is taken from 790 to 810°C.

To explain the changes in properties of self-lubricating bronze bearings with the rise in sintering temperature, it is important to look into the structure formation mechanism in the sintering of such bearings. According to Geotzel⁵⁵, after the melting point of tin at 232°C is crossed the tin melts, and with increasing temperature and time the molten tin diffuses rapidly into the surrounding copper particles so that after the sintering temperature is reached and the compact remains there for a length of time, a homogeneous solid solution of alpha bronze is formed. According to colour photomicrographs taken by Hall⁴² [as reported by Goetzel⁵⁵] actual phase changes that occur during sintering are shown. Diffusion between tin and copper is said to commence after one minute at the temperature where tin-rich transitory phases are formed. After around 25 minutes, a homogeneous alloy of alpha-bronze is obtained. The X-ray corroboration with the microstructural properties are given by Carter and Metelke⁵⁶. According to them the porosity and the phase distribution of the material is sharply influenced by the peritectic reaction

temperature at 798°C . According to Goetzel⁵⁵ the schematic representation of the sintering mechanism has been given by Saurwald⁵⁷.

According to Jones¹², the mechanism of structure formation of bronze bearings during sintering of elemental powder mixes is quite complex. According to the copper-tin phase diagram a number of intermetallic phases may make their appearance with increasing temperature, either at the interface or in the tin melt. According to him the more important of these are first η (approximately 60% tin) at low temperatures, followed by ϵ (approximately 38% tin) stable upto 670°C , and then finally at higher temperatures γ and β and then the copper-tin solid solution α . Finished sintered bronzes generally contain either only α (which may or may not be homogeneously diffused) or sometimes a mixture of α and δ produced by the decomposition of the β and γ phases. In this case it can be assumed that the diffusion process is not complete and the sintering does not proceed to the complete formation of α , but leaves behind some β phase. According to him there is some divergence of opinion as to whether the residual δ phase is beneficial or not. The rate of solutioning of solid copper in liquid tin is very high, and it is probable that, within seconds of the melting of tin the first copper particles (less than 15 microns) are completely dissolved. The compact has excess of copper so the rate of solutioning quickly decreases as copper content of molten tin

rises. Solution of copper in the tin with the formation of the η and then the ϵ phases proceeds rapidly and unless the heating up is very rapid the compact is wholly solid by the time 500°C is attained. Then the microstructure should have copper particles, with some enveloping α phase formed by diffusion of tin into the copper lattice, surrounded by zones of δ and ϵ phases. He agrees that the course of the subsequent diffusion is not known with certainty, but he says that probably tin diffuses from these phases into the copper lattice, though the reverse process could also be possible. When sintering temperature is taken above the first peritectic reaction temperature at 798°C , any residual β phase liquifies, and the homogenization process is speeded up.

The pores consists partly of the previously existing pores in the compact along with some of the volume that was previously occupied by the tin particles. The copper particles however expands because of diffusion of tin into them. Also the melting of tin allows stress relieving and repacking of the particles, and probably the tin moves to zones of least pressure. The graphite only acts as a barrier to the fast diffusion process.

It is generally agreed that the growth observed in the bronze compacts depends on the alloying of tin into copper. According to Berry³⁸, on melting the tin tends to alloy in the regions of copper particle junction, the increase in volume produced by diffusion causing the copper

particles to move apart and growth to occur. While alloying is producing an increase in volume, there is an opposing sintering process in action reducing the surface area of the pores. Diffusion must be considered a two way process, and in the case of the copper tin system the diffusion of tin in copper is greater than that of copper in tin. Asaeda⁵⁸ maintains that growth occurs in a copper based system where diffusion in copper is greater than in additives, while shrinkage is favoured if the diffusion in the additives is greater than that in copper.

Daver and Ullrich⁵⁹ carried out some work on the structure formation mechanism in copper tin systems (90 copper 10 tin) commonly used for sintered bronze bearings. The work was undertaken to study the liquid phase sintering with the help of hot-stage microscope. Their findings in a nutshell describes the theory of structure formation mechanism of 90 copper - 10 tin compacts. According to them, as soon as the tin melts, it reacts with the copper particles forming intermediate phases - first η (60% tin) followed by ϵ (38% tin). The phases are formed at the interface and not in the tin melt. The areas originally occupied by the tin phase leaves behind pores of approximately the same size and shape. At around 700°C crystal formation and metallurgical bonds develop rapidly. The phases that now exist are α and δ . The δ phase is retained at the room temperature (when cooled) as it decomposes to α plus ϵ only under complete equilibrium

conditions. When 800°C . is crossed diffusion increases tremendously accompanied by concentration leveling, homogenization and solidification. The structure is α bronze with evidence of twinning, pore migration and spherodization.

Znatokova and Likhtman⁶⁰ agree that from the experimental data obtained by them, they have not categorically proved the structure formation mechanism. They have pointed out that existing theories relating to the mechanism of structural transformations in the copper tin systems are contradictory.

According to them, during the sintering of a copper tin mixture the constituents diffuse into each other leading to the formation of intermetallic compounds, and in the long run, to the formation of a homogeneous solid solution of tin and copper. In their model experiments carried out at $200 - 250^{\circ}\text{C}$ they found that it is copper which diffused into tin forming new phases on the copper tin boundary and within the volume of tin. When sinterings are carried out at temperatures below the melting point of tin a transitional diffusion layer is found, consisting of two phases, ϵ phase bordering upon the copper and η phase bordering upon the tin. When the temperature is taken above the melting point of tin (232°C), the transitional layer on the tin side has an uneven edge with stretched and often torn crystals of η phase. The η phase is brilliant white and the ϵ phase is gray in colour. These new phases have different microhardnesses from that of

tin. Microhardnesses of tin, η (white phase), and ϵ (gray phase) are 16-25, 460-610, 179-285 Kg/mm^2 respectively.

On a further rise in temperature the process develops in the direction of an increase in the volume of ϵ phase, both through the decrease in the volume of η phase and through the surrounding copper. On heating upto 400°C , all traces of η phase disappears from the areas rich in tin which then consists of entirely ϵ phase. Then on heating to 420°C , on the periphery of these areas there appears a thin layer of a new phase called δ phase, which is still richer in copper and also white in colour like the η phase. With increasing temperature this layer extends deeper absorbing the ϵ phase and at 500°C this process is nearly complete. In addition to this, in the temperature region of $400 - 500^\circ\text{C}$ there is extensive α solid solution formation through diffusion of tin and copper, accompanied by breakdown of the intermetallic compounds that have formed, and this process is nearly complete at 600°C . At this temperature solid solution forms every where with traces of crushed α - δ eutectoid. At 600°C the solid solution which was heterogeneous (microhardness $165-233 \text{ kg/mm}^2$) becomes nearly homogeneous at 700°C with the δ phase being restricted to very small areas. At 800°C a homogeneous α solid solution is obtained (hardness $213-233 \text{ kg/mm}^2$).

Znatokova and Likhtman⁶⁰ have compared their results with the other published ones^{12, 38, 55, 61-63}. According to

them, many authors are of the opinion that copper tin system should be regarded as a system containing a liquid phase within a wide temperature interval. After melting tin is drawn by capillary forces into micropores between the copper particles and it spreads over the surface of these particles and envelops them in a thick film. Furthermore, with increasing sintering temperature the process of diffusion penetration of tin into copper is intensified and leads to the formation of new phases and finally to the formation of homogeneous α solid solution. However, from the work of Znatokova and Likhtman⁶⁰ the process of sintering of the copper tin system cannot be considered as taking place in the presence of a liquid phase. Even if heating is sufficiently rapid for the tin to remain unaffected upto the melting point, then the liquid phase forming is immediately enveloped in a thin but rapidly thickening layer of solid α phase, arising as a result of diffusion of copper in tin, and preventing the tin from spreading. Thus it is not possible for liquid phase to remain for an extensive length of time at temperatures above 232°C , since η phase disappears at 400°C , i.e. below its melting point, and is replaced by the more refractory ϵ and then by δ phase. The latter also breaks down, forming α solid solution at 600°C , i.e. again below its melting point.

1.2.3.b Sintering time : According to Jones¹² an important point that is to be noticed, but is not realized, is that the whole thermal cycle is usually very short. Time varies with

different manufacturers, but it is quite customary for the temperature of the compacts to be raised to the sintering temperature in 2 to 5 minutes, and for the final sintering treatment to last no more than 3 to 5 minutes. Cooling generally arranged by water jackets around the furnace muffle, takes longer, but the compacts reach 100°C in less than 10 minutes. In his work, Hall⁴² found that with 25 to 27 minutes at the sintering temperature the alloying is substantially completed, as evident from the appearance of α bronze.

Kosho⁶⁴, in his detailed work, studied the final properties as a function of sintering times (0 to 240 minutes) and of the tin particle size and of sintering temperatures of 790°C and 810°C . At 790°C , porosity gradually decreases with sintering time. When sintering at 810°C , the porosities are lower when compared to the ones sintered at 790°C . At 810°C also, with sintering time the porosity decreases. Finally, he also observed that the tendency of contraction of oil holes is there with the contraction of sintered body when held at 790°C - but closed pores are not formed. However, when the temperature is held at 810°C , more and more closed pores forms with sintering times.

In the article by Taubenblat and Smith⁶⁵, 90/10 bronze bearings are sintered at 843°C for 3, 5 and 13 minutes. According to the microstructures taken at the three times it is seen that the shortest time of sintering produced an

undersintered structure consisting of uneven grain sizes with particles of unalloyed copper remaining. The K-factor of this is found to be around 18,000 psi. Sintering for 5 minutes gives good optimum structure consisting of a single phase matrix, with small and uniform grain size, and a K-factor of 31,000 psi. However when sintering for 13 minutes the tin is completely diffused into copper which results in a single phase structure, but with excessive grain growth. The grain sizes are bigger when compared to the samples sintered for 5 minutes and it gives a K-factor of 29,000 psi which is lower than the optimum sintered one.

May⁶⁶, studied the electrical resistance during inductive liquid phase sintering of copper-tin mixes. He observed that the resistance drops as the sintering temperature increases from room temperature to the melting point of tin. As soon as the melting point of tin is crossed there is a sudden rise in the resistance value - followed by a continuous decrease till about 800°C is reached. As soon as a temperature of 800°C (which corresponds to the first peritectic reaction temperature at 799°C) is crossed there is again a sharp increase in the resistance value till the point at which the maximum sintering temperature is reached. It is seen that on holding at the maximum sintering temperature, the resistance value gradually decreases with time, and then with still further holding passes through a hump. The author has however failed to give much explanation for the nature of the curves.

Elliot³¹ working on some factors which affects the growth of copper-tin compacts, showed that the samples reached 800^oC in about three minutes. On reaching the sintering temperature, the growth remained fairly constant for several minutes, and after ten minutes a slight reduction in overall growth occurred. Following the growth which arises during the initial period required to reach the sintering temperature, it seems that the porous structure which is established is dimensionally stable. The increase in the shrinkage factor, which could be expected to develop with time, did not manifest itself until the end of the sintering cycle.

Berry³⁸ also working on effects of sintering time on the growth of 90 copper / 10 tin compacts concludes, that holding at temperatures for times much longer than 5 minutes does not appreciably reduce growth under the sintering conditions of the test.

1.2.3.c Heating rate: That heating rate will affect the final sintered properties of bronze bearings is one of the conclusions drawn up by Jones¹². According to him it will affect the time upto which a part of the compact remains in the liquid state. "Solution of copper in tin with the formation of the η and then the ϵ phases will rapidly proceed, and very probably, unless the rate of heating up is very rapid, the compact is wholly solid again by the time 500^oC has been attained". However, according to Znatokova and Likhtman⁶⁰ the process of sintering of the copper-tin

system cannot be considered as taking place in the presence of a liquid phase, even if heating rate is sufficiently rapid for the tin to remain unaffected upto its melting point. The liquid phase forming is immediately enveloped in a thin but rapidly thickening layer of α phase, thus preventing the liquid phase from spreading.

Work done by Elliot³¹ shows that in conveyor furnace the growth is 2.25% whereas in batch furnace it is observed to be 3%. This increase can be attributed to the higher rate of heating in batch furnace, which has a substantial influence upon growth. Berry³⁸ also working on growth of copper-tin compacts agrees that under rapid heating rate that prevails in practice, it is likely that some liquid phase is present throughout sintering until the final solidification above the peritectic reaction temperature occurs. According to him the growth increases as the time to reach the maximum temperature is decreased. Increase in heating rate effectively reduces the extent of tin diffusion before the peritectic temperature is reached. More liquid phase is thus produced and causes a greater growth of the compacts.

Detailed work on effect of heating rate on the properties of 90 copper / 10 tin bronze bearings is reported by Kosho⁶⁴. In his work, the presintering temperature used is 400°C, heated upto it at the rate of 15°C / minute, and held there for 60 minutes. Then from 400°C to 790°C the heating rates are varied from 3 to 80°C / minute. He observed

that porosity increases with an increase in the heating rate, but the interconnected porosity is not much affected by the increase in porosity. Very poor results are obtained by heating at the rate of $3^{\circ}\text{C} / \text{minute}$ but a rapid improvement in the interconnected porosity is noticed with an increase in the heating rate. Almost a normal state of 85% of total porosity is reached when heating rate is $15^{\circ}\text{C} / \text{minute}$, and it remains constant above this heating rate level. Samples heated at the rate of $80^{\circ}\text{C} / \text{minute}$ shows unusual distortion. From microstructural observations he noted that with the increase in the heating rates the globular pores grows larger.

1.2.3.d Sintering atmosphere : According to Goetzel¹³, "Sintering is also exclusively conducted in continous furnace in a protective atmosphere, usually consisting of partially combusted hydrocarbons or natural gas, but in certain instances protection against oxidation during sintering is achieved by simply packing briquettes together with coke or charcoal inside closed metal boxes. Hydrogen and Dissociated Ammonia are not generally used because of the higher costs involved".

Studies on effect of atmosphere on properties of bronze bearings are few . However Mitani⁵³ working on dialatometry, obtained an abnormal expansion when the temperature crossed the first peritectic reaction. He considered that the abnormal growth can be reduced by using an atmosphere containing a minimal hydrogen content, since his findings indicate that a significant proportion of the

expansion is caused by evolution of dissolved hydrogen on solidification.

Berry³⁸ and Meyer et al⁶⁷ has shown that decomposition of lubricants are influenced by the atmosphere. Berry³⁸ showed that a negative growth can be produced if the volatiles on delubrication are of a reducing nature, particularly where lean atmospheres are used.

The influence of sintering atmosphere on the pores are briefly described by Fleming⁶⁸. It is known that sintering affects the porosity in the following manner a) the total number of pores decreases progressively during sintering at all temperatures (b) the average pore size existing in the compact increases with the sintering time, (c) there is, for each conditions of sintering, a pore size which occurs in maximum number in the size scale, and this maximum shifts towards larger pore size as sintering proceeds, (d) late in the sintering process there exist pores which are larger than any present at the beginning of sintering.

These factors are independent of whether sintering occurs in a reducing or neutral atmosphere, or in vacuum. The affects of vacuum sintering or sintering in a reducing atmosphere for a single - component metal powder compact cannot be described in a simple manner as it depends on the surface condition of the powder. There is a considerable variation in activation energy which determines the rate of

sintering, and this depends strongly on the sintering atmosphere. However, it may also be stated that, (a) sintering in vacuum results in minimum porosity, (b) the vacuum sintered compacts have the minimum number of fine, and a maximum number of coarse pores, whereas in the hydrogen sintered compacts the maximum number of pores lies in the medium pore size range, (c) it is also known that the pore size distribution determines the grain size in the sintered compact, and it may therefore be concluded that the sintering atmosphere directly affects the final grain size of the sintered compact.

However this theory is seemingly applicable for single phase components. What happens when sintering proceeds through a number of intermetallic phases and where a transient liquid phase appears and disappears as in case of sintering of 90 copper / 10 tin components is not established. The work of Fleming⁶⁸, however does give a general idea as to what effect should be obtained if the sintering of 90 copper / 10 tin bronze bearings are to be carried out under a vacuum atmosphere, instead of the conventional reducing gas atmospheres.

AIM AND SCOPE OF THE PRESENT WORK

With the present global oil and natural gas crisis, alternative to conventional processes (using petroleum or its by products) are being hotly pursued in every field. A glance at the warnings that have been issued by various bodies

to conserve petroleum and its by products, drives the point home that more stringent measures are to be taken for conserving the limited resources. One of the reports published in the "World Energy Resources 1985-2000" dealing with oil and gas resources⁶⁹ says that, "By raising the problem of oil supply to the industrialized countries, the events of recent years have drawn attention to the problem of the exhaustion of worldwide petroleum resources. Until then the public had been only vaguely aware that whereas mankind had only about 30 years of petroleum reserves, a short and alarming length of time, these thirty years were constantly moving forward,

These worries have led to a proliferation of futuristic surveys during the last two or three years. The opinion that is generally expressed is that by the end of the century the world is in serious danger of lacking crude oil as the result of a decrease in production that should begin around 1990. The most pessimistic, combining the political dangers of a slowing down of production and the assumption of relatively high economic growth rate, even consider that difficulties of supply will appear during the coming decade".

The recent Iraq Iran war has added a new dimension to this grave problem and has also resulted in a spurt of price rise of crude petroleum barrels.

So, to reduce the dependence on petroleum products or natural gases which are obviously becoming dearer (and its resources are also dwindling) it was decided to try vacuum as the sintering atmosphere for one of the most conventional powder metallurgy product, namely the self lubrication bronze bearings.

In recent years vacuum technology is taking large strides and is gradually encroaching into totally alien territories. Specially with the advent of continuous vacuum furnaces in the market, the main argument which was used against the vacuum sintering atmosphere, "that its a batch process", is fast loosing its ground. The interaction of market needs and equipment development is always giving new solutions to old problems and creating openings to tackle completely new problems. This has led to a rapid development of vacuum furnaces and their applications. It is now in the offing that a number of P/M part manufacturers will using vacuum as the sintering atmosphere in the near future.

Vacuum furnaces have already entered the metallurgical market in a big way owing to its obvious advantages. The boom in the aerospace industry has called for an expansion in the vacuum heat - treatment furnaces. It is on the cards that we shall see further advances in vacuum heat-treatment technology in the near future. Already liquid quenching vacuum furnaces are coming to the market as described by Buckley⁷⁰. In an article in Metallurgia⁷¹ it is stated that "the whole

industry is in a state of technological evolution in which vacuum heat-treatment will doubtless play an increasingly important role". A new vacuum furnace is also reported in Metallurgia⁷² which is a twin zone one, believed by its manufacturers, Wentgate Engineers, to be the first of its kind.

Vacuum sintering furnaces are also making inroads into the powder metallurgy industry⁷³. A new model of vacuum furnace, it is claimed, provides more uniform sintering temperature. Batch vacuum units from GCA International (European representatives of GCA Vacuum Industries, USA) is introduced to facilitate complete cycling processing of sintered hard metals. The new furnace offers $\pm 5^{\circ}\text{C}$ temperature uniformity throughout its 36 inch long, 18 inch wide, 12 inch high work zone.

Another continuous vacuum furnace for powder metallurgical products is designed by Degussa. This furnace consists of three zones, one pre-sintering zone under atmosphere, one sintering zone and one cooling zone under vacuum. In an article by Bauer⁷⁴ on recent developments in automated vacuum sintering, he says, "During the last few years, Degussa has presented the powder metallurgy world with another greater vacuum sintering furnace for hard-metals which is of double the capacity compared to the former one. The automated vacuum sintering plant, called 'Sinterautomat' is a very good solution for sintering mass produced hard metal parts".

The advantages of vacuum atmosphere over the other normal gas atmospheres are numerous

- (1) Excellent temperature uniformity,
- (2) No environmental pollution by toxic materials, heat or fumes,
- (3) Less distortion problems,
- (4) Easier material degassing and complete elimination of surface oxidation or deterioration,
- (5) Significant reduction in labour costs both in the furnace operation and by elimination of subsequent cleaning operation,
- (6) It gives much more efficient energy usage.

Tamalet⁷⁵ in his article on "How to decrease the Energy Demand of Powder Metallurgy Furnaces" has said that "we cannot refer to atmosphere without mentioning vacuum. This solution is obviously radical, to cut 50% of energy costs in the sintering operation". He has described a vacuum sintering furnace the 'Metafram Sedimec Furnace', which is a continuous car type furnace. It has a pre-heat zone, a process zone, a cooling zone and two locks one for product entry and the other for exit. The furnace production may reach 150 kg/hour and a maximum temperature of 1400^o C. The products obtained in this furnace always shows better properties than those obtained in conventional furnaces.

How the heat-transfer in vacuum takes place is discussed in details by Limque et al⁷⁶. According to them vacuum plays a double role in terms of heat transfer. Comparing vacuum atmosphere with gas atmospheres (eg. Argon) it is said that in vacuum the heat insulation efficiency of ceramic wool is increased by 60%. Additionally, better insulation and lower heat losses allow lower heat input in a state of equilibrium, with consequent smaller temperature differences. The temperature distribution in a loaded chamber is maximum $\pm 5^{\circ}\text{K}$ even at 600°C .

From the following discussions it is obvious that vacuum technology has a lot to offer to the powder metallurgists in form of sintering atmospheres. The shift to vacuum atmosphere is further prompted by the energy conservation drive, low petroleum and natural gas resources and soaring price of petroleum and its byproducts. Obviously, from the energy and product quality viewpoint, the vacuum furnace gives, by far the best results, but its use is as yet limited owing to its price being much higher than the conventional furnaces. But, as more and more manufacturers shift their alliance towards vacuum atmosphere, it is expected that the price of the furnaces will fall rapidly. One of the good signs for vacuum technologists is the number of big names in the furnace manufacturing world laying stress, and committing themselves to huge fiscal investments for the development of vacuum furnaces.

So, with the developments in the continuous vacuum sintering furnaces, and with the ever increasing cost of production by the conventional route, it becomes timely to investigate the feasibilities of production of porous bronze bearings through vacuum sintering.

It is proposed to look into the feasibility of sintering self lubricating bronze bearings in vacuum. The investigations would cover the influence of high and low vacuum on properties of bearings produced and also help in determining the type of vacuum set up essential for proper sintering of such materials. The other important investigations will include evaluation of types of copper powders, the suitable pre-sintering and sintering temperature and time, the heating rate, the compacting pressure, the tin contents that would be suitable for vacuum sintering. It is also proposed to compare some of the vacuum sintered bronze bearings with bearings sintered under similar conditions but in hydrogen atmosphere.

Some of the properties to be determined are the total, open and closed porosities as a percent of volume ; closed porosity as a percent of total porosity ; sintered density ; percent theoretical density and the K-strength constants. It is also proposed to look into the structures to try and understand its effects on the final properties of porous bronze bearings. This work may help to establish vacuum sintering as an alternative to the conventional gas sintering of self-lubricating bronze bearings.

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