INFLUENCE OF PROCESSING VARIABLES ON THE PHYSICAL PROPERTIES OF POWDER METALLURGY PRODUCTS

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INTRODUCTION

Powder metallurgy is the technology of transforming powdered metals, alloys, oxides or salts into finished or semifinished products by mechanical and thermal operations which are performed at temperatures below the melting point of at least the major part of the metal composition.

The powder metallurgist either manufactures ingots, which are subsequently shaped by plastic deformation or machining, or he produces immediately the finished part, thus eliminating working and machining operations.

Powder metallurgy is, however, not only a technology, but also a science, the main field of this branch of research being the understanding of all reactions which take place during the transformation of metal powders to powder metallurgy products. The scope of powder metallurgic research also includes the analysis of technological and other properties of the finished products as compared with those of materials of identical chemical composition produced by other methods.

The main operations of powder metallurgy are:

1. The production and analysis of the raw material, which is the basis of all powder metallurgy processes, namely the powdered metals or alloys;

2. The compacting process, during which suitably prepared powder mixtures are subjected, at normal or elevated temperatures, to considerable pressures;

3. The sintering process, in which the pressed "green compacts" are subjected to a thermal treatment which imparts to them the required mechanical strength as well as other desired properties. Compacting and sintering are frequently followed by re-pressing and annealing or resintering and/or other afterworking treatments. In all cases, the performance of the material during processing, as well as the properties of the finished products, depends to a large extent upon the basic characteristics of the powder material (3).

The importance of powder metallurgy lies in the ability of this technique to produce complicated metal shapes within a close limit of tolerance by a process requiring much less time and skill than machining, and much lower temperatures and fewer finishing operations than casting. Moreover, the products of powder metallurgy may possess almost all the physical characteristics of those made by the other methods, as well as many which can not be obtained thereby, for instance, controlled porosity. This fact causes a widening of scope for powder metallurgy.

Powder metallurgy is also known as "metal ceramics", while the products are often called "sintered metals", both terms indicating the method of production. (7)

The powder metallurgy industry is firmly established in every major country in the world, and its products used throughout a wide variety of industries. Utilization of this method within general industry is now an accepted practice and the average American car contains in excess of 120 sintered components as compared with the average English car of around 85 (an indication of the well known conservative attitude within British industry.) (11)

In the automobile industry, for example, the applications are very numerous and range from shock absorbers to distributors, starting motors, car door locks and components in the steering mechanism. Shortly there will be more highly stressed applications within gear box and internal combustion engines. (11)

Each day more and more people are becoming aware of the advantages of this unusual method of producing engineering components with the result that the volume of pieces produced by the process is growing rapidly.

Without any shadow of doubt, powder metallurgy is one of the industries of the future although it is true to say that a lot more development is required.

The powder metallurgy industry does not exist in Turkey, and the metal powders used for nonmetallurgical purposes, such as pigments, welding rod constituents, etc. are imported. One of the intentions in undertaking this subject was to gain experience by going into investigations in powder metallurgy, for the first time in this country.

A small and modest laboratory was established, mainly by using substitutes for the needed equipment. The experimental work is carried out personally by the student with the counsel of an experienced adviser. By doing so, the proper way to attack a new problem, methods of study, experimentation techniques, the difficulties involved, and the possible solutions were observed and experienced.

The specific problem was to investigate the influence of processing variables on the properties of powder metallurgy products. Although optimum conditions have been developed in practice, the literature on the subject shows a lack of analysis or evaluation of the processing variables, probably for the reason that the details of the physical and chemical mechanisms involved are not understood in any quantitative sense. Some points which are left vague in the literature were investigated, such as the effect of compaction in vacuum, the size effect and the effect of "dwell-time", as well as the common processing variables such as compacting pressure, sintering temperature and time. The major measurable property was taken as the total porosity, i.e., the approach to theoretical density of the products. The reasoning behind this choice is that for most materials, the physical properties such as hardness, tensile strength, compressive strength, fatigue strength, and electrical conductivity are directly and sometimes linearly proportional to the density. (Fig. 1).

The results of these investigations will be reported in a later chapter.

Numerous difficulties encountered in establishing the laboratory, and specially in obtaining the powders caused a delay of three months in starting the experiments, and the short time of two semesters limited the extent of investigations. However, it is understood that such investigations in powder metallurgy will probably continue in Robert College as subjects of graduate theses, and a section of "Recommendations" for the interested investigators is included at the end.

REVIEW OF LITERATURE

HISTORY AND DEVELOPMENT OF POWDER METALLURGY

The essential features of powder metallurgy are the production by mechanical or chemical means of a metal powder, and consolidation of this powder at a temperature below the melting point of the major constituent, into a reasonably strong solid form. The coalescence of the particles requires the application of pressure and heat. An important trend in modern powder metallurgy is to apply the pressure to the hot powder.

It is interesting to note that, one of the earliest metallurgical processes employed these principles. Furnaces that would melt nearly pure iron were not available until the 19th century; yet iron was used at least as early as 3000 B.C. In the usual primitive process the pure oxide ore was heated in a charcoal fire, generally aided by a blast from bellows, to reduce it to a metallic condition. The resulting metal sponge while still hot was then hammered to weld the particles together and give a cohevent metallic mass which could be forged into a usable shape. The product was often unsound and full of slag, but excellent samples were occasionally produced. (1)

At the present time sintered metallic objects are limited in size to pieces weighing a few ounces -- or at most pounds - yet the smiths of India some 1600 years ago produced the famous Delhi pillar weighing 6 1/2 tons and other pieces even larger. (1)

Powder metallurgy was used in Europe at the end of the 18th century for working the then infusible (since there were no furnaces capable of melting it) metal platinum. It is astonishing to find that it had been used for the same purpose by predecessors of the Incas in Ecuador and by the Incas themselves in that locality for a considerable period before Columbus made his famous voyage. Several samples of platinum have been found that had been worked by a process not unlike that used in preparing sintered hard carbides today: The grains of native refractory platinum (separated from the ore by washing and selecting) were cemented together by a metal of lower melting point which wet them and drew the particles together by surface tension to form a strong lump, fit for further work. (1)

Many writers on powder metallurgy have referred to the work of Wollaston in producing malleable platinum, published in 1829. Wollaston kept his process secret until the end of his life and is said to have received a large income from its use. His process, was essentially as follows: Ammonium chloro-platinate was ignited to give metallic platinum as a fine powder. Wollaston cautioned against heatin the powder at too high a temperature and advised that it be broken up gently in a wooden mortar to avoid burnishing it, for this would prevent later cohesion. The powder was washed with water and while wet put into a brass mold 6.75 in. long, tapering from 1.12 in. diameter at the top to 1.23 in. at the bottom, where it was closed with an iron plug. The use of water suspension was supposed to give a more uniform mass in the cylinder. The powder was pressed in by hand with a wooden plug, then covered with a copper plate and pressed in the ingenious simple "Toggle Press". The resulting cake was hard and firm enough to be handled without danger of breaking and was heated to redness on a charcoal fire to drive off moisture and oil and to give a small degree of cohesion. The cake was next heated in a wind furnace, resting on clean quartz sand and covered with an inverted refractory pot. The wind furnace (fired with coke) burned for about 20 minutes from the time of lighting. The cake was removed from the furnace and while still hot struck squarely on top with a heavy hammer. Thereafter the metal was sufficiently consolidated to permit further forging like any other metal. (1)

This is the process generally mentioned as the beginning of modern powder metallurgy. A lot was done on platinum before Wollaston's work by various men but his chief innovation seems to have been the use of a press in making cold compacts prior to heating for consolidation by hot working.

It was also stated (1) that an independently developed Russian method was in operation in the year 1826. The sifted platinum powder was pressed in a cast iron cylinder of the desired size, fitted with a steel punch actuated by a powerful screw press. The compacts were fragile but could be handled. They were rendered workable by annealing for one and a half days at the very high temperature of a porcelain-firing kiln. If the platinum had been well purified, and especially if it had been properly washed, it was then very malleable and suitable for any use.

This seems to be the first commercial use of a high temperatur sintering operation applied to a previously compressed mass of powder, as distinct from the earlier method of hot pressing.

The important modern use of powder metallurgy to form intricately shaped articles by pressing and sintering was suggested over a century ago. In 1830, when determining the atomic weight of copper by the reduction of its oxide in hydrogen, the chemis, G. Osann, noticed that the reduced metal sintered to a compact mass. In his paper, published later, he gives full details of his process for maxing impressions of medals and the like from copper powder produced by the reduction of precipitated copper carbonate. (1)

An important use of the sintering process was for making the filaments of incandescent electric lamps. This process was probably a direct offshoot of the methods used in making carbon filaments by the extrusion and subsequent sintering of the carbonaceous materials. (2)

The first metal filament was the osmium one, made by mixing osmium or its oxide with a reducing material that served also as a binding agent. The mixture was extruded to form a filament which was subsequently heated to reduce the oxide and to sinter the metal into coherent form. Similar techniques were used for the production of filaments made of tungsten, vanadium, zirconium, tantalum and other metals. (1)

The first commercially successful metal filament was of tantal drawn from vacuum-fused lumps and not made from powder metal. Before Coolidge's important discovery that tungsten could be worked in a certain temperature range and would then retain its ductility at room temperature, filaments had been made by mixing tungsten powder with as little as 2 to 3% nickel, pressing, and sintering the compact in hydrogen at a temperature slightly below the melting point of the nicke The resulting bars could be drawn, and the final filaments were freed from nickel by a vacuum treatment at high temperature. This process was not commercially satisfactory but is important as an antecedent to the sintered hard carbides. (1)

The next stages were the production of contacts and electrode materials (a logical offshoot of tungsten production); porous metal bearings (a real innovation); the cemented carbides; the development of a wide range of special magnetic materials; and finally the use of powder metals to make certain objects more cheaply than can be done by conventional methods of casting, working and machining, for example gears.

PROCESSING

METAL POWDERS

CHARACTERISTICS: The properties of the finished powder metallurgical product, as well as the performance of the material duri pressing and sintering, and thus the economy of the process, depend to a large extent upon the physical and chemical characteristics of the metal powder. These characteristics in turn, depend upon the method of powder preparation. The selection of the most suitable powder for a particular job is dictated by the intended application of the finishe product. The final selection must be based on the performance of the powder when it is subjected to the actual pressing and sintering operations. However, the determination of the powder characteristics by laboratory tests permits a preliminary choice of samples for performanc tests, besides the determination and control of characteristic properties is essential for securing uniformity in different powder lots.

PHYSICAL CHARACTERISTICS: Apart from chemical composition anc purity, the basic characteristics of a metal powder are:

particle size and size distribution;
particle shape;
particle porosity;
particle microstructure;
apparent density;
flow factor;
specific surface;
compressibility

for some specific applications some other characteristics become essential; for example; electric and magnetic properties for electric and magnetic parts, or thermal conductivity for the manufacture of frictio materials. (3)

In industry, particle size and size distribution, apparent density and flow factor are most widely employed in specifications and control routine. This is due to the fact that they are the most important factors in production. For example, the apparent density is important because commercial operations employ a volumetric fill for each mold. Therefore, if the apparent density varies, more or less powder will be fed into the die, depending upon whether the density has been increased or decreased, and when pressure is applied, provided it is applied to a constant pressure, the green compact will be shorter or longer than desired. If pressure is to a definite volume, the porosity and density will be affected.

Methods for determining these three characteristics are standardized by A.S.T.M. (4)

<u>CHEMICAL CHARACTERISTICS:</u> In general, it is not difficult to produce metal powders of a purity well above 99%. In many cases 99.99% purity is attainable.

The percentage of impurities permissible depends on their chemical nature and their location. It is stated that a 97% powder may be preferred to a 99% powder, if the impurities in the high-purity powder are more abrasive than those in the 97% powder. (3) The distribution of the impurities in the powder particles is also highly important. Surface oxides, for example, may, under certain conditions, be eliminated by sintering in reducing atmospheres, while occluded oxides may not be attacked under identical conditions. If oxide occurs on the surface of the particle it does not interfere very markedly with the molding operation or subsequent strength of the product. It appears that surface oxide in the form of a thin film is displaced during processing, and the place from which it has been removed presents a fresh metallic surface to promote adhesion. This oxide may subsequently be reduced during the sintering operation if it is carried out in a reducing atmosphere. If the sintering takes place in a neutral atmosphere the oxide will of course remain unchanged, but apparently it does not metarially affect the physical properties dema of the product. If the oxide is occluded, however, there is nothing the production cycle which has any tendency to remove it, and a weak spot remains within every particle in which oxide is present. Theref the resulting product will be somewhat weaker. (2)

The amount of occluded oxide can be decreased by grinding th powder and subjecting it to a reduction operation. (3)

The chemical composition of powders and the presence of impurities are determined by standard methods of chemical analysis. Information regarding the location of impurities can be obtained by sta dard metallographic methods as well as by the "loss of weight in hydrogen", which is determined by sintering in hydrogen under specifi conditions, and represents a relative measure of the amount of reduci impurities accessible to hydrogen. (3)

Besides oxygen some other impurities, such as carbon, silica and sulfur also receive some attention.

Carbon is important in ferrous powders. If it is residual a free carbon, it does no harm to most products, and may aid the produc tion cycle by slightly lubricating the dies. If it is combined with iron, the hardness of the iron is increased and its malleability reduced. This in turn lowers the cohesive strength of the compact, necessitating higher pressures.

Silica is to be avoided because of its abrasive action on t dies and because it acts as an interfering phase and reduces metalli cohesion. (2)

Sulfur creates acidic conditions and gases during sintering, shortens equipment life, and makes it difficult to control the porosity, size and shape of the finished products.

PRODUCTION: A great variety of methods are employed for the production of metal powders; but it is possible to gather these methods into three general classes;

1. Mechanical,
2. Physical,
3. Chemical.

Powders widely differing from each other in particle size and shape, chemical purity, and microstructure are produced by these methods. However, many of them are suited only for nonmetallurgical uses, for example as pigments, catalysts, etc.

Most powders intended for use in powder metallurgical processes are produced by one of two methods:

1. reduction of oxides (and other solid compounds);
2. electrolysis

Due to their importance these two methods will be discussed briefly in separate sections.

Other methods used for the production of the starting material of powder metallurgical processes are:

3. atomization,
4. mechanical comminution (by crushing, milling, etc.),
5. thermal decomposition of carbonyls,
6. intergranular corrosion.

Methods of only minor interest in powder metallurgy include:

7. condensation of gaseous metals,
8. decomposition of alloys,
9. other chemical methods (reduction of solutions and fused salts, and thermal decomposition of solid compounds),
10. other mechanical methods (mechanical comminution by machining, and solidification of liquid metals by shotting and graining). (3)

1. REDUCTION OF OXIDES (and other solid compounds): The most widely employed process of producing powders for pressing and sintering is the reduction of oxide ores, the reaction being performed at temperatures below the melting points of the oxides and metals. Gases, such as H_2, CO, coal gas, or alkali metal vapors, carbon or metals are employed as reducing agents. (3) The powder thus produced is sponge like and lends itself to shaping by cold pressing because of its softness and plasticity. (5)

In some processes, the metal is obtained in the form of spongy agglomerates, which are easily comminuted to powders by mechanical means.

The main advantage of the reduction method is its flexibility. By varying the particle size and shape of the oxides (the oxides are generally brittle), the temperature of reaction, the type of reducing agent, and, in the cases of gaseous agents, the pressure and rate of flow of the gas, it is possible to control, within very wide limits, the particle size and also the particle shape, apparent density, and related characteristics of the powder. (3)

The powder is, however, nearly always slightly porous; and if any oxide remains, it is more significant than the oxide which is so frequently present in mechanically produced powders. The latter is primarily a surface oxide whereas the oxide which may remain in a powder obtained by reduction is primarily that part of the original oxide which has not been reduced and therefore, lies in the center of the particle. (See Chemical Characteristics) (2).

The reduction process is employed exclusively for the technical production of tungsten and molybdenum powders, is used for the production of most iron powders, and also for copper, nickel and cobalt powders. (5)

2. <u>ELECTROLYTIC METHODS:</u> Metal powders are produced by electrodeposition from solutions, as well as from fused salts. The electrolysis of solutions is employed for the commercial production of metals such as Fe, Cu, Ni, Zn, Cd, Sn, Sb, Ag and Pb. The electrolytic

process has the advantage that within wide limits, though not to the same extent as in the reduction method, a control of powder characteristics, particularly particle size, is possible.

Means of control are the regulation of current density, temperature, composition and circulation of the both, size and arrangements of the electrodes.

Three different types of electrodeposition are in practical use:

1. deposition as a hard, brittle mass, which is subsequently ground-for example, in hammer mills;

2. deposition as a soft spongy mass, only loosely adherent to the electrode and easily disintegrated to powder;

3. direct deposition as powder.

The removal of the deposit from the cathode -- either continuously or at regular intervals -- is essential, since accumulation of deposit increases the active cathode surface and thus decreases the current density. (3)

The deposit is removed by mechanical means such as scrapers or stiff bristle brushes, or by the use of rotating cathodes, or by rapid circulation of the bath. (5)

Electrolytic powders deposited in powder form are generally characterized by a dendritic, fernlike shape of low apparent density, the latter property frequently necessitating a densifying aftertreatment of the powder. (3)

CONDITIONING METAL POWDERS FOR USE: Before the pressing operations, the powders are frequently subjected to special treatments, generally of mechanical or thermal nature. The purpose of mechanical treatments may be densification, mixing and blending, or coating; that of thermal treatments, either purification or softening. Powder particles may also be coated with materials different from that of the particles.

MECHANICAL TREATMENTS

DENSIFICATION: Powders consisting of very porous particles or of voluminous particle aggregates (so-called secondary particles) may exhibit an apparent density too low for satisfactory performance during pressing and sintering, as well as unsatisfactory flow characteristics. The apparent density of such powders can be considerably increased by prolonged ball-milling. (3)

Another method of densification consists in agglomerating powder by mechanical compression and converting the resultant coherent cake into powder by mechanical comminution. (3)

Generally, mechanical densification results in work hardening and necessitates a subsequent softening by annealing.

MIXING AND BLENDING: Mixing operations are applied, either for the blending of different lots of the same powder (to eliminate variations due to production fluctuations), or for the blending of powders of identical chemical composition but of different physical characteristics, such as particle size; and particularly for mixing differing powder materials, such as the powders of different metals, or metal powders with nonmetallic powders.

For these operations, conventional mixing equipment such as mixers and ball mills are employed. The current industrial procedure consists of ball milling the mixture in stainless or carbide lined mills with carbide balls in the presence of a non-reactive organic liquid as, for example, acetone. (6)

Wet mixing aids in securing a homogeneous blend.

BLENDING METALLIC WITH NONMETALLIC POWDERS: Nonmetallic powders admixed to metal powders may represent alloy constituents, such as graphite and phosphorus, or their function may be the improvement of compressing characteristics as binders and lubricants, or the control of properties such as porosity. The distinction between these classes is not distinct, for example, graphite may represent an alloy constituent but may at the same time act as a lubricant, while many organic additions act as lubricants and at the same time increase the porosity of the finished part. (3)

The function of nonmetallic binders and lubricants is the improvement of compressing characteristics by reduction of interparticle friction and friction between particles and die walls. Graphite and stearic acid are the most commonly used lubricants. (3)

The organic additions evaporate or are decomposed during the sintering process, or they are boiled out in a low-temperature baking process before sintering. Additions which leave traces of carbon as residues in the sintered product can not be used in applications where carbon is harmful. This evaporation or decomposition of organic auxiliaries increases to some extent the porosity of the finished parts, and in some cases additions are made for this purpose. (3)

Other nonmetallic powder constituents may be required for particular applications: thus, friction-producing powders, usually abrasives, are added to metal powders intended for use as friction materials.

COATING: When mixing powders of different metals, segregation occurs due to marked differences in particle sizes. This can be overcome by causing the fine particles to form adherent coatings upon the surfaces of the coarser metal. Coating of metal powders is also employed for purposes of other than prevention of segregation, such as modification of the plastic or chemical surface characteristics of a powder, or insulation of the individual metal particles.

Coatings on metal particles can be produced by various methods:

1. ball-milling relatively coarse particles of a hard material with a small proportion of a fine powder of a soft material;

2. electroplating, the powder particles to be plated forming the cathode in an electrolytic cell;

3. chemical precipitation (cementation) of a metal from its salt solution upon the surface of a less noble metal particle. (3)

THERMAL TREATMENT:

The purpose of a thermal powder treatment may be purification (including drying) or softening.

A heat treatment with reducing gases, usually hydrogen, is frequently effective in keeping surface oxides, traces of moisture, absorbed or entrained gases at a minimum, and also in removing excessive C, S, and P. In order to prevent a reoxidation or a reabsorption of moisture or gases, the heat treatment should immediately be followed by the pressing operation. (3)

Powders as received from the supplier are often in a more or less cold-worked condition and hence have little plasticity. This is, of course, particularly true of powders prepared by a mechanical comminution process. Annealing such powders will allow higher as-pressed densities to be obtained as the softer powder cold-welds better than the more brittle cold-worked powder. The hydrogen cleaning operation also allows some softening to occur; hence the two conditioning operations of cleaning and annealing can often be combined. (9)

In powders prepared either electrolytically or by reduction with more electropositive metals, embrittlement may be caused by the absorption of nascent hydrogen. The ductility of such hydrogen-embrittled powders is restored when the absorbed gas is expelled by treatment. It is reported that electrolytic powders must always be annealed. (3)

Ferrous powders may be softened by decarburization, by decomposition of iron carbide, or by modifying the carbide structure. All these changes may be produced by an appropriate heat treatment.

An ingenious method of annealing metal powders without sintering has been devised by Von Batchelder and Strauss. These investigators mixed gold, silver, and iron powders with sodium chloride in the ratio of one part of metal to ten parts of salt. The metal-salt mixture is then annealed in the normal fashion, the large excess of salt preventing metal-to-metal contact and hence sintering of the metal powders. The particle size of the salt should be comparable to the metal powder size. After annealing, the salt is readily removed from the metal powder by washing in water. There seems to be no reason why other salts could not be used, provided they are sufficiently stable, inert and high melting. (9)

COMPACTING:

The purpose of the compacting process is the shaping of metal powders to compacts with sufficient coherence to permit the transfer to the sintering furnace, and with characteristics ensuring satisfactory performance during sintering as well as the desired properties of the sintered product.

The compacting is most commonly performed by pouring the conditioned powder into a die and subjecting it to the action of one or more punches (plungers) operated by a press. This operation may be accomplished either hot or cold.

Two other methods of compacting, namely compacting by extrusion and compacting by centrifuging are also practiced. (3)

Powder under pressure does not follow the laws of hydrodynamics; that is to say, the pressure is not uniform throughout the powder. However, the finished part is supposed to be of uniform density. To achieve this, proper die and punch designs as well as the proper press operation must be adapted.

If the part is relatively thin and of uniform height, the powder may be compacted by "single action", that is, by compression from one side only. (3)

If thicker parts of uniform thickness are to be pressed, it is necessary to use "double action" cycles - that is, to have the lower punch take part in the compressing step. (3)

In the main, the same considerations as have been given above for two types of very simple designs apply when the part to be manufactured has different thicknesses, or has curved upper or lower surfaces. (3, 10)

The press operation consists of the following steps:

1. The die cavity is filled with powder (filling).
2. The upper punch is lowered until it contacts the powder (closing).
3. The upper (and lower) punch (es) advances further and compresses the powder.
4. The maximum pressure is reached and maintained for a definite period of time (Dwell time). (3)

Compacts exhibit a small elastic expansion when removed from the die, and this expansion prevents them from falling back into the die cavity with the retreating lower punch. If compacts of considerable height are produced, their green strength may be insufficient to permit ejection by the action of the lower punch or punches. In this case, so-called split, or segment dies are used - that is to say, dies composed of segments which can be seperated for the removal of the compact. These dies may require considerable horizontal pressures to hold the segments together during compression. In this procedure, the horizontal pressure does not take part in the compressing action; however, a new press which permits the application of horizontal, in addition to vertical pressures have been developed by the Hydraulic Press Manufacturing Company. This modification increases the uniformity of pressure and powder distribution and may permit the pressing of designs which cannot be achieved by vertical pressures only. (3)

In any compressing cycle, speed and pressure of the punch or punches will not be constant during the entire cycle, and the control of these factors provides another means of promoting uniform powder distribution throughout the compact.

High speed of punch advance during compression may result in non-uniform powder distribution and in entrapment of excessive amounts of air, the escape of which, during the sintering process, introduces complications. (3)

The optimum conditions for the compression cycle depend not only on the powder characteristics and the efficiency of the added lubricants, but also on the conditions of the sintering process; and the optimum conditions for the sintering process depend in turn on the conditions of the compacting process. (3)

These interrelations will be discussed in a later section.

PRESSES:

Presses used for compacting metal powders are either mechanical or hydraulic presses, or they combine mechanical with hydraulic action.

The majority of the presses used in the western hepisphere for powder metallurgy operations are of the cam actuated type, providing the total press tonnage does not exceed 100. Where total tonnages greatly exceed this figure then obviously hydraulic equipment is utilized. Pressures applied vary from 10 to 50 tons/sq.in. depending upon the required density. (11)

In general the presses are equipped with feeding devices for filling the die cavity with the loose powder, and permit the automatic ejection of the pressed compact as well as the automatic removal of the ejected compact from the die table. (12)

FEEDING:

The cavities are usually filled by volume - that is to say, the cavity is filled to overflow and then leveled off flush with the top face of the die, so that the amount of powder is determined by the powder characteristics (see Physical Characteristics) and the volume of the die cavity. Some feeding devices have been designed to carry out this operation automatically, and in order to control the reproducibility of the method special devices such as electric vibrators and stirrers have been developed.

Another method which is also in practical use is, filling by weight. This method is a necessity with powders of poor flow qualities, and is often carried out by hand. (3)

SPEED OF PUNCH ADVANCE:

The speed of punch advance is also varied within wide limits. For high production rates, maximum speed will be employed for the closing step of the cycle (bringing punch in contact with the powder), as well as for the withdrawal of the punch after compression; while speed and pressure during compression are limited not only by their effects on the uniform distribution of the powder, but also by the wear of the die materials. (3)

STROKE CONTROL AND PRESSURE CONTROL:

As it was explained earlier, in order to control the punch movements and the pressures during pressing, there are two principal means:

1. Control of the stroke, which is exclusively employed in mechanically operated presses. The maximum pressure is determined by the stroke of the punches.
2. Pressure control, usually employed in hydraulic presses. In this method the stroke is determined by the fixed maximum pressure.

Nonuniformity of powder characteristics will have different effects on the products pressed by these two different methods (see Physical Characteristics).

DIES

DIE MATERIALS:

The punch and die equipment is an important factor in powder metallurgy, especially when the pressures and rate of production are high. The material for these tools must be carefully selected with respect to the durability offered. Generally, high-grade alloy steels, and even hard carbide alloys, are used for the dies and punches. Satisfactory dies are made from air-hardening alloy steels containing a high percentage of carbon and chromium. Special alloy punch steel is recommended for the punches, and usually this steel is oil hardened. (5)

The inner die surfaces must be carefully polished with polishing rouge, and operation which has to be carried out by lapping in the direction of the stroke. Wear is also reduced by lubrication of the die with graphite flakes, stearic acid, glycerin, or other lubricants. (3)

DIE DESIGN:

Factors determining powder metallurgical die design are the practically complete absence of lateral flow of powder during compression and the relatively high compression ratios, which approaches in most practical applications a value of about 3.

The performance during the processing operations following the compacting, as well as the quality of the finished part, depends upon the uniform distribution of the powder throughout the compact; and designs are limited to types permitting a satisfactory uniformity of the powder.

The limitations resulting from these considerations are summarized in the following rules:

Structures which cannot be pressed are:

1. holes perpendicular to the direction of pressing;
2. re-entant angles and grooves;
3. undercuts.

The following features should be avoided:

1. large and abrupt thickness changes;
2. uneven cross sections;
3. very narrow and deep splines;
4. sharp corners;
5. internal angles without fillets. (3)

However, die design for high speed production is not only based on previous experience and judgement but also on extensive studies with cheaper experimental or hand dies. All factors must first be determined with briquettes pressed in experimental dies. With this information the designer is able to make proper drawings for a production die. (13)

PRODUCTION RATES:

The rate of production depend upon the size and shape of the product and the type of press used.

A complete compression cycle consists of, filling. closing, compression proper, return of punches, ejection and removal of the ejected compact from the die table. On conventional presses production rates range from 3 to 100 pieces per minute.

However, a considerable speeding up at the production rate can be accomplished by the use of rotary presses on which multiple sets of dies are mounted. Bailey, who gives a very instructive historical review of the development of pressing machinery (14), reports production rates on rotary presses with automatic feeding and removing equipment of 500 pieces per minute.

If the usual hardened-steel dies are used they will yield up to 150,000 parts before wearing out of tolerance. If hard carbide alloys are used production often runs over a million parts before such a die wears out of size. (10)

HOT PRESSING:

Hot pressing draws attention because it is relatively easy to secure compacts of theoretical density, whereas, cold-press, sinter methods rarely closely approach ultimate densities, except in the case of liquid-phase sintering. Hot pressing has not found much favor for commercial operations, because it is a slow process, a single pressing often requiring several minutes and even hours to complete.

Heating of the powder can be performed by setting the whole die in a resistance furnace, or in a high-frequency coil; by passing electric current through the punches; or by using graphite as die material and passing the current through the die. (3)

The powder may be introduced cold into the die, or it may be preheated. Another way is to prepress the powder cold, heat it in a furnace, and compress it in a cold die while still hot, thus avoiding the special equipment for the heating of the die.

The temperatures employed range from 100° to 500°C. for non-ferrous materials and from 600° to 1,100°C. for ferrous materials. For temperatures up to approximately 600°C high-speed steel dies are used. Graphite dies are required for higher temperatures. (9)

Hot pressing method, in general require the use of protective atmospheres, to prevent oxidation, and hence necessitating additional special equipment.

SINTERING

After the compressing operation the "green compacts" are sintered by furnacing, in a controlled reducing atmosphere at a temperature largely dependent upon the major constituent metal, (generally within the range of 2/3 to 4/5 of the melting point, in °K). A reducing atmosphere is essential throughout this cycle to prevent oxidation and, in the case of iron carbon alloys, decarbonization. Temperature and time of sintering as well as the rate of heating and cooling are controlled to very close limits. The optimum conditions for the production of specific mechanical properties and dimensions of the sintered part depend, however, not only on these sintering conditions but also, to a large extent, on the properties of the green compact, which in turn are determined by the powder characteristics and pressing conditions. These factors will be discussed in detail together with some other processing variables in a later section.

Sintering induces strength and duetility by permitting diffusion to take place between the particles of compressed powders. A good analysis of this process is given by Wretblad and Wulff (15). The related theories will be discussed in later sections.

FURNACES:

As it was mentioned earlier, proper sintering requires a close control and regulation of heating rate, heating time, maximum temperature, sintering atmosphere and cooling rate.

Special furnaces are developed to achieve absolute control over these variables, the most modern one being the continuous furnace, containing various zones. A detailed description of sintering furnaces and control methods is given by Webber. (16)

HEATING METHODS:

Sintering furnaces are heated almost exclusively by electricity

Gas heating, the other alternative, has only minor importance.

The maximum working temperature is in most furnaces, limited by the temperature resistance of the muffle materials rather than by the efficiency of the heating method. The ideal muffle material must be nonporous and must withstand, in contact with inner and outer atmospheres, the maximum temperatures, as well as all temperature changes involved in the sintering cycle. (3)

A number of muffle materials have been developed for satisfactory service in certain ranges of temperature.

RESISTANCE HEATING:

Resistance heated furnaces are most frequently used in sintering work.

Four different types of resistor elements are in use:

1. Wires, ribbons, etc., of metals and alloys which can be freely exposed to furnace atmospheres (up to 1,260°C, 2300°F)

2. Globar elements, made of silicon carbide and ceramic filling material, which also can be freely exposed to furnace atmospheres (1,260°-1,400°C, 2,300°-2,550°F)

3. Heating elements consisting of high melting metals, such as Ta, Mo, or W, which require a protective, reducing atmosphere (up to 1500°C, 2,750°F).

4. Stratit elements in which the resistors - rods of Mo or W - are enclosed in gastight containers and surrounded by vacuum (up to 1,600°C, 2,900°F). (3)

OTHER METHODS OF ELECTRIC HEATING:

A. Direct passage of the current through the piece to be sintered. In the case of tungsten, temperatures in excess of 3,000°C (5,400°F) are reached.

B. Graphite-tube short-circuit furnaces are employed for the sintering of hard alloys and permit temperatures up to about 1,480°C (2,700°F).

C. High-frequency induction furnaces are also employed to obtai temperatures up to 3,000°C (5,400°F). (3)

In powder metallurgic practice, however, the actual operating temperatures generally do not exceed about 1,980°C, (3,600°F).

Special high frequency furnaces are developed for sintering in vacuum.

SINTERING ATMOSPHERES:

The control of the sintering atmosphere is more important in powder metallurgy than in other metallurgic heat treatments. This is due to the large surface areas exposed to the sintering atmosphere.

Koehring (17) defines sintering, as "the process of heating the article to a temperature below the melting point of the highest-melting constituent for such a length of time and in such an atmosphere as will import to that article the properties which will permit it to serve its useful purpose."

The functions of the sintering atmosphere are, in general two-fold:

1. It must prevent undesired reactions, such as oxidation, carbonization, and decarbonization.

2. It must perform desired reactions, such as the reduction of surface oxides and the removal or replacement of absorbed gases. (3)

A number of sintering atmospheres (including vacuum), their production methods and the principles of selection of suitable atmospheres are explained thoroughly in references 3 and 17.

The effects of these atmospheres on the physical properties of the product will be discussed later together with the effects of other processing variables.

LIQUID-PHASE SINTERING:

This process is only feasible when there are two phases of quite widely different melting points, and when the amount of the liquid phase present is small. Also, the liquid phase must thoroughly wet the solid phase. Another condition is that there must be enough of the higher melting powder to form a self-supporting, skeletal network, thus the shape of the compact is not destroyed when the other powder melts. The liquid metal, by means of capillary action penetrates the skeletral network, filling all the voids and thus makes a completely dense two-phase structure. (9)

INFILTRATION METHODS:

Sometimes more satisfactory liquid-phase sintering is obtained by pressing the high-melting network powder first, and in a second operation causing the liquid phase to penetrate the porons structure in the same manner as water is taken up by a sponge. One advantage of this technique is that the volume reactions can be controlled quite accurately by controlling the high-melting network powder pressing conditions. (9)

TREATMENTS SUBSEQUENT TO SINTERING

Dependent upon tolerances and the application of the part, the sintered component may then be "sized" or "coined" to: --

a. rectify and deformation caused by sintering
b. achieve close dimensional accuracy
c. improve surface finish
d. increase physical properties
e. calibrate porosity
f. give a combination of any of the above features

The plastic deformation obtained by re-pressing at room temperature is considerably lower than that produced by conventional working methods. (18) Therefore, the increase in plasticity with temperature is sometimes utilized in hot re-pressing methods. This consists of taking hot compacts out of the sintering furnace and dropping them immediately into preheated dies.

The sintering and recoining operations may be repeated again at this stage to induce additional strength, after which the metal sintering can be considered a usable part. As one of the features of metal sinterings is porosity, impregnation is carried out in the majority of cases to provide self-lubricating properties by the utilization of oils, greases, waxes, or dry lubricants such as molybdenum disulphide. (11)

Alternatively, or in addition, further operations may be executed such as: --

a. Orthodox machining operations where a desired characteristic cannot be incorporated in the powder metallurgical tooling- for instance annular grooves, drilling of cross holes, tapping or rolling of threads etc. (see Die design).

b. Heat treatment (hardening)

c. Surface finishing, etc.

The component may then be considered ready for service. (9)

INVESTIGATION

EFFECTS OF DESIGN AND PROCESSING VARIABLES ON THE PHYSICAL PROPERTIES OF POWDER METALLURGY PRODUCTS

Dr. Schwarzkopf (3) summarizes the most important factors determining the final results of a powder metallurgic production process as follows:

1. The characteristics of the metal powder used as raw material:
    a. Susceptibility of the powder material used, to plastic deformation;
    b. size, size distribution, shape, and porosity of the powder particles together with other characteristic such as apparent density, compression ratio, and flow, which are mainly determined by particle size, shape, and porosity;
    c. purity of the powder, and the nature as well as the distribution of the impurities.

2. The compacting conditions:
    a. Maximum pressure during compacting;
    b. timing of the pressure application - that is to say, the rate of pressure increase during the compression and the time during which maximum pressure is maintained;
    c. shape of the compact or die cavity;
    d. manner in which the pressure is applied upon the powder (number and direction of punches);

e. temperature at which the compression is performed;
f. lubricants within the powder mixture and lubrication of the die walls.
g. die material.

3. The sintering conditions:
   a. maximum temperature;
   b. timing of heat treatment, characterized by the time-temperature curve of the entire sintering cycle (rate of heating, time during which maximum temperature is maintained, rate of cooling);
   c. sintering atmosphere;
   d. pressure applied to the compact during sintering;
   e. type of heat supply.

Hausner (7) considers two more factors, namely;

1. Subsequent working, and
2. Composition.

Gurland (6), in his investigations of factors which influence the performance of sintered carbides of WC-Co, groups these factors into two, namely;

1. Design variables,
2. Processing variables.

In this classification, powder characteristics, size and shape of the compact, some of the subsequent treatments (heat treatment, surface finish), composition and rate of loading, etc. are classified as design variables, whereas mixing procedures, compacting conditions, sintering conditions and some of the subsequent treatments such as re-pressing and re-sintering are included among the processing variables.

Our objective is to investigate the effects of some processing variables on the physical properties of the powder metallurgical products.

Therefore, we will state the effects of design variables rather briefly, to understand the sacrifices we have made by not controlling them. (Due to the limitations imposed by the capacity of our experimental equipment and the rather short time of two semesters). Then we will summarize the effects of the processing variables as determined by various investigators so as to have some comparison with our results. We will also have a summary of the underlying theories.

In our investigations, especially the effects of these variables on the density of the finished products are emphasized. The reason for this is that the physical properties, such as hardness, tensile strength, compressive strength, fatigue strength, and electrical conductivity of the powder compacts are directly and sometimes linearly proportional to the density for most materials. (Figure 1).

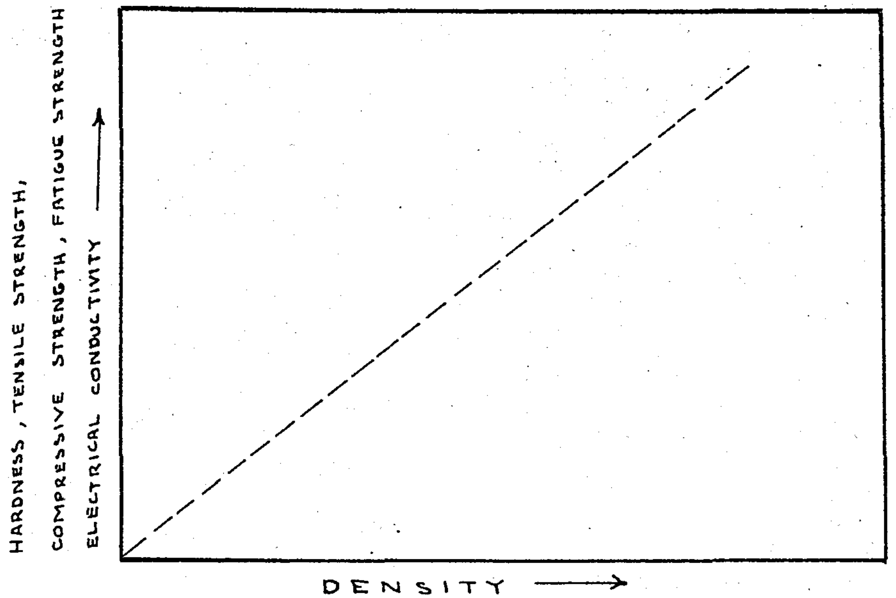


FIGURE 1

EFFECT OF DENSITY ON PHYSICAL PROPERTIES OF POWDER COMPACTS.

(Figure reproduced from REF. 7, pp-13)

DESIGN VARIABLES

POWDER CHARACTERISTICS

SUSCEPTIBILITY TO PLASTIC DEFORMATION: The susceptibility to plastic deformation depends, to a large extent upon the crystal structure.

Generally it can be stated that;

a. The higher the susceptibility to plastic deformation under the influence of external stresses, the lower is the compacting pressure required to produce briquettes of sufficient cohesion for further handling, and the higher is the permissible rate of pressure increase;

b. The higher the susceptibility to deformation, the lower is the porosity of the green compact for the same compacting pressure;

c. The higher the susceptibility to deformation, the easier it is to produce points of contact between particles in the compact, which is a necessary condition for the bonding to be effected by the sintering process. (3)

This property of the powder can be increased by annealing and purification (see Thermal Treatments).

The following table given by Eilender and Schwalbe (3) is included here to indicate the total effect of sintering and of purification.

TABLE I

EFFECT OF ANNEALING TEMPERATURE ON GREEN COMPACTS OF COARSE IRON POWDER PRODUCED BY ATOMIZATION.

ANNEALING TEMPERATURE	700°C. (1,290°F.)	800°C. (1,470°F.)	900°C. (1,650°F.)	1,000°C. (1,830°F.)
Height of cylindirical green compact (mm.) produced at a compacting pressure of 30 tsi.	17.5	16.6	16.2	16.0
Density (g./cm.^{3}) of compact after sintering for 1 hr. at 1,200°C. (2,190°F.) in H_2.	5.92	6.35	6.52	6.61
Hydrogen Loss (Loss in weight during sintering, indicative of amount of reduced oxides.	1.32%	0.85%	0.4%	0.01%

(Table reproduced from Ref. 3., pp - 84).

Hausner (7) also gives a diagrammatic sketch of the effect of the hardness of the metal on the density of the compressed powder and also of the compacting pressure on the density.

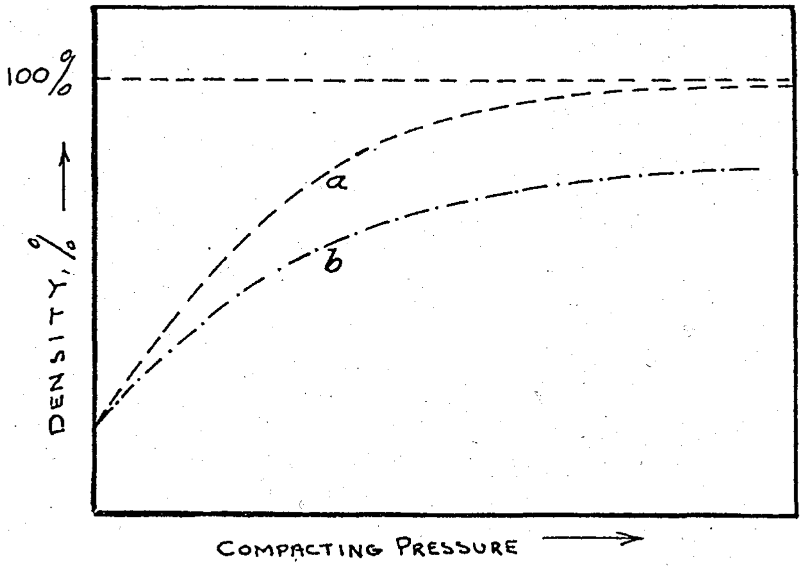


FIGURE 2

DENSITY OF COMPRESSED AND SINTERED SOFT AND HARD POWDERS AS A FUNCTION OF COMPACTING PRESSURE.

SINTERING TEMPERATURE AND SINTERING TIME WERE CONSTANT

CURVE a : SOFT POWDER
CURVE b : HARD POWDER

(Figure reproduced from REF. 7., pp- 15)

PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION: Regardless of the type of basic material used, the particle size of the metal powder has great influence on the properties of the compact. It is a general rule that the density of a metal compact is a function of the particle size, and the larger the grain size of the powders, the lower will be the density of the compact, the other variables being kept constant.

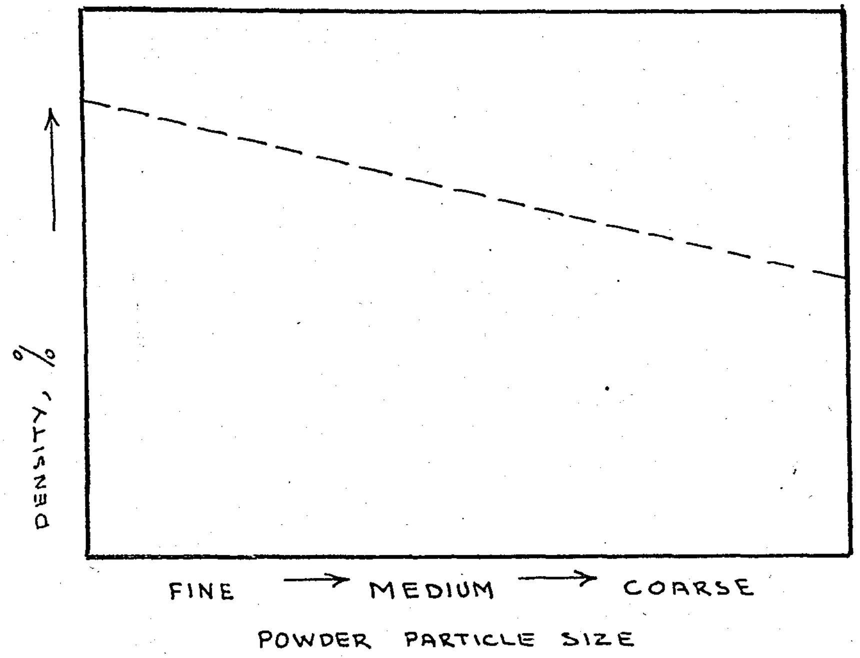


FIGURE 3.

DENSITY OF POWDER COMPACTS AS A FUNCTION OF THE PARTICLE SIZE OF THE POWDER

SINTERING AND COMPACTING CONDITIONS ARE CONSTANT

(Figure reproduced from REF. 7., pp. 13).

However, in the powder metallurgical practice rather wide particle size distributions are used because of the packing effects they produce, minimizing the possibility of bridge formation.

The results of Libsch, Volterra, and Wulff (8) illustrate this superiority of wide size distributions.

TABLE II.

PHYSICAL PROPERTIES OF ELECTROLYTIC IRON POWDER COMPACTS PRESSED AT 33 TONS PER SQ. IN. AND HEAT TREATED IN DRY HYDROGEN AT 825°C. FOR 4 HR.

POWDER SIZE IN MESH	BRINNEL HARDNESS	TENSILE STRENGTH	ELONGATION	DENSITY
100 to 200 (coarse)	40.3	28,600 psi.	15.2 %	7.20
200 to 325 (medium)	41.5	26,400 psi.	13.5	7.06
325 to 500 (fine)	45.4	30,000 psi.	13.0	6.90
Mixed*	39.4	31,000 psi.	16.5	7.27

---

*66% coarse, 17% medium, 17% fine.

(Table reproduced from REF. 8., pp. 390).

PARTICLE SHAPE:

The particle shape has a marked effect on the packing of a powder, and thus on its apparent density. The packing effects obtainable with particles of substantially spheroidal form can be mathematically predetermined (3). In this case the apparent density can be increased by an approximate mixing of larger and smaller particles, according to well-established mathematical relationships. Powders with irregular shapes (due to their method of production) have somewhat lower apparent densities than powders of regular shape. These powders also favor the formation of bridges, which again lowers the apparent density. In addition, the compression of these powders involves more deformation than that of regular particles (3).

Not only the over-all particle shape but also the surface smoothness has an effect on the compactibility, the direction of this effect, however, being still the subject of great arguments (8).

INTERNAL PARTICLE POROSITY:

The apparent density of the powder is also dependent on the internal porosity of the powder particles. Powders of high internal porosity usually exhibit excellent compactibility (there are, however, some exceptions) (8).

A disadvantage is that the increase of internal surface will also increase the amount of adsorbed gases and the surface impurities, particularly oxides. The effect of adsorbed gases and surface impurities depends, to a large extent, on the type of particle porosity, i.e., whether the pores are interconnected with each other and connected with the outer particle surface since this point determines the efficiency of the sintering atmosphere. The average pore size is also important since it determines the amount of adsorbed gases and surface impurities uneffected by sintering atmospheres and remaining in the closed pores as weak points.

The other powder characteristics, namely the apparent density, compression ratio and the flow depend on these characteristics explained above.

The effects of impurities and their distribution was explained together with the chemical characteristics of the powders in an earlier section (see Chemical Characteristics).

OTHER DESIGN VARIABLES:

The other design variables, namely the rate of loading and some of the subsequent treatments such as heat treatment and surface finish are concerned with the intended use of the products and will not be treated here. The rate of load application and the time of loading is particularly important for the strength of the brittle materials (6).

Composition alone effects the final properties more than any other variable. Experimental results are available for certain compositions, however, the behaviour of new and unusual compositions still constitute the subject matter for the majority of research work in powder metallurgy.

PROCESSING VARIABLES:

MIXING PROCEDURES:

The importance of mixing and blending of metal powders was explained earlier in another section. The effectiveness of a number or alternate mixing methods were compared by Gurland (6), using definite procedures for each method. The alloy composition used was: 90% WC - 10% Co. After a number of preliminary tests the optimum mixing times, loads, liquid to powder ratios, etc. were established. The mixing methods were evaluated by comparing the properties of compacts sintered for 1 hour at 1,400^{o}C. The results are shown in Table 3.

TABLE III

EFFECT OF MIXING PROCEDURES ON PROPERTIES

Mixing Method	Density	Hardness	Transverse Rupture Strength ($\times 10^3$ psi)	
	g/cc	R_A	Average	Range
Hand mixing, dry	13.84	88.3	177 (1)	174 – 178
Stirring, water	13.86	88.5	171 (1)	160 – 179
Stirring, acetone	13.92	89.1	194 (1)	163 – 200
Blender, dry	13.66	85.9	110 (2)	107 – 113
Blender, water	13.79	88.6	209 (2)	200 – 217
Blender, vythene	13.89	88.6	214 (2)	201 – 221
Ball mill, acetone	13.89	89.3	270	243 – 294

(1) Average based on 4 samples only.

(2) Average based on 3 samples only.

(Table reproduced from REF. 6., pp. 22).

Characteristic defects associated with unsatisfactory mixing procedures were found to be; porosity associated with insufficient mixing and decarburization associated with oxidation by mixing in water

COMPACTING CONDITIONS

<u>COMPACTING PRESSURE:</u> The application of pressure decreases th porosity and at the same time increases the cohesion between particles by increasing the number of points of contact, as well as by causing particles of irregular shapes to interlock.

In general, a rapid density increase at low and medium pressures is followed, on further pressure increase, by a slower densification. (3)

The maximum green density attainable by cold pressing depends not only on the applied pressure but also on the nature (origin) of the powdered metal, which determines the powder characteristics mentioned earlier.

These effects are illustrated in Figure 4.

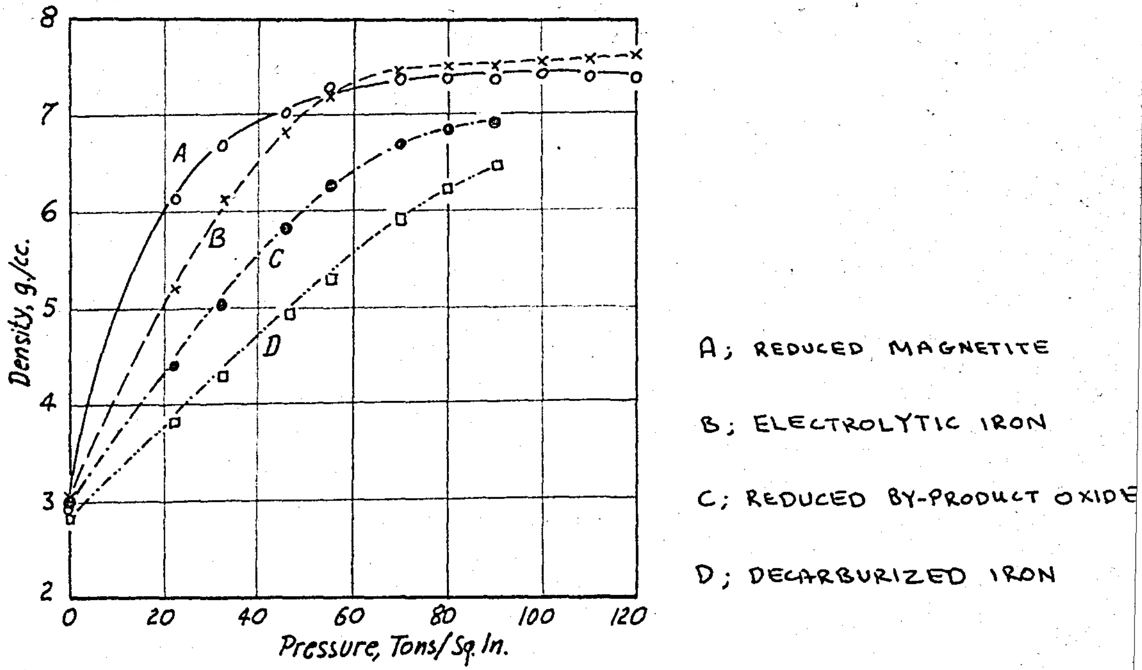


FIGURE 4.

DENSITY OF IRON COMPACTS, AS RELATED TO COMPACTING PRESSURE AND NATURE (ORIGIN) OF THE POWDERED METAL.

Samples in curves C and D were cracked at a compacting pressure above 90 tons per sq. in.

(Figure reproduced from REF. 8., pp. 383).

However, when we consider the density of the sinteredpart, although the density usually increases with increasing compacting pressures, we can not generalize this relationship. The shrinkage during sintering has a marked effect on the final densities. This shrinkage is generally greater in compacts formed at law and medium pressures than in compacts produced at high pressures. Extremely high pressures may even produce growth instead of shrinkage (3).

PRESSING SPEED:

In order to achieve high production rates, very high pressing speeds are used. A limitation is imposed however, by the air entrapped during pressing because of the shortness of escape time.

Variation in the pressing speed has minor influence on the density of the pressed piece; however, compacts pressed at high speed generally show a decrease in density when compared with compacts compressed slowly. These effects are shown in Fig. 5.a

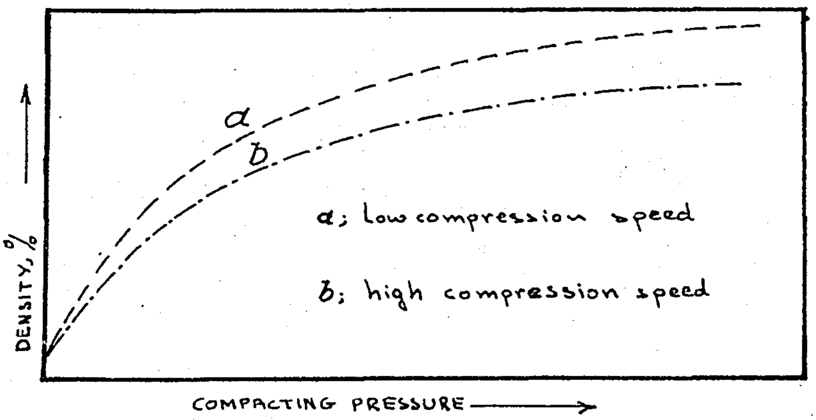


FIGURE 5.a

RELATIONSHIP BETWEEN THE DENSITY OF METAL POWDER COMPACTS AND THE SPEED OF COMPACTING PRESSURE.
(Figure reproduced from REF. 7., pp-16).

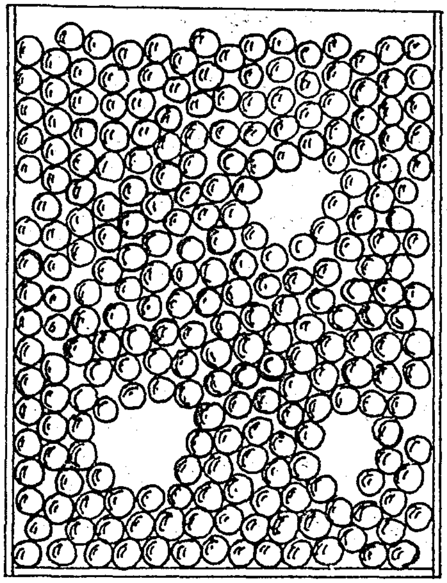


FIGURE 5. b.

BRIDGE FORMATION DURING THE PACKING OF SPHERICAL PARTICLES

(Figure reproduced from REF. 3., pp. 87)

Slow pressure increase reduces friction losses and increases the uniformity of pressure distribution, and thus of powder density throughout the compact; particularly, with powders having a tendency to bridge formation, and in cases of compact designs characterized by relatively high thickness in the direction of compression (3).

TYPE OF PRESSURE APPLICATION (Number and Direction of Punches) AND EFFECTS OF LUBRICANTS:

The nonuniform pressure distribution during compacting, which is due to the fact that powders do not follow the hydrodynamic laws results in nonuniform density as well as hardness in the green compact.

In the case of compression from one side only, the density of the compact will decrease with increasing distance from the advancing punch and will be higher in the neighborhood of the die walls. As pointed out earlier (see Compacting), the decrease of uniformity with increasing distance from the advancing punch necessitates the application of compression from two directions, when the thickness of the part exceeds a value. This maximum value depends on the over-all design of the compact, on the required strength of the finished part, and particularly on the powder characteristics. The powder characteristics however, can be greatly influenced by the addition of lubricants.

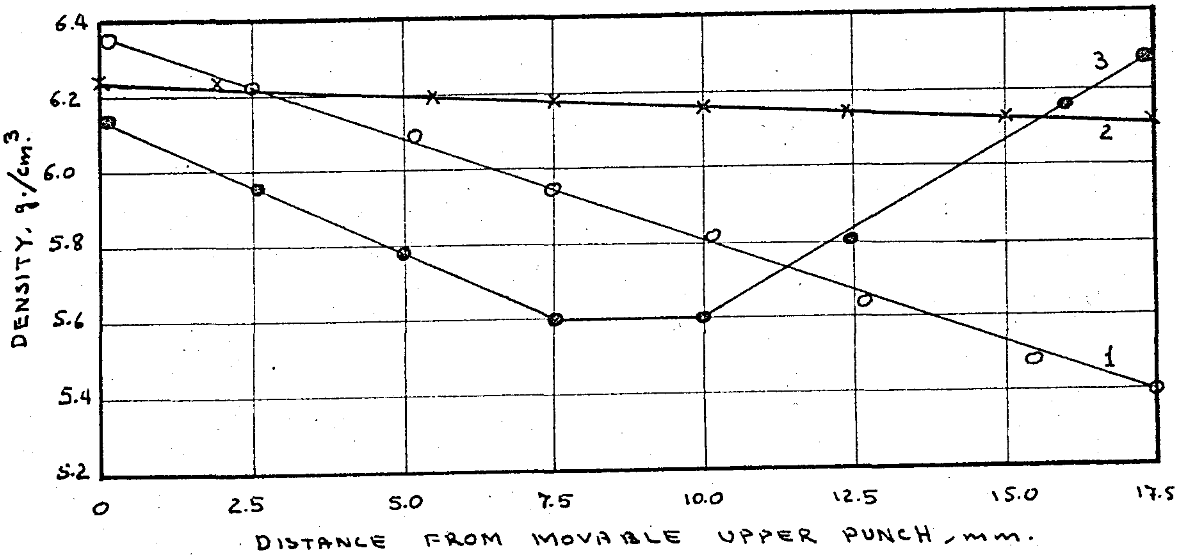


FIGURE 6.

1. ELECTROLYTIC COPPER, PRESSED IN SINGLE ACTION.
2. ELECTROLYTIC COPPER, CONTAINING 4% GRAPHITE, PRESSED IN SINGLE ACTION.
3. ELECTROLYTIC COPPER, PRESSED IN DOUBLE ACTION.

REF 3, pp 98)

EFFECT OF TEMPERATURE ON COMPACTING:

The advantages of hot pressing, due to the increase of plastic deformability with increasing temperature have already been indicated (see Hot Pressing). The densities, tensile strengths, and hardness values of hot-pressed products are frequently far superior to those of cold-pressed products and approach the corresponding values of cast metals. Hot-pressing eliminates the shrinkage effects of a normal sintering process, and the maintenance of dimensions is one of the main advantages (3).

SINTERING CONDITIONS

SINTERING TEMPERATURE: Densities and other physical properties of powder metallurgy products tend to increase with increasing sintering temperature. In the case of iron, the results obtained by Libsch, Volterra, and Wulff (8) indicate a marked increase of density, tensile strength, and elongation with increasing temperatures (Fig. 7).

This figure illustrates the effect of sintering temperature on the physical properties (TENSILE STRENGTH, DENSITY AND ELONGATION) of electrolytic iron compacts.

The compacts were pressed at 33 tsi. and sintered in hydrogen.

Particle size : 66 per cent 100 to 200 mesh.
17 per cent 200 to 325 mesh.
17 per cent — 325 mesh.

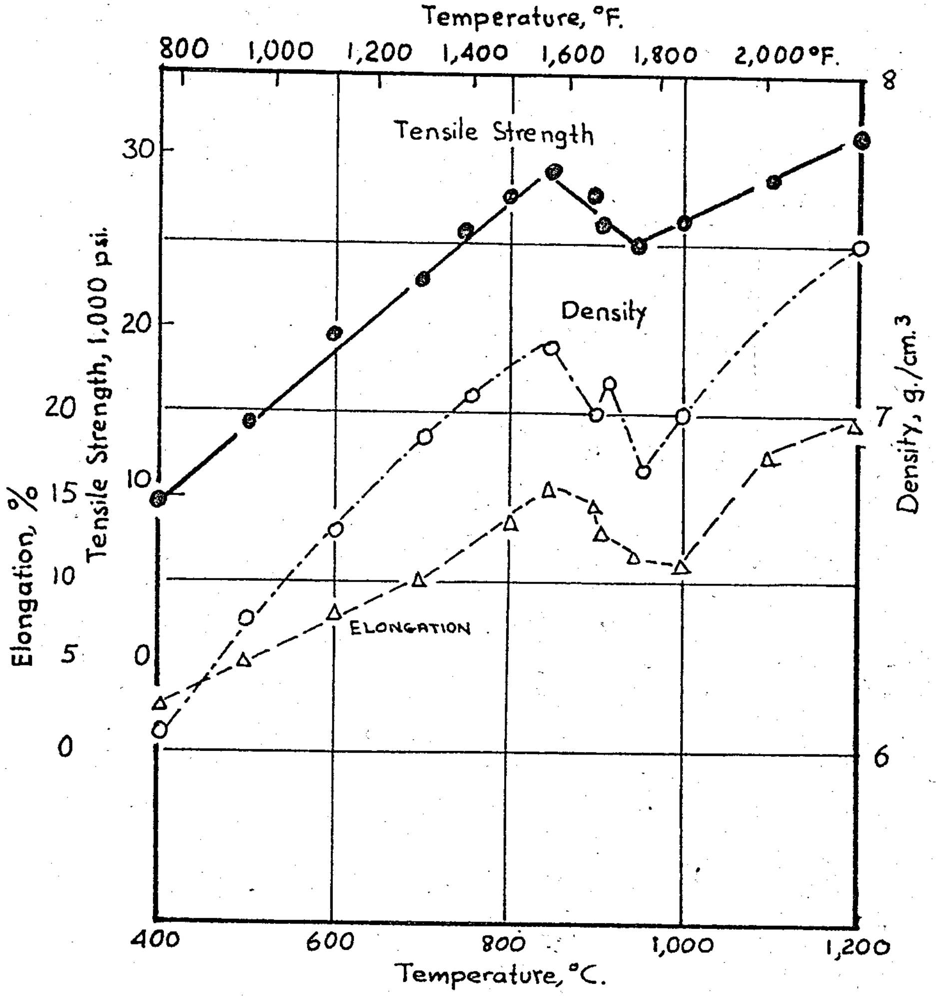


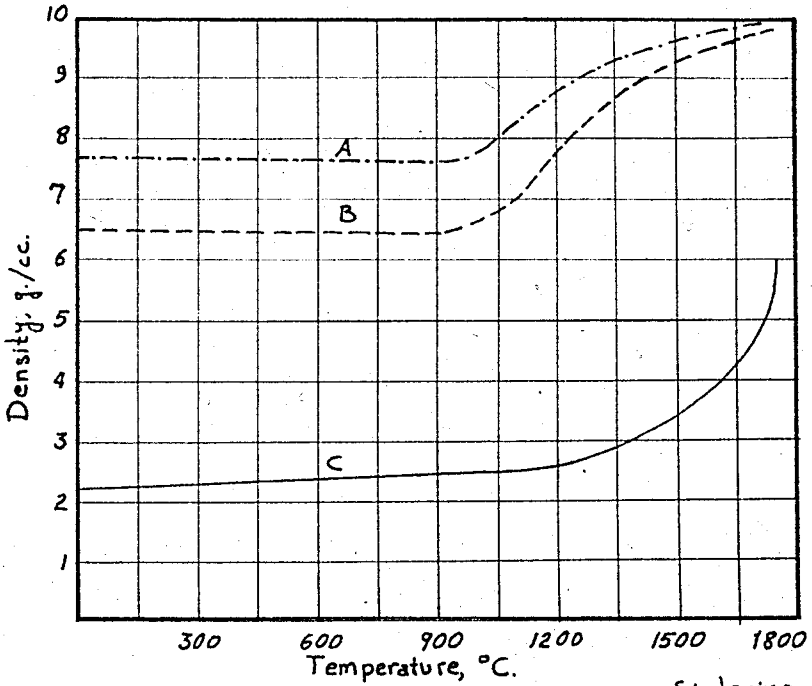
FIGURE 7.

(Figure reproduced from REF. 8., pp. 386).

The observed minima correspond to the $\alpha \rightarrow \gamma$ transformation of iron, and similar minima have been found in the study of the properties of hot pressed iron compacts (19).

Goetzel explains this by connecting it with the allotropic change in the iron, indicating that the compacts when entering the austenitic condition, are more resistant to pressure than when still in the ferritic condition.

The effect of sintering temperature depend on the pressure applied during the compacting operation. The effect of compacting pressure and sintering temperature upon the density of Mo compacts has been studied by Grube and Schlech. Their results are illustrated in Figure. 8.



Sintering time: 3 hr.
Sintering atmosphere: hydrogen.

FIGURE 8.

EFFECT OF SINTERING TEMPERATURE AND COMPACTING PRESSURE ON THE DENSITY OF MOLYBDENUM POWDER.

CURVE A : compact compressed at 6000 kg. per c.c.
CURVE B : compact compressed at 3430 kg. per c.c.
CURVE C : loosely filled powder, not compressed.
(Figure reproduced from REF. 7., pp. 100).

Powders pressed at extremely high pressures frequently show a decrease of density with increasing sintering temperature. In these cases, the density produced by compression is very high and is reduced, during sintering, by growth due to the escape of gases (3).

This effect is schematically represented in Figure 9.

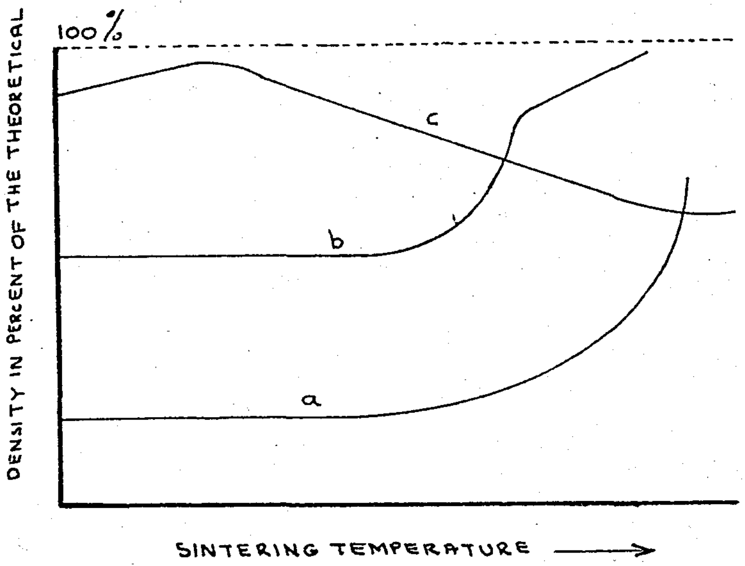


FIGURE 9.

EFFECT OF SINTERING TEMPERATURE ON DENSITY
a: loose powder.
b: moderate compacting pressures.
c: high compacting pressures.
(Figure reproduced from REF. 3., p.p. 103).

SINTERING TIME:

Schwarzkopf (3) states that, generally, it is possible to obtain similar effects with short sintering periods at high temperatures and with long sintering periods at low temperatures.

This indicates that the effect of sintering time is in the same direction as the effect of sintering temperature. However, the investigations of various people reveal that this effect is less pronounced.

Figure 10 illustrates the effect of sintering time at 850°C on the 66% coarse, 17% medium and 17% fine mix of electrolytic powder pressed at 33 tons per sq. in.

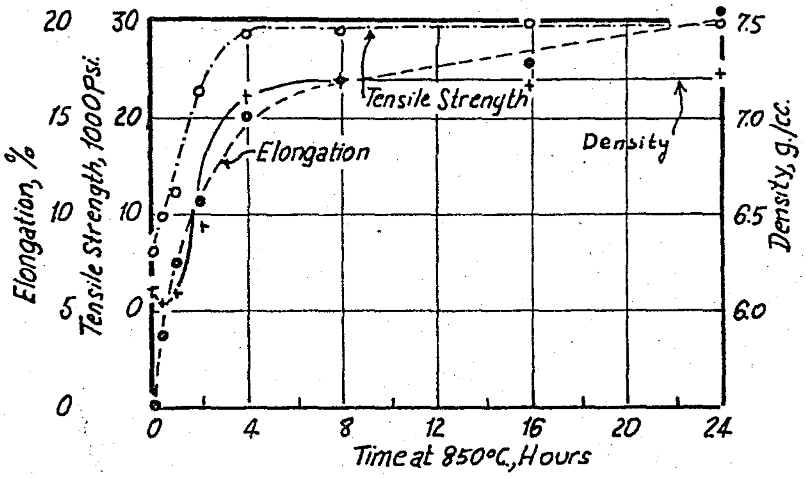


FIGURE 10.

PHYSICAL PROPERTIES OF ELECTROLYTIC IRON COMPACTS AS INFLUENCED BY SINTERING TIME.

(Figure reproduced from REF. 8, pp. 387).

The figure also illustrates a common conclusion of various authors, namely that the effects of sintering time on the physical characteristics of the product is more marked during the initial stages of sintering.

The discussion of the effects of sintering conditions has been, so far, restricted to homogeneous one-metal powders, In the case of powders composed of more than one component, it is necessary to take additional factors into account. The most important of these factors is the extent of homogenization by diffusion (3).

The effects of composition together with the effects of sintering temperature and time is illustrated in Figure 11 for WC-Co alloys.

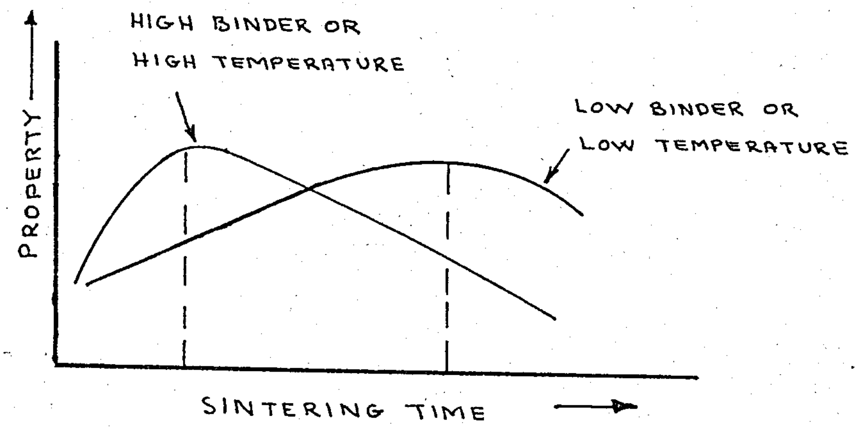


FIGURE 11.

SCHEMATIC ILLUSTRATION OF VARIATION OF PROPERTIES WITH SINTERING TIME.

Figure reproduced from REF. 6., FIG. 12).

SINTERING ATMOSPHERE:

The importance of sintering atmospheres were discussed together with the other stages involved in powder metallurgy practice (see Sintering Atmospheres).

Data concerning the effects of this variable on the density of products is not available in literature. Figure 12 shows the effects of sintering atmospheres on the strength of the product.

With powders of low oxide content, sintering in vacuum may result in products superior to those sintered in hydrogen. As a rule, however, sintering in a reducing atmosphere is a necessity for the production of sintered parts with satisfactory characteristics (3).

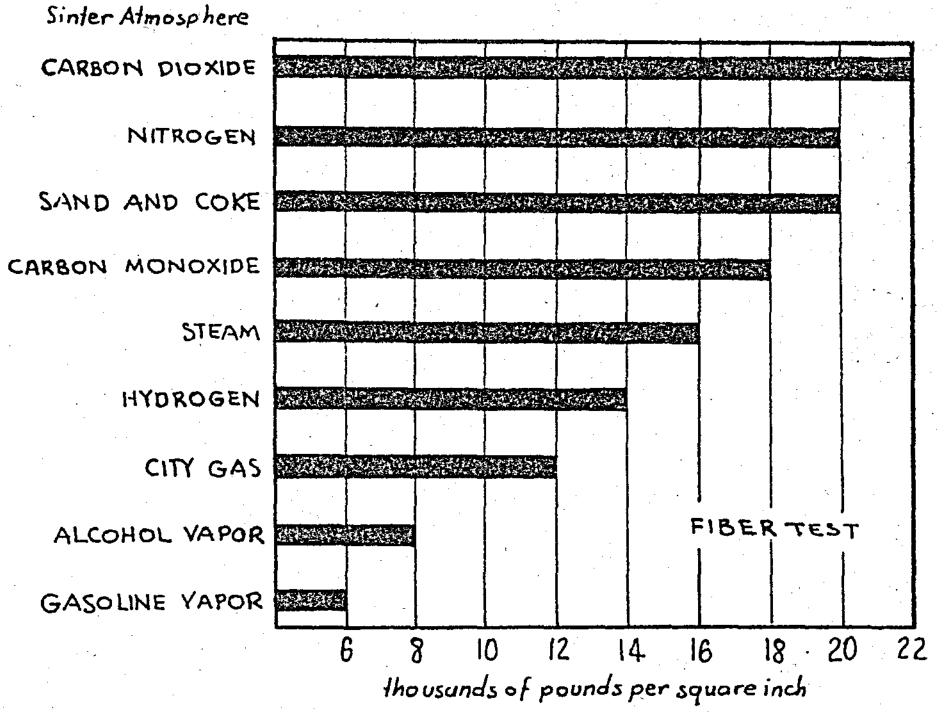


FIGURE 12.

SINTER ATMOSPHERE VS. STRENGTH FOR GRAPHITED BRONZE
(Figure reproduced from REF. 2., pp. 86).

SUBSEQUENT TREATMENTS:

The density of a compact obtained by pressing a metal powder and by applying a single sintering treatment very seldom approaches the density of the cast metal. In many cases the density of the sintered compact lies between 70 and 95 percent, and only at very high compacting conditions it reaches 97 percent, of the density of the respective cast metal. The mechanical properties of the compact, therefore, are usually not achieved with one sintering treatment, and subsequent working, such as re-pressing, re-sintering, forging, extruding, rolling, drawing, is often necessary to obtain the desired physical and mechanical properties.

Although it is a general rule that a reduction in volume, such as is achieved by re-pressing or other methods, causes an increase in strength, a lowering in strength may occur when the reduction is exaggerated (7).

Attempts to increase the density of Sn+WC alloys produced the results shown in Figure 13 (20)

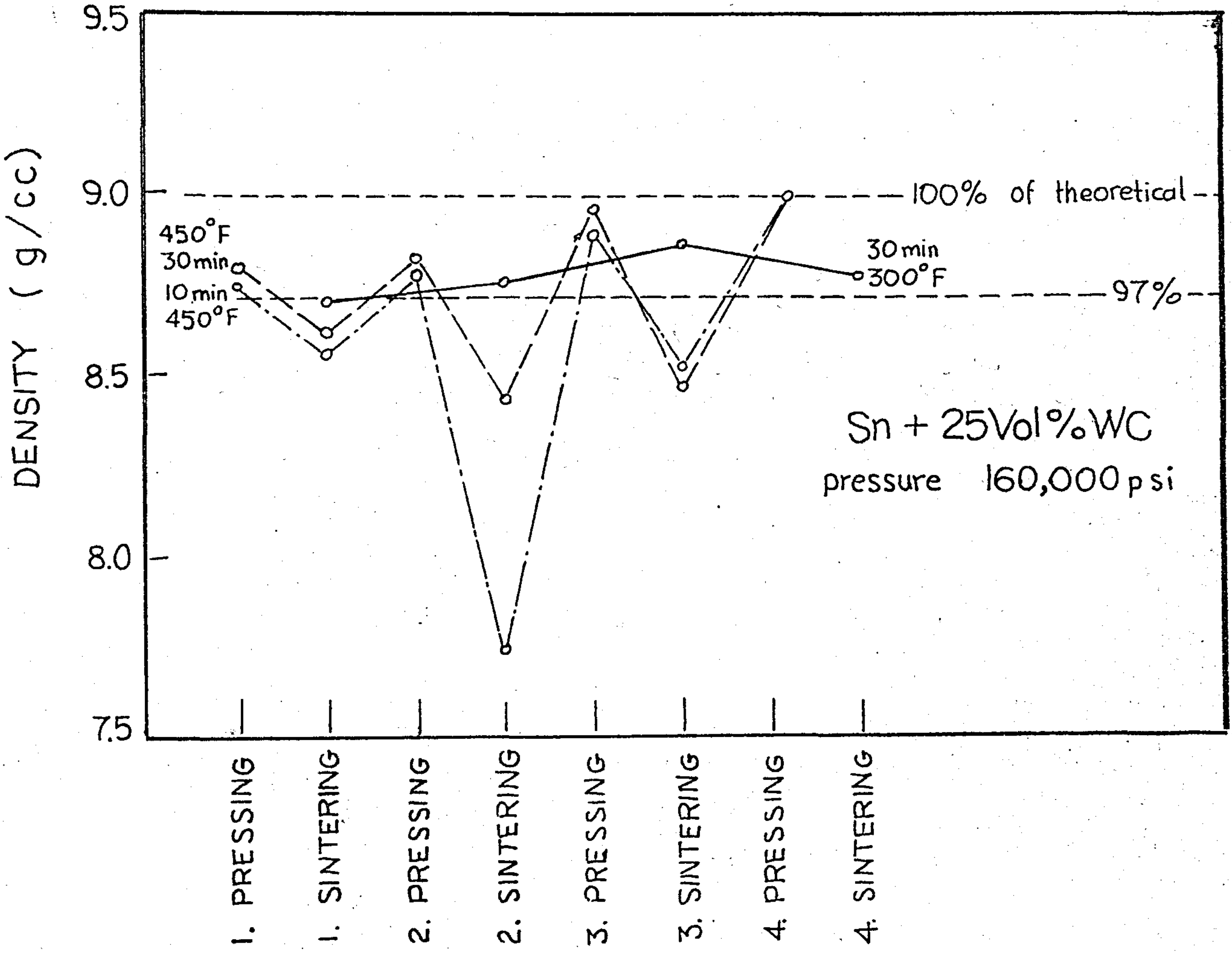


FIGURE 13.

(Figure reproduced from REF. 20., FIG. 8)

EFFECT OF REPEATED PRESSING AND SINTERING CYCLES.

It is seen that by repeated pressing it is possible to obtain almost 100% of the theoretical density. But in all cases density decreases upon sintering. It is also noticed that by using a lower sintering temperature, it is possible to obtain higher densities by repeated pressing (20).

THEORETICAL PRINCIPLES

As it is stated in the introduction, although optimum conditions have been developed in practice, the literature on the subject shows a lack of analysis or evaluation of the processing variables, probably for the reason that the details of the physical and chemical mechanisms involved are not understood in any quantitative sense.

In spite of this, however, this chapter, summarizing the existing theoretical principles is included to facilitate discussions of our results. (This chapter is a combined summary of references 2, p. 56-75, 3, p. 273-287, 15, 18 and 21, p. 418-439.)

There is probably no more disputed factor in metallurgy, and certainly not in powder metallurgy, than cohesion. Baeza classifies the existing theories as:

1. difference of potential between the surfaces,
2. surface-tension activity,
3. an interatomic force,
4. mechanical interlocking.

These theories, however, lack scholarly explanations and the available explanations are usually in contradiction.

It was Sauerwald (22-23) who, in 1922 raised the first theory of compacting and sintering mechanisms. He recorded the temperature of beginning grain growth as observed on metallographic specimens. He found this temperature to be independent of the compacting pressure and to be characteristic for each particular metal. He assumed that any deformation taking place during compacting would manifest itself in a lowering of the grain-growth temperature, and concluded from the constancy of the observed grain-growth temperatures for different compacting pressures that no deformation takes place during compaction.

Later on however, he was compelled to admit the existance of work hardening produced by the compression of the powder. In his revised theory, although he admits the presence of work hardening, he still maintains that recrystallization processes can take place in sintered metals without previous plastic deformation. This assumption would indicate a principal difference between the recrystallization processes in sintered and reguline metals, since we know that according to the concepts of recrystallization and grain growth, reguline metals do not exhibit recrystallization without plastic deformation.

Sauerwald distinguishes different ranges of compacting pressures. Only at high pressures deformation involves the entire particle as does recrystallization during sintering. However, the recrystallization temperatures (as indicated by the effect of annealing after cold work) are below the sintering temperatures (as indicated by the strength and hardness increases observed during sintering). He concludes, therefore, that the sintering mechanism is not affected by recrystallization due to recovery from cold work, since this recovery is completed before sintering starts. His conclusion is that except for very high pressures, the consolidation taking place during sintering is due to adhesion and not recrystallization. In discussing the prerequisities for adhesive attraction, however, he makes use of concepts, such as surface mobility and exchange of atoms, and thus refers to processes which are not readily distinguishable from those taking place during recrystallization.

The experimental results obtained by various other investigators are in contradiction with Sanerwald's conclusions. Trezebiatowski and others, after extensive studies proved that strong work-hardening effects take place during compaction.

Trezebiatowski also offers an explanation for the density decrease taking place during the sintering of highly compacted powders. This density decrease is produced by the evolution of gases which have been occluded during compacting. While gases retained in compacts pressed at comparatively low pressures can escape at low sintering temperatures, the expansion of gases occluded at high compacting pressures causes volume increases and blistering.

Balshin (26 - 30) introduced a number of new concepts. He believes that the energy expended during compacting is mainly determined by three factors:

1. the energy expended on overcoming the cohesion between powder particles;
2. the energy expended on deformation and fragmentation of particles;

3'. the energy expended on overcoming elastic and residual stresses.

He also puts these assumptions in a mathematical formula, using the concepts of fluid mechanics. The validity of his assumptions are highly doubtful, however, because, for example if we consider the total compaction process, it is necessary to take into account the fact that the particles are bound by cohesive forces in the final as well as in the initial state, and that the energy liberated by the formation of new cohesive bonds must be considered. His theoretical discussions are rather oversimplified. The author's concepts regarding the sintering process appear to be based on sounder foundations than is his compacting theory. According to Balshin, the principles differences between reguline and sintered metals are the relative weakness of adhesive forces between particles in the case of powder compacts, and the presence of pores between these particles. The strong bonds between grains of cast metals, as well as the low degree of porosity, oppose any change of structure except growth of one grain at the expense of another. In compacts, on the other hand, bonds are more readily broken, and the pores permit an expansion which is not at the expense of neighboring particles. Thus recrystallization in compacts may easily manifest itself in forms other than grain growth: for instance, in breaking of bonds, changes in particle shape, and migration of particles.

The processes taking place during sintering are subdivided in three classes:

1. change of relative position of powder particles;
2. internal changes of structure of individual particles;
3. external changes involving more than one particle and not limited by particle boundaries.

In discussing the effects of the sintering process, Balshin distinguishes between processes which promote shrinkage and those which oppose it. Adhesive forces can be assumed always to promote shrinkage. Recrystallization, however, can both increase and decrease the density of sintered products, depending on the location of the recrystallization center. If recrystallization starts at the boundary between particles, the effect will in general be external (involving more than one particle) and will result in grain growth and density increase. If, however, recrystallization does not start at particle boundaries, internal recrystallization will more probably occur. In the majority of instances, internal recrystallization will tend to produce equiaxial particle shapes, and this will result in an increase of porosity, thus acting counter to the processes which promote shrinkage.

The characteristic feature of Balshin's theory of sintering is the consideration of groups of forces acting against each other. Interpreting experimental results in the light of this concept, Balshin discusses the increase in dimensions of coarse powders during sintering. It is assumed that work hardening during compaction is distributed unevenly, and in the case of fine poroders, is strongest at points of contact between particles. This selective work hardening results in selective recrystallization during sintering, changes being confined mainly to particle surfaces and resulting in shrinkage by smoothing out of surface irregularities.

In the case of large powder particles, however, the specific surface area is comparatively small, and recrystallization centers are formed chiefly in the interior of the particles. This will tend to produce equiaxial particles and thus increase the dimensions. As a result, shrinkage and mechanical strength will show a continuous decrease with increasing particle size. At a critical value of the particle size, the dimensions will not shrink during sintering.

Another theory was raised by Jones (31-32), based on experimental evidence of cohesion between surfaces of massive metals. This cohesion, named as "cold-welding" can also be observed at low temperatures, provided the metal surfaces are free from contamination. Temperature increase and increase of contact area by plastic deformation favor cohesion. The contact area is decreased by oxide films, but these films can be at least partly eliminated mechanically by motion of particles in relation to each other.

According to Jones, the effects of compacting pressure are: a filling up of large pores by small particles; a deformation of particles that keys them one into the other; and the reduction of porosity on an atomic scale by flattening of microscopic and submicroscopic surface projections.

Dawihl (33) also follows the same ideas, in considering the forces that cause strength and density increases during sintering. The forces are free molecular forces, basically identical with the forces that give strength to molten metals. Since these forces decrease with increasing temperature, experimental evidence leads to the conclusion that obstacles preventing sintering at low temperatures are removed by heating. Once the obstacles are removed, by increased mobility of the atoms or other causes, the sintering proceeds with high speed.

Surface tension activity is considered by Balke (34). Balke considers the surface tension of the solid metal as the force bringing about the sintering. According to him, the rupture of intervening surface films, with consequent formation of points of contact during the compacting process, creates deep cracks which, during sintering are gradually filled up by action of the surface tension. This picture explains the shrinkage occuring during sintering. The role of temperature in the sintering mechanism is to increase plasticity, which allows the surface tension to become effective in reasonable time.

Hüttig (35-37) at the end of systematic studies distinguishes between several sintering steps which take place at increasing temperatures. In comparing different metals, corresponding sintering steps are found to take place at temperatures which represent approximately the same fractions of the absolute melting temperatures. The sintering steps are the following:

1. The adhesion period at low temperatures, determined mainly by pure adhesion or cohesion effects. During this period, the surface area available for processes such as adsorption is reduced, but no noticeable shrinkage is observed.

2. The period of surface diffusion. The surface mobility causes atoms to migrate into capillaries between particles and produces bonding between particles, which result in consolidation and shrinkage.

3. The period of boundary displacements. Growth of particles occurs at the expense of other particles. The growing particle need not necessarily have been originally larger than the consumed particle.

4. The period of lattice diffusion, which takes place over the entire cross section of the crystallites, and produces bonding between crystallites.

5. The period of formation of new crystallization centers. This process, taking place at high temperatures, results in complete recrystallization.

The primary processes taking place during sintering and resulting in the sintering steps outlined above, are:

1. Changes taking place in individual crystals.
2. Changes involving the formation of single crystals from two primary crystallites in contact with each other. The forces producing changes of the second type may be:

    a. adhesive forces;
    b. surface diffusion;
    c. diffusion in the crystal lattice;
    d. recrystallization processes.

Wretblad and Wulff (15) consider the sintering process fundamentally as a bonding by atomic forces. In accordance with previous theories, particularly that of Jones, these authors point out that cohesion by atomic forces can take place even at room temperature. However, they place more emphasis than do Jones and other authors on the role of plastic deformation taking place during compaction and subsequent recrystallization. The increase in density and strength usually observed at the recrystallization temperature is considered by them to indicate that at this temperature the sum of the thermal energy of the atoms plus the potential energy due to cold working of a considerable number of atoms surpasses a critical value and thus permits the atoms to move accross grain boundaries. This mobility of atoms causes recrystallization and at the same time facilitates sintering. The sintering temperature is thus linked with recrystallization. It is stressed that recrystallization - even when associated with grain growth - increases the strength of sintered products. Contrary to the concepts of Balshin and others, grain growth taking place within individual polycrystalline powder particles is considered of only minor importance. Wretblad and Wulff also pointed out that Sauerwald's concepts, according to which the temperature of spontaneous grain growth is independent of compacting pressure as well as of such powder characteristics as purity and particle size, are not in agreement with out knowledge of grain growth.

Schwarzkopf (3) discusses and compares these theories and draws the following conclusions: Recrystallization of reguline metals is brought about by instability in the lattice arrangement, produced by cald-working. It is obvious that similar instabilities produced by other means might bring about similar recrystallization effects. During sintering, metal particles of different orientations are brought into contact with each other, and the contact areas where crystals of different orientations meet will necessarily represent areas of instability. In the case of solidified metals, the boundaries between grains have been produced at the temperature of solidification; the boundaries are therefore, stable at this or at any lower temperature. In compacts produced from metal powders at room temperature, the increased atomic mobility at higher temperature will enable the atoms to assume, in the contact areas, an arrangement which is more stable than the accidental arrangement produced by compacting. In other words, instability resulting from the contact between differently oriented crystallites will induce recrystallization effects in fundamentally the same way as will instabilities resulting from work hardening. It can, therefore, be assumed that the same laws of crystallization processes which have been established for solidified metals can be applied to the sintering process and this can be done independently of the final answer to Sauerwald's question.

As outlined in the preceding review, a great deal of the theoretical discussion has been concerned with the distinction between adhesive and crystallization effects. Schwarzkopf draws two final conclusions:

1. Same laws control crystallization processes in sintered and in cast metals;

2. There is no distinction between adhesive and crystallization effect since both of these effects are produced by atomic forces.

MATERIALS AND APPARATUS

MATERIALS:

The most important materials required for our investigations were;

a. Metal powders,
b. Lubricants,
c. Sintering atmosphere.

METAL POWDERS: Metal powders were obtained from a number of sources. As it was previously stated in the introduction, metal powders are not produced in Turkey. Therefore, the first attempt was to order them from the well known American suppliers. Being unsuccesful in this the local industry was consulted. Iron, titanium oxide and ferromanganese powders are used for the preparation of coatings for welding rods, copper powder is used in current collector brushes of electric motors and zinc dust was imported to be used as a part of experimental rocket fuel mixture.

Chemical compositions were available only for the first three of these powders. Specific gravities and particle size distributions were determined by the student. The results are given in Appendix A, together with the methods used.

LUBRICANT: Lubricants most suggested in the literature are graphite and stearic acid. Graphite flakes with a size of -100 mesh could not be found in the market. Instead stearic acid (specific gravity = 0.849) (38) was grinded and sieved from a 100 mesh sieve to be used as a lubricant.

SINTERING ATMOSPHERE: No controlled atmosphere furnaces were available for sintering work. Therefore, a rough method is used. Compacts were embedded in charcoal powder in closed containers and therefore, sintered in carbon monoxide. The disadvantages of this very sample and safe method will be discussed together with other points in a later section.

Another material used was "vacuum seal", since as high a vacuum as possible is needed. LUBRISEAL (High vacuum), of Arthus H. Thomas Co. Philadelphia, U.S.A. was used to obtain air tight hose connections.

APPARATUS:

It is felt that a brief explanation of some equipment used is justified by the fact that these were only some type of substitutes found for the special equipment required by this technique.

For compacting, a small press, essentially an automobile jack with an attached pressure gage was used. This hand operated press was capable of producing 120,000 psi. on our compacts.

No attempt was done to produce the die, because of the manufacturing difficulties in obtaining the required tolerances. Substitutes were searched. Baeza (2) suggests bushings such as those made by F.A. Baumbach Company and the Danly Machine Company, both of Chicago. These are guaranteed to ± 0.0001 in. variation from 0.5 in I.D. For the pucnhes he suggests the dowel pins manufactured by the same companies. Such elements do no exist in the market and the problem is solved by using the fuel injection pump element and its plunger of a 24 hp Deutz marine diesel engine.

The punch was surface hardened steel and it did not allow any buckling. Therefore, centering the punch with the axis of the press was necessary to minimize buckling.

This die is illustrated in Appendix B, together with its plugs, centering cap and ejection pipe.

Sintering boxes were simply 3 in. cast iron pipe pieces, one ends closed by welding. They are also illustrated in Appendix B, together with a detailed description all apparatus.

METHOD OF PROCEDURE

MIXING THE POWDER: The first step in the preparation of powder metallurgy products is the mixing of the constituent powders. Proper amounts are weighed to 0.01 g. and each case 0.5% of stearic acid powder (-100 mesh) by weight is added as a lubricant. Powders and lubricant are hand mixed by mortar and pestle, combining and blending and shearing action. Mixing time = 15 minutes.

Load = 50 grams of powder.

CALCULATING THE VOLUME PERCENTS: To calculate the proper amount of each powder in volume percent mixtures the following formula is used;

$$\gamma = \frac{W}{V} \qquad V = \frac{W}{\gamma}$$

For example for 75% Fe and 25% TiO_2 the calculation was;

$$V_{Fe} = \frac{74.6}{7.46} = 10\ cm^3 \quad \text{(taking } W_{Fe} = 74.6 \text{ g. for simplicity)}$$

$$V_{TiO_2} = \frac{1}{3} V_{Fe} = 3.33\ cm^3 \text{ and } W_{TiO_2} = 3.33 \times 4.16 = 13.85 g.$$

therefore, to each 74.6 g. of iron 13.85 of titanium oxide must be added.

HANDLING POWDER AND FILLING THE DIE: When the powders are mixed the die is loaded. (Sometimes by volume and sometimes by approximate weight of powder.) The die is first brushed with a test tube brush to clean the remining particles from the previous compacting. Then the tip of the brush is dipped in stearic acid powder and the die walls are lubricated by brushing. The stationary lower punch is placed and the die is ready for filling.

Care was used to avoid segregation and breakdown of the mix. The hole in the die is filled with a broad-bladed spatula. The easier method of transferring powder to the die cavity with the aid of a creased paper is avoided, because as the powder ran down the paper, automatic classification would occur. This rather clumsy method of loading is deliberately used to reduce classification and segregation to a minimum. When the die is filled, it is tapped slightly on four sides by the handle of spatula to avoid any bridging and also for obtaining a flat powder surface in the die for uniformity. The plunger is inserted and pressed slightly against the powder by hand.

PRESSING: Pressing is done with the press explained above. The loaded die is transferred to the press and the powder is compacted by regular slow strokes until the maximum pressure is reached. (The pressure gage is calibrated in terms of the punch diameter.) This pressure is maintained a definite period of time, (Dwell time). The pressure is then released, the stationary lower punch is removed and the "extraction support" is placed under the die. The upper plate of the press is carefully brought in contact with the die plunger and the green compact is extracted smoothly. The compact is observed through the "peek hole" in the "extraction support" as it comes out.

These compacts are strong enough for handling and even permit the use of a punch for marking by a quick, sharp blow.

The irregularities on the upper ends of these compacts (due to the tapered plunger end) is corrected by emery paper.

MEASUREMENT OF GREEN DENSITIES: Green densities are obtained by weighing the cylindirical compact to 0.01 g. and taking two micrometer readings. (Length and diameter, to determine the volume.) These values are recorded for the calculation of "bulk densities" of the green compacts.

Bulk density is defined as mass over the total volume including the open and closed pores. (33)

SINTERING: When the proper number of cores are made (usually 2 or 3, and more if unconsistency is observed) and measured, they are transferred to the sintering boxes. The lower level of these boxes have previously been filled with charcoal about 1/2 in. thick. The compacts are set horizontally side by side about 1/4 in. apart. The boxes are now filled with charcoal, a piece of asbestos is placed on top, slightly pressed by hand and an iron plate of 1 cm. thickness is placed over the asbestos as weight.

Since the pressure in the box is larger than the atmospheric pressure due to evolving gases it is understood that no air enters the box at temperatures higher than room temperature.

The temperature of the furnace is brought to 100°C higher than the required sintering temperature and the boxes are placed in the furnace, near the thermocouple. This difference of 100°C is necessary to compensate the heat losses during loading, namely;

1. Losses due to opening the furnace door,
2. Losses due to bringing the temperature of the box and its contents to the sintering temperature. The temperature is maintained carefully during the time of sintering. The stated sintering time in our experiments corresponds to the actual time elapsed between insertion and removal of the sample from the furnace. This includes the time required for the sample to attain the sintering temperature, namely, 20 minutes (6).

Before the boxes are placed into the furnace they are marked with ordinary chalk. It is observed that this identification persists throughout the heat cycle: and since this can easily be erased, it serves very admirably to our purpose.

When the sintering time has elapsed the box is removed from the furnace and allowed to cool to room temperature while it is still closed. The contents are then dumped on a 3/8 in. sieve and the products are shaken free of charcoal.

The charcoal is used repeatedly, each time adding about 20% of fresh charcoal to each charge of used charcoal. 100% fresh charcoal is never used since the excess amounts of gases produced might cause some small explosions, strong enough to force the boxes open.

SUBSEQUENT MEASUREMENTS AND OBSERVATIONS: The cores are measured and weighed exactly in the same manner as the green compacts. These readings are recorded for the calculation of bulk densities, and total porosities.

If a Rockwell hardness test is run the hardness of each core is determined at three points. The first point is determined near one end. The core is then turned 60° and the next reading taken in the center. It is then turned another 60° and the final reading taken at the other end. The high-end readings and the low-end readings are grouped separately. The two or three (or more) sets of readings are averaged and the report on the hardness of the cores contain the average high, the average low and the center hardness, as well as the absolute high reading and the absolute low reading.

Some cores are polished and their porosity is observed under a microscope (no etching). Some pictures of the structure is taken by a polaraid camera.

KEEPING THE CORES FOR FURTHER TESTS AND REFERENCE: The products are kept in separate match boxes. A label is attached to the box and the composition, compacting pressure, sintering temperature and time are indicated. If the effects of other variables such as, pressing in vacuum, thickness effect or dwell time is investigated "vacuum", the approximate weight of powder used or the dwell time is also indicated on this label.

PRESENTATION OF DATA AND RESULTS

A brief summary of our experimental results would contain the effects of the following processing variables on the physical properties of powder metallurgy products:

1. Influence of compacting conditions.
    a. Compacting pressure,
    b. Dwell time,
    c. Type of pressure application (thickness effects),
    d. Compacting in vacuum.

2. Influence of sintering conditions,
    a. Sintering temperature,
    b. Sintering time.

During the course of our experiments about 300 compacts were produced and their properties studied. The data obtained is carefully screened and only typical data bearing heavily on the subject is included. These data will be presented in the following pages as tables and graphs together with the results obtained.

Discussion of these results will form the subject matter for the next chapter. (Discussion of Results.)

In the experiments all variables other than the one being investigated is kept constant. The powder used was homogeneous, one-material powder unless otherwise stated.

DENSITIES (GREEN)

COMPACTING PRESSURE psi.	Fe		Cu		Zn		Fe + 25% Vol. TiO_2	
	$g./cm^3$	% th.	$g./cm^3$	% th	g/cm^3	% th	g/cm^3	% th
20,000	3.77	53.2	5.31	61.9	5.18	75.7	3.81	59.4
40,000	4.65	65.0	6.41	74.8	5.61	81.9	4.43	69.1
60,000	5.21	72.7	7.08	82.6	5.81	84.8	4.85	75.6
80,000	5.55	77.6	7.54	88.0	5.94	86.7	5.10	79.5
100,000	5.78	81.0	7.80	91.0	DIE TROUBLE		5.30	82.7
110,000	5.83	81.6	DIE TROUBLE				DIE TROUBLE	

TABLE IV.

EFFECT OF COMPACTING PRESSURE ON GREEN DENSITIES OF Fe, Cu, Zn and Fe+25% Vol. TiO_2 COMPACTS.

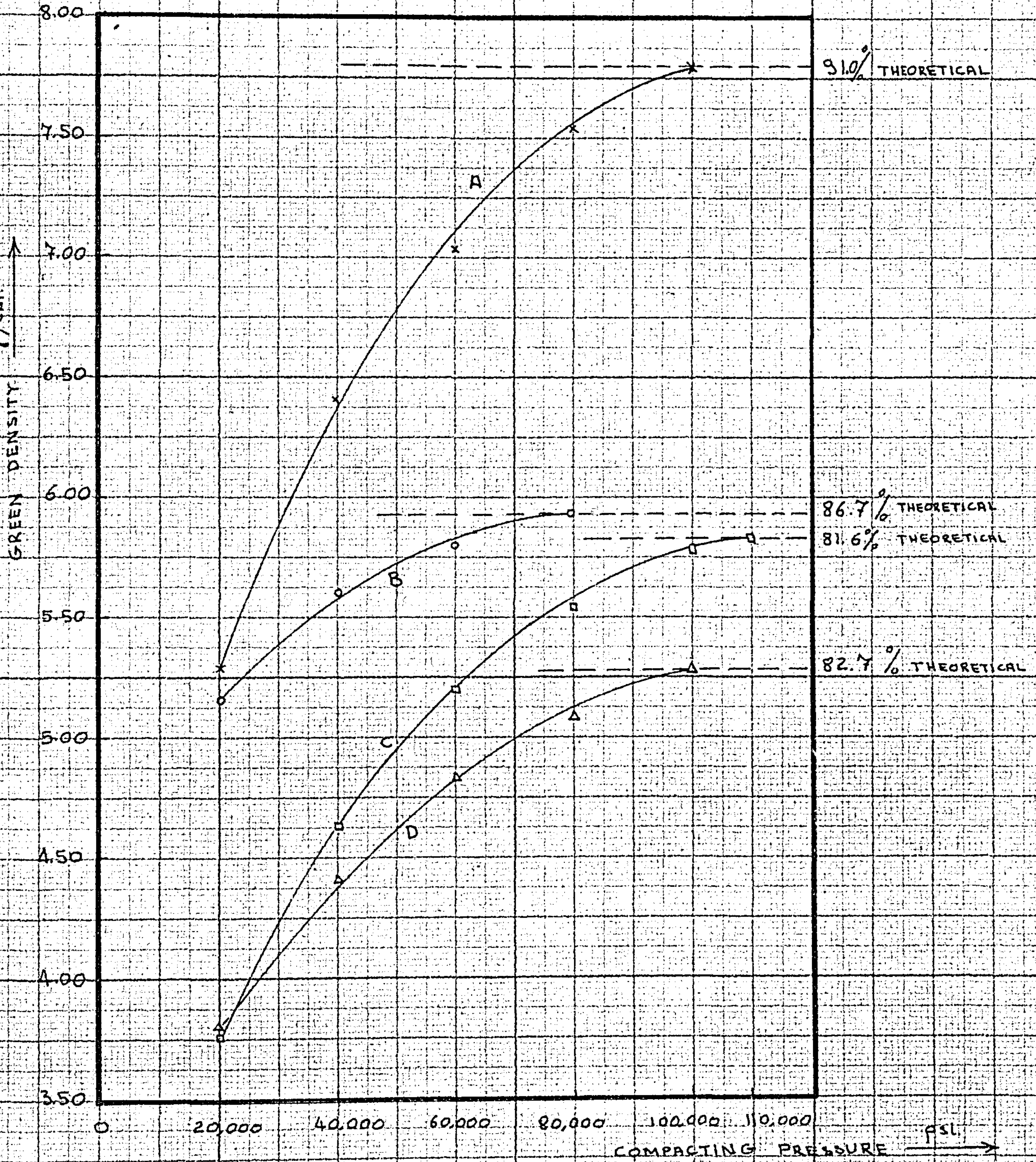


FIGURE 14

COMPACTING PRESSURE VS. GREEN DENSITY

CURVE A. COPPER
CURVE B. ZINC
CURVE C. IRON
CURVE D. Fe + 25% VOL TiO$_2$

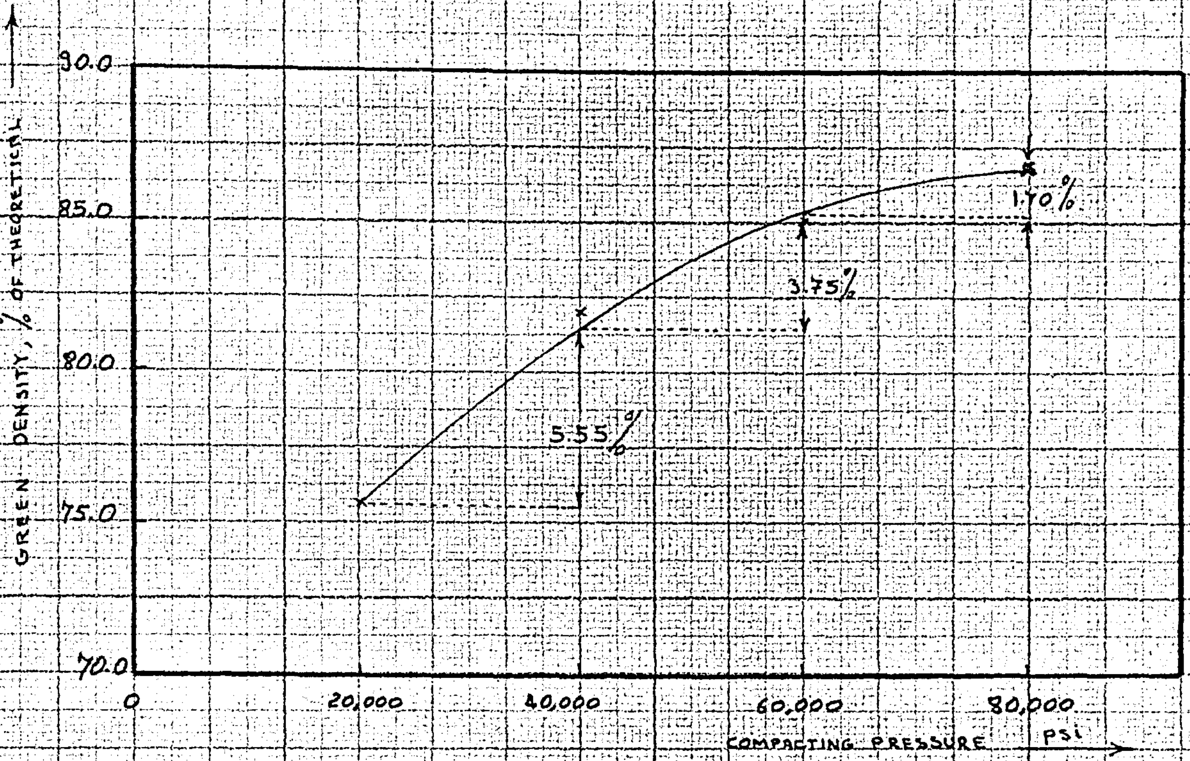


FIGURE 15.

COMPACTING PRESSURE VS GREEN DENSITY OF ZINC.

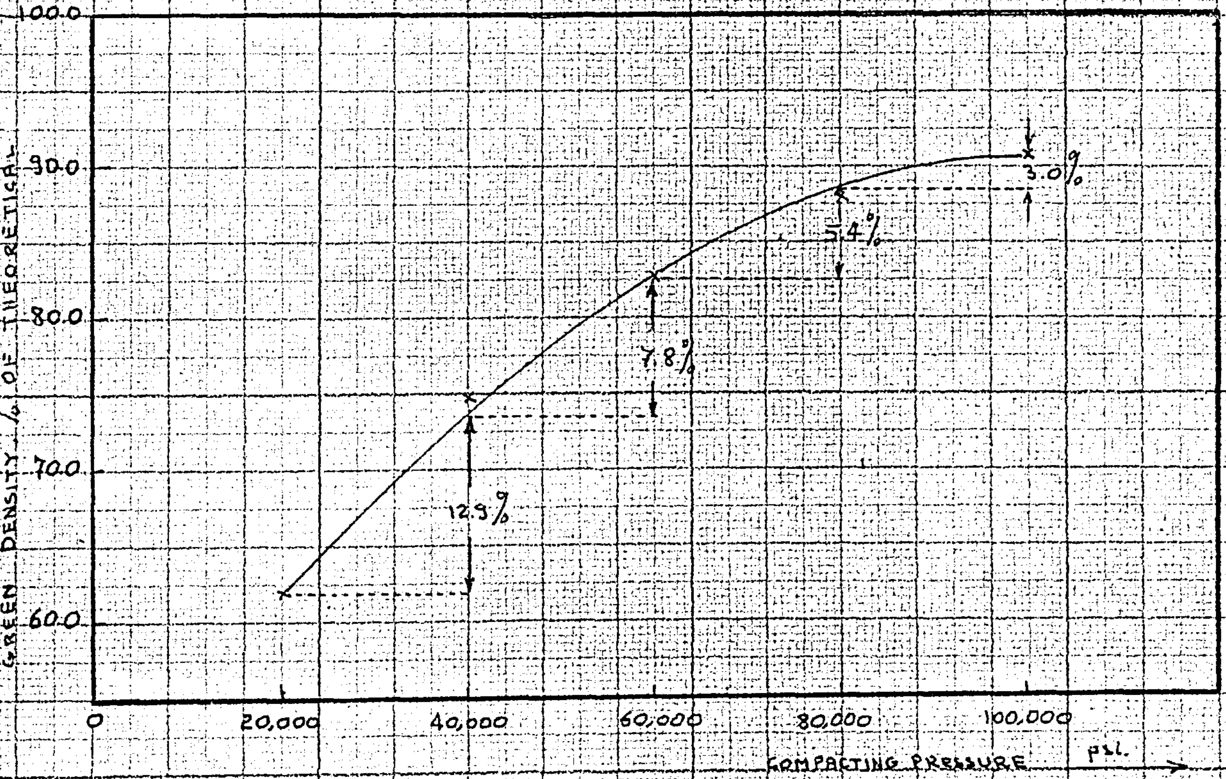


FIGURE 16.

COMPACTING PRESSURE VS. GREEN DENSITY OF COPPER.

Fe
Sintering Temp: 850°C
Sintering time: 4 hrs. HARDNESS, ROCKWELL H

COMPACTING PRESSURE psi.	AVERAGE			ABSOLUTE	
	HIGH	CENTER	LOW	HIGH	LOW
20,000	—	—	—	—	—
40,000	36	19	—	37	—
60,000	58	54	24	59	12
80,000	78	72	59	81	55
100,000	84	81	63	84	60

TABLE V.

Fe
Sintering Temp: 1200°C
Sintering time: 4 hrs. HARDNESS, ROCKWELL K

COMPACTING PRESSURE psi.	AVERAGE			ABSOLUTE	
	HIGH	CENTER	LOW	HIGH	LOW
20,000	—	—	—	—	—
40,000	47	35	24	51	17
60,000	62	50	22	62	20
80,000	85	80	70	85	68
100,000	92	84	78	92	77
110,000	91	86	70	91	69

TABLE VI.

Cu
Sintering Temp: 750°C
Sintering time: 2 hrs. HARDNESS, ROCKWELL H

COMPACTING PRESSURE psi.	AVERAGE			ABSOLUTE	
	HIGH	CENTER	LOW	HIGH	LOW
20,000	—	—	—	—	—
40,000	33	19	1	35	1
60,000	60	57	46	61	42
80,000	69	69	55	69	53
100,000	80	82	73	82	71

TABLE VII.

Cu
Sintering temp: 750°C
Sintering time: 2 hrs.

COMPACTING PRESSURE psi.	DENSITY, % TH.	
	GREEN	SINTERED
20,000	61.9	65.3
40,000	74.8	76.4
60,000	82.6	84.0
80,000	88.0	87.9
100,000	91.0	90.7

TABLE VIII.

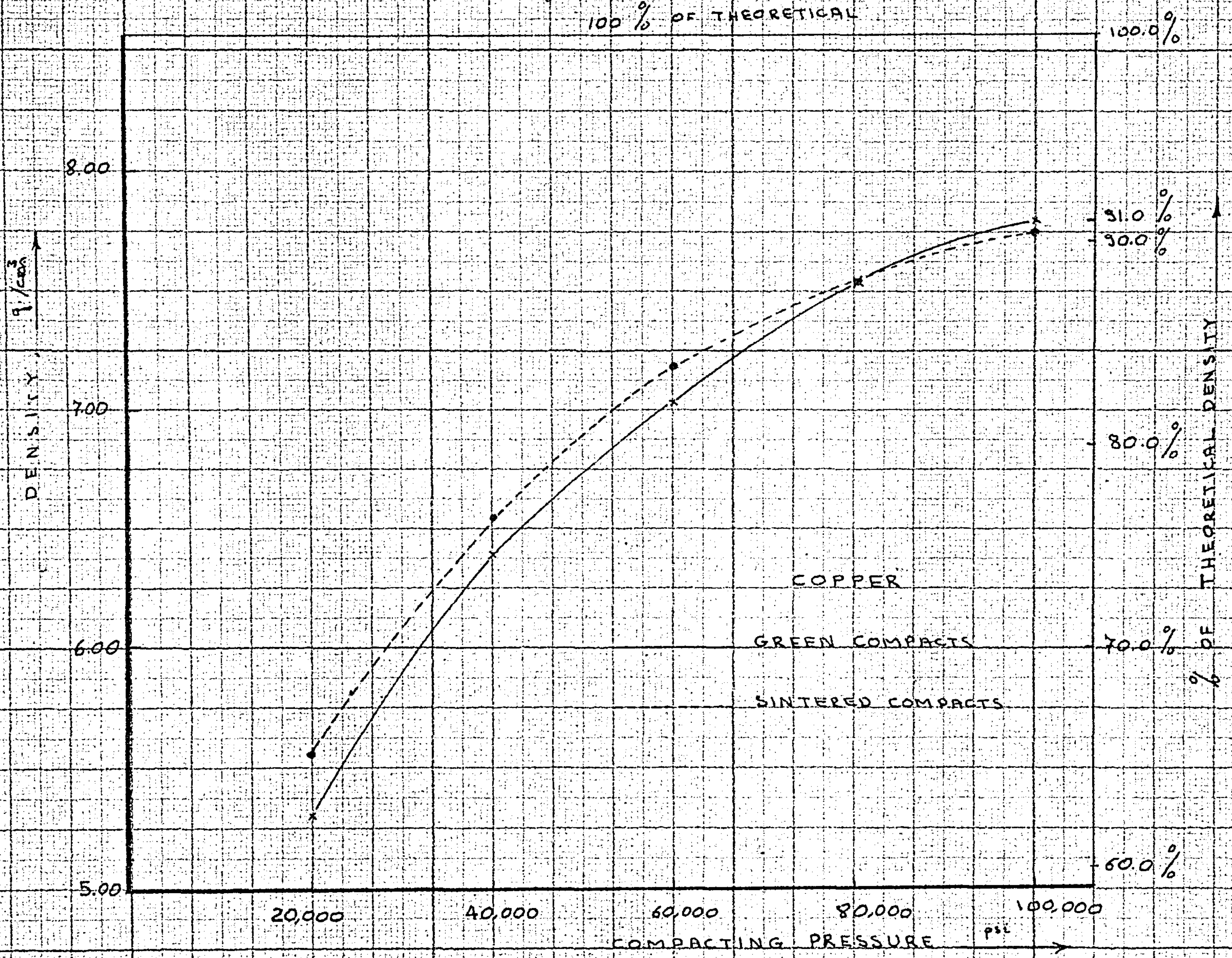


FIGURE 17.

DENSITY (GREEN AND SINTERED) VS COMPACTING PRESSURE FOR Cu POWDERS

Fe
$P = 100{,}000$ psi

$T = 900$ °C
$t = 2$ hrs.

DWELL TIME SECONDS	DENSITY	
	GREEN, % TH	SINTERED, % TH
0	83.90	81.50
10	83.40	80.80
30	83.00	80.25
60	83.80	80.70
180	84.90	82.25

TABLE IX.

DWELL TIME VS. DENSITY OF IRON COMPACTS

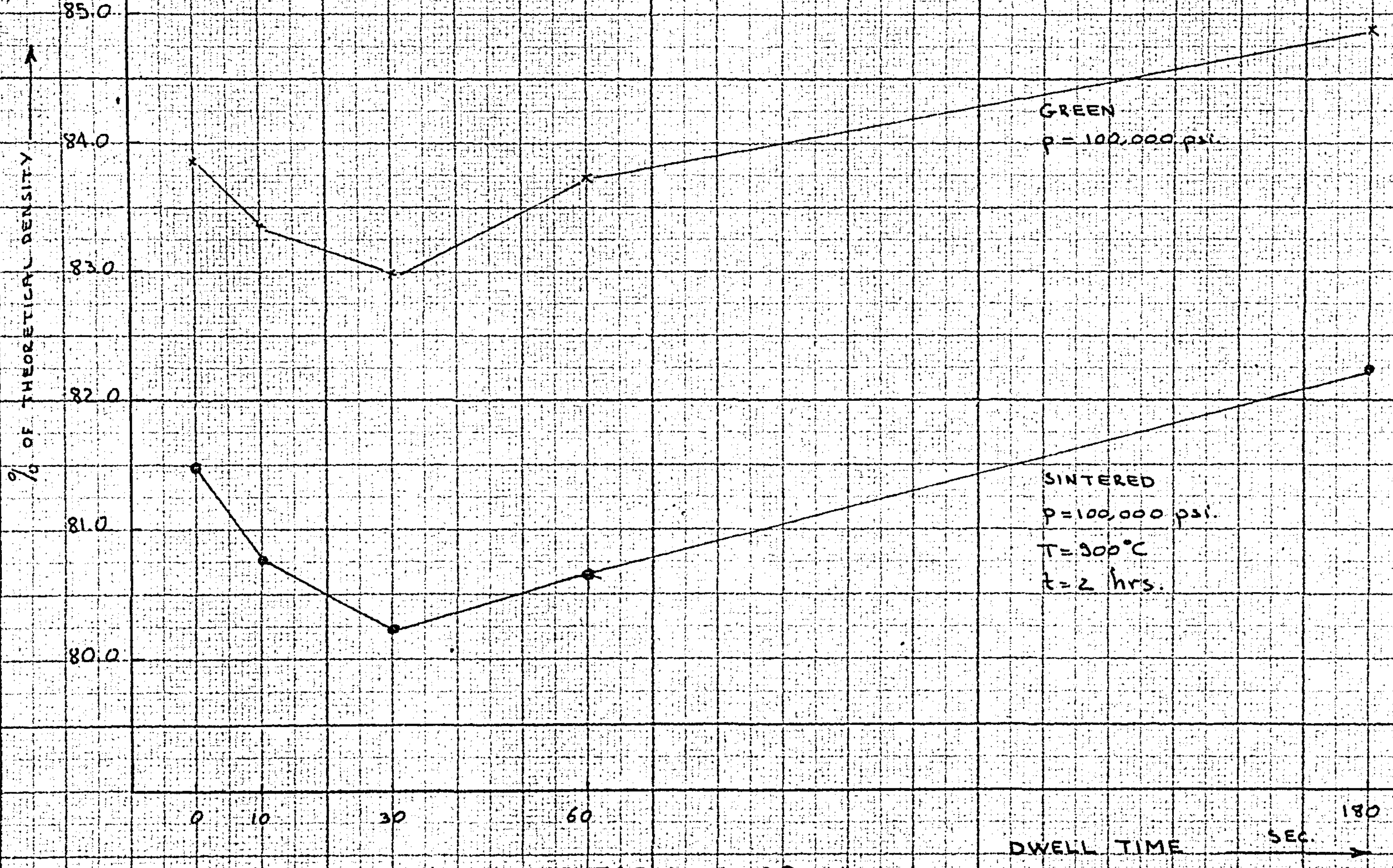


FIGURE 18.

DWELL TIME VS. DENSITY OF IRON COMPACTS

Fe
p = 100,000 psi. T = 900°C , t = 2 hrs.

Approximate wt. of powder g.	LENGTH in mm.	GREEN DENSITY		SINTERED DENSITY	
		Density g/cm^3	Density % Theoretical	Density g/cm^3	Density % Theoretical
7	18.15	5.96	83.4	5.78	80.08
5	12.80	5.98	83.7	5.81	81.30
3	7.60	5.98	83.7	5.82	81.50
1	2.52	6.00	83.9	5.74	80.02

TABLE XI. THICKNESS EFFECT FOR IRON COMPACTS

Cu
p = 80,000 psi. T = 750°C , t = 2 hrs.

Approximate wt. of powder g.	LENGTH in mm.	GREEN DENSITY		SINTERED DENSITY	
		g/cm^3	% Theoretical	g/cm^3	% Theoretical
9	18.60	7.52	87.7	7.58	88.6
6	12.25	7.58	88.5	7.60	89.0
3	6.14	7.62	89.0	7.62	89.0
2	4.02	7.60	88.7	7.68	89.6
1	2.06	7.56	88.3	7.78	90.08

TABLE X. THICKNESS EFFECT FOR COPPER COMPACTS.

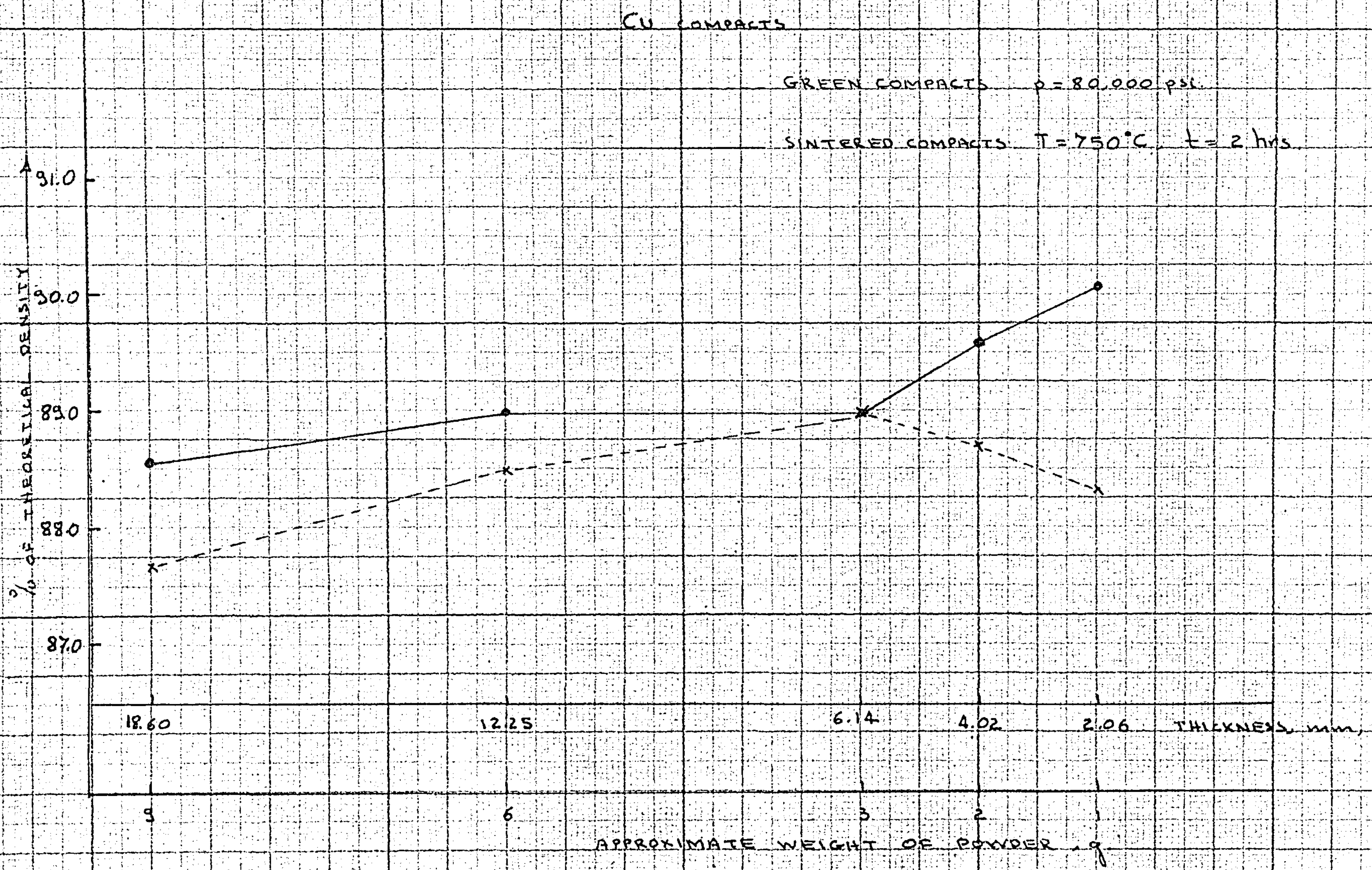


FIGURE 18

THICKNESS EFFECT FOR COPPER POWDERS

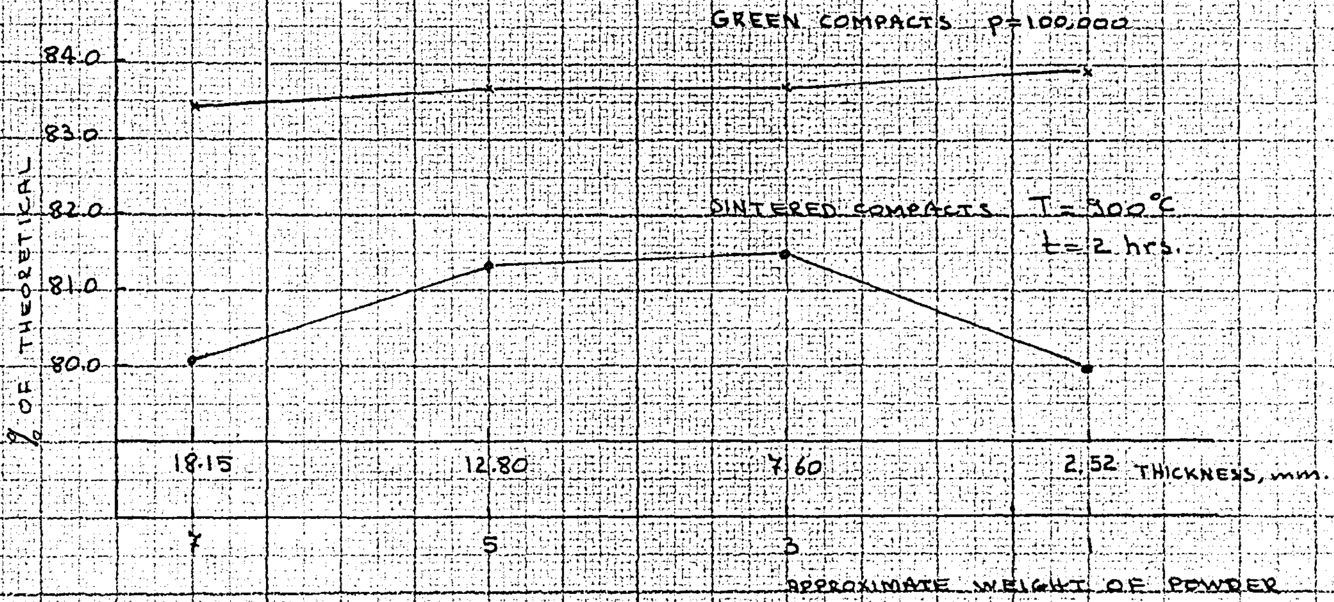


FIGURE 20.

THICKNESS EFFECT FOR IRON POWDERS

p=100,000 psi.

T= 900 °C

t= 2 hrs.

Fe

$p = 40{,}000$ psi. , $T = 1200°C$, $t = 4$ hrs.

Distance from the moving punch. mm.	LAYER DENSITY	
	g/cm^3	% OF THEORETICAL
1.23	5.26	73.5
3.58	5.11	71.4
6.01	4.94	69.1
8.44	4.95	69.3
10.99	4.85	67.8
13.71	4.81	67.3
17.46	4.63	64.8
22.98	4.43	62.0

TABLE XII.

DISTANCE FROM THE MOVING PUNCH VS. DENSITY OF IRON COMPACTS.

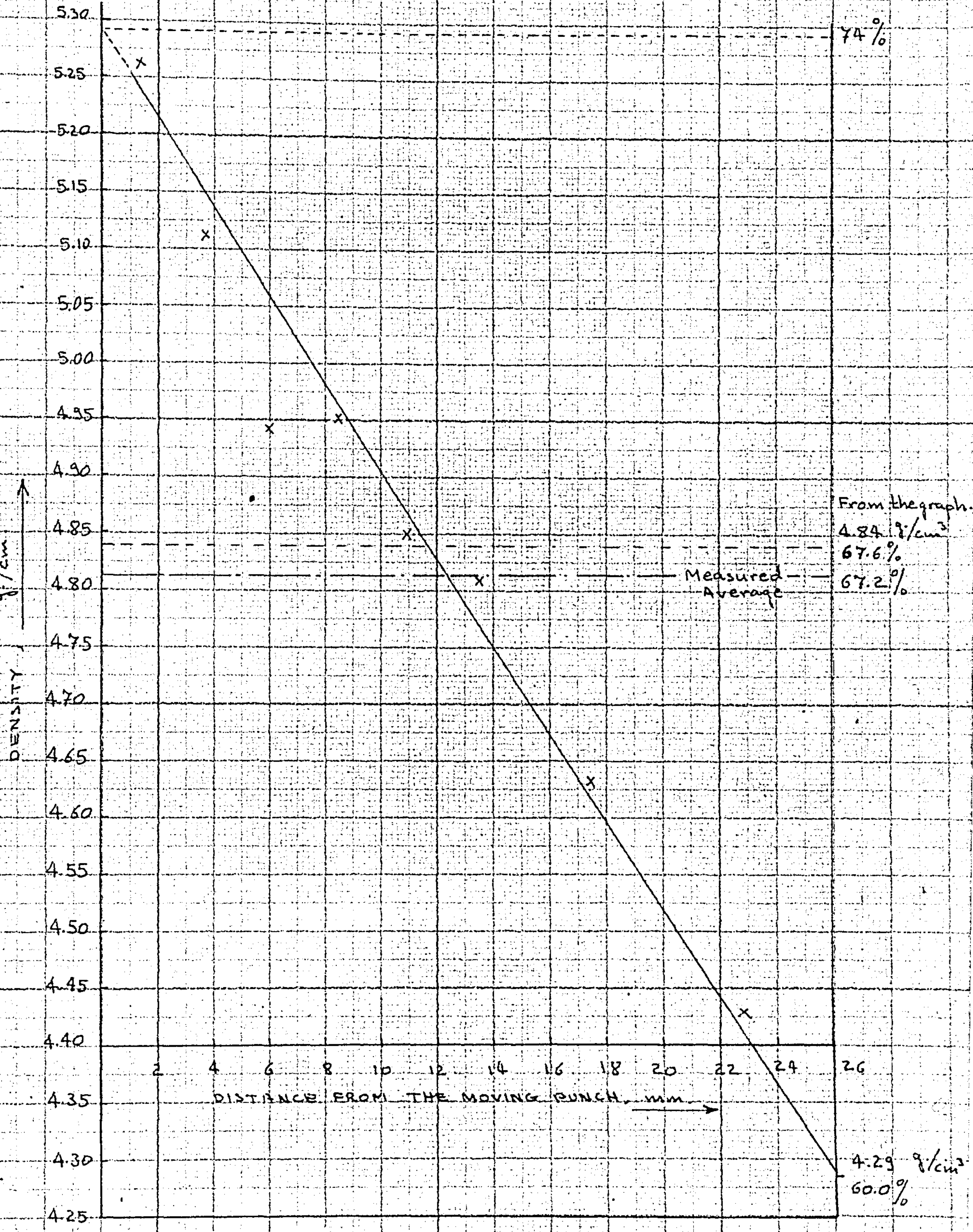


FIGURE 21

DISTANCE FROM THE MOVING PUNCH VS. DENSITY OF IRON COMPACTS
p = 40,000 psi.
T = 1200°C
t = 4 hrs

Cu

p = 100,000 psi., T = 750 °C, t = 2 hrs.

Distance from the moving punch. mm.	LAYER DENSITY	
	g./cm^3.	% OF THEORETICAL
1.00	8.39	96.8
1.72	8.22	95.7
5.02	7.96	92.9
7.69	7.88	91.9
9.66	7.85	91.5
11.82	7.73	90.1
14.01	7.80	91.0
16.09	7.77	90.6

TABLE XIII.

DISTANCE FROM THE MOVING PUNCH VS. DENSITY OF COPPER COMPACTS.

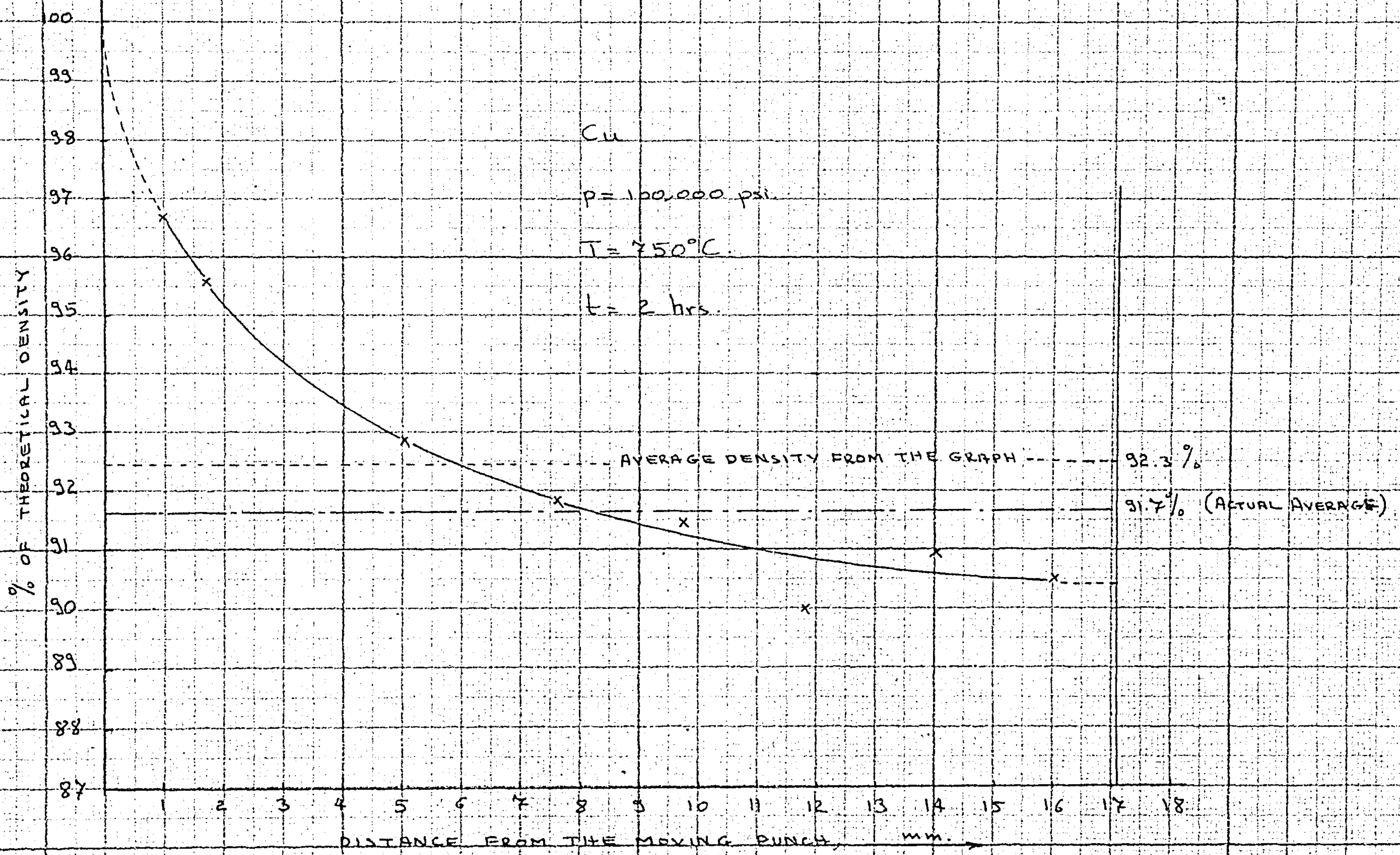


FIGURE 22.

DISTANCE FROM THE MOVING PUNCH VS DENSITY OF COPPER COMPACTS.

Cu
$p = 80{,}000$ psi.
$T = 750°C$
$t = 2$ hrs.

APPROX. WEIGHT OF POWDER g.	DENSITY (% OF THEORETICAL)			
	NO VACUUM		VACUUM	
	GREEN	SINTERED	GREEN	SINTERED
9	87.7	88.6	87.5	88.9
6	88.5	89.0	88.7	89.4
3	89.0	89.0	88.6	88.7
2	88.7	89.6	88.5	90.06
1	88.3	90.08	87.7	89.8

TABLE XIV.

EFFECT OF VACUUM DURING COMPACTING, TOGETHER WITH THE THICKNESS EFFECT, ON THE DENSITY OF COPPER COMPACTS PRESSED AT 80,000 psi. AND SINTERED 2 hrs. AT 750°C.

EFFECT OF VACUUM DURING COMPACTING TOGETHER WITH THE THICKNESS EFFECT ON THE DENSITY OF COPPER COMPACTS

PRESSED AT 80,000 PSI
Sintered at T=750°C
t=2 hrs

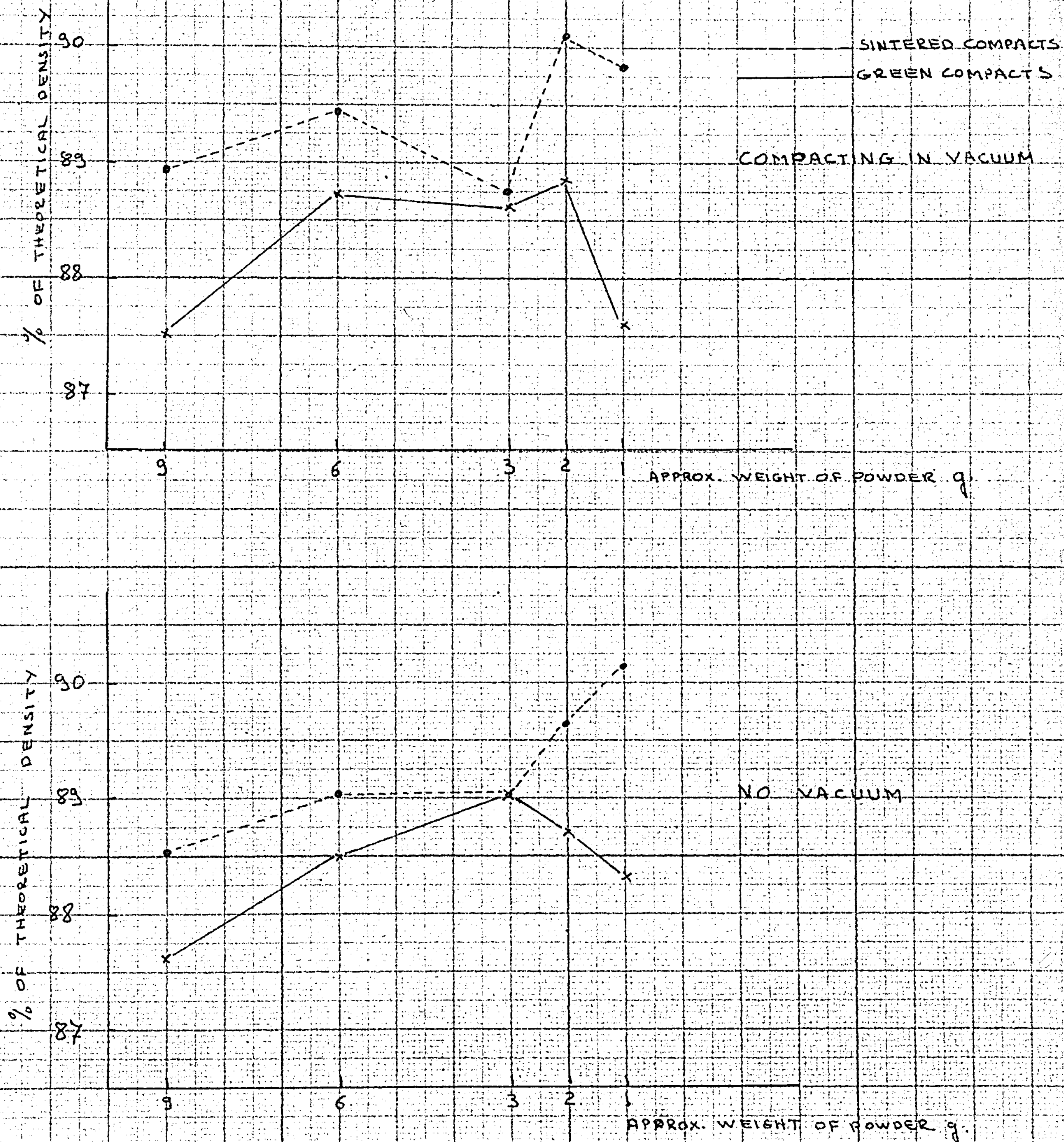


FIGURE 23.

Cu
p=100,000 psi.
T=750°C
t = 2 hrs.

APPROX. WEIGHT OF POWDER g.	DENSITY (% OF THEORETICAL)			
	NO VACUUM		VACUUM	
	GREEN	SINTERED	GREEN	SINTERED
9	90.5	91.0	90.8	91.2
6	91.4	91.9	91.8	92.7
3	92.5	92.6	93.0	93.0

TABLE XV.

EFFECT OF VACUUM DURING COMPACTING, TOGETHER WITH THE THICKNESS EFFECT, ON THE DENSITY OF COPPER COMPACTS PRESSED AT 100,000 psi. AND SINTERED 2 hrs. AT 750°C.

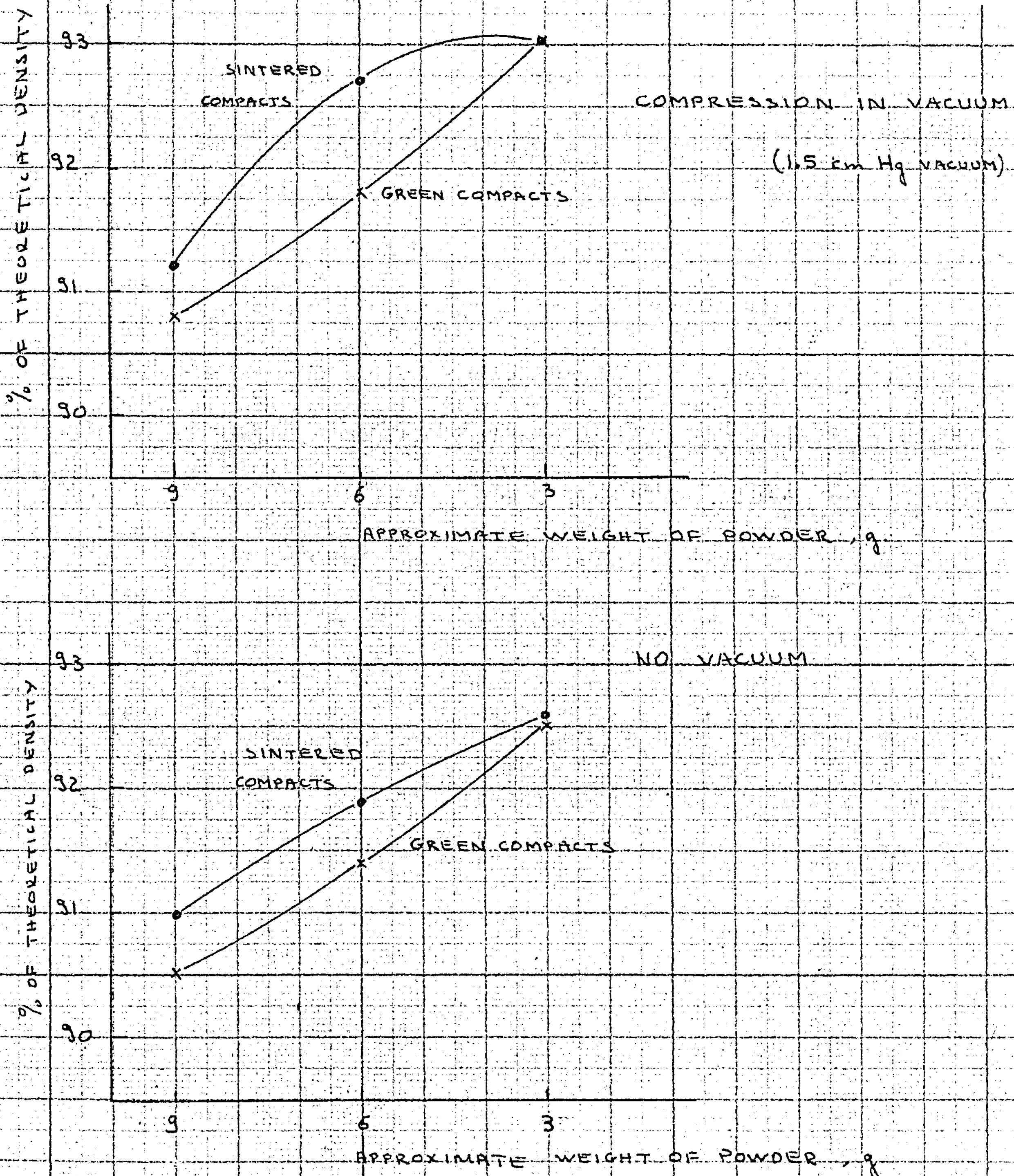


FIGURE 24

EFFECT OF VACUUM DURING COMPACTING TOGETHER WITH THE THICKNESS EFFECT ON THE DENSITY OF COPPER COMPACTS PRESSED AT 100,000 psi AND SINTERED 2 HRS AT 750°C

Fe

DENSITIES

COMPACTING PRESSURE psi.	GREEN		T = 850°C t = 4 hrs.		T = 1200°C t = 4 hrs.	
	g/cm^3	% OF THEORETICAL	g/cm^3.	% OF THEORETICAL	g/cm^3	% OF THEORETICAL
20,000	3.77	53.2	3.75	52.4	3.74	52.3
40,000	4.65	65.0	4.50	62.9	4.62	64.6
60,000	5.21	72.7	5.01	70.1	5.15	72.0
80,000	5.55	77.6	5.41	75.6	5.52	77.2
100,000	5.78	81.0	5.66	79.2	5.75	80.4
110,000	5.83	81.6			5.82	81.5

TABLE XVI.

EFFECT OF SINTERING TEMPERATURE AND COMPACTING PRESSURE ON THE DENSITY OF IRON COMPACTS.

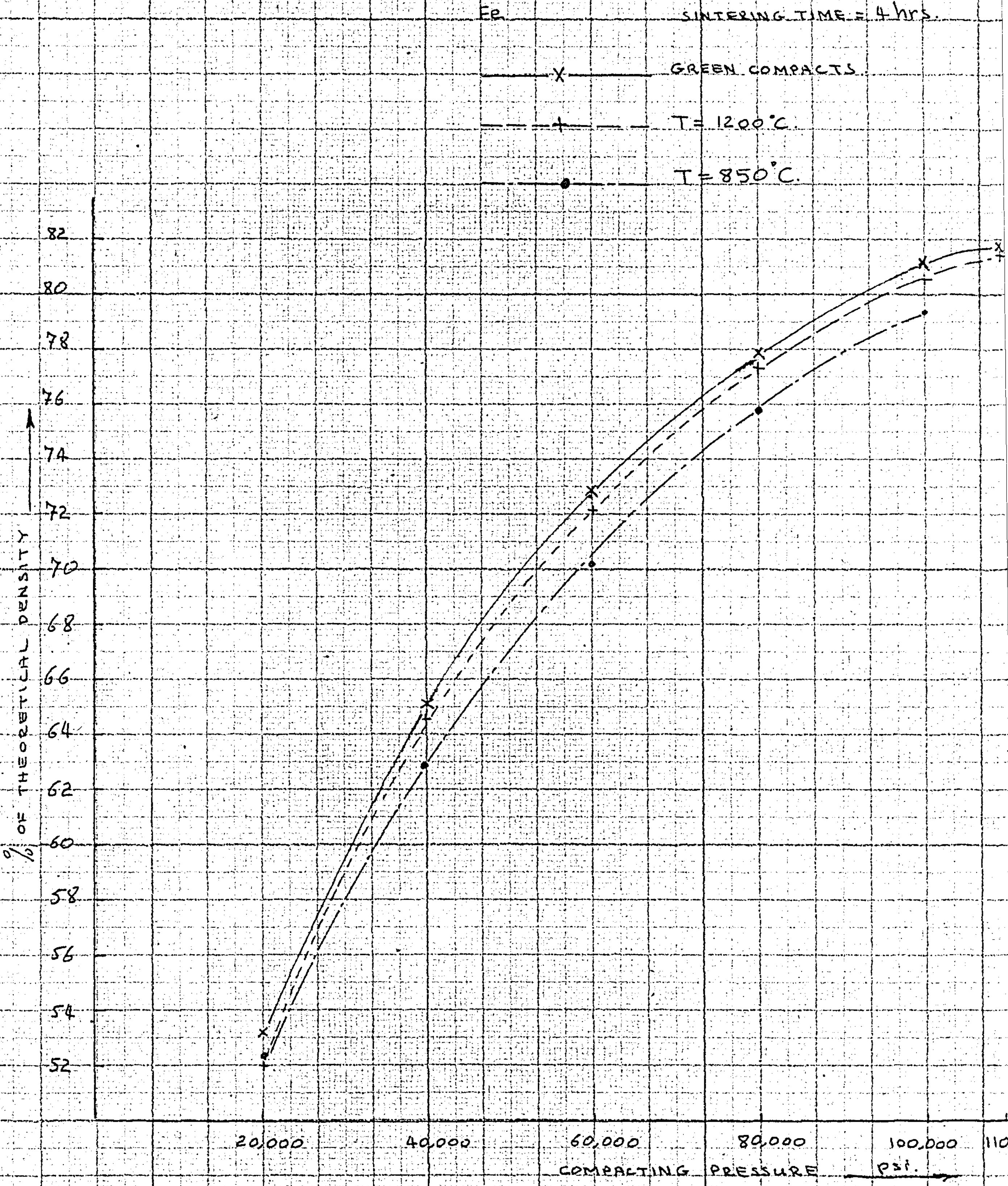


FIGURE 25

EFFECT OF SINTERING TEMPERATURE AND COMPACTING PRESSURE ON THE DENSITY OF IRON COMPACTS.

Fe + 25 Vol.% TiO_2

COMPACTING PRESSURE psi.	DENSITIES (% OF THEORETICAL)			
	GREEN	T = 850 °C t = 2 hrs.	T = 1000 °C t = 2 hrs.	T = 1150 °C t = 2 hrs.
20,000	59.4	58.5	58.3	56.9
40,000	69.1	67.9	67.1	66.4
60,000	75.6	74.0	73.8	73.1
80,000	79.5	77.2	76.9	77.2
100,000	82.7	80.05	80.00	79.6

TABLE XVII.

EFFECT OF SINTERING TEMPERATURE AND COMPACTING PRESSURE ON THE DENSITY OF Fe + 25 Vol.% TiO_2 COMPA

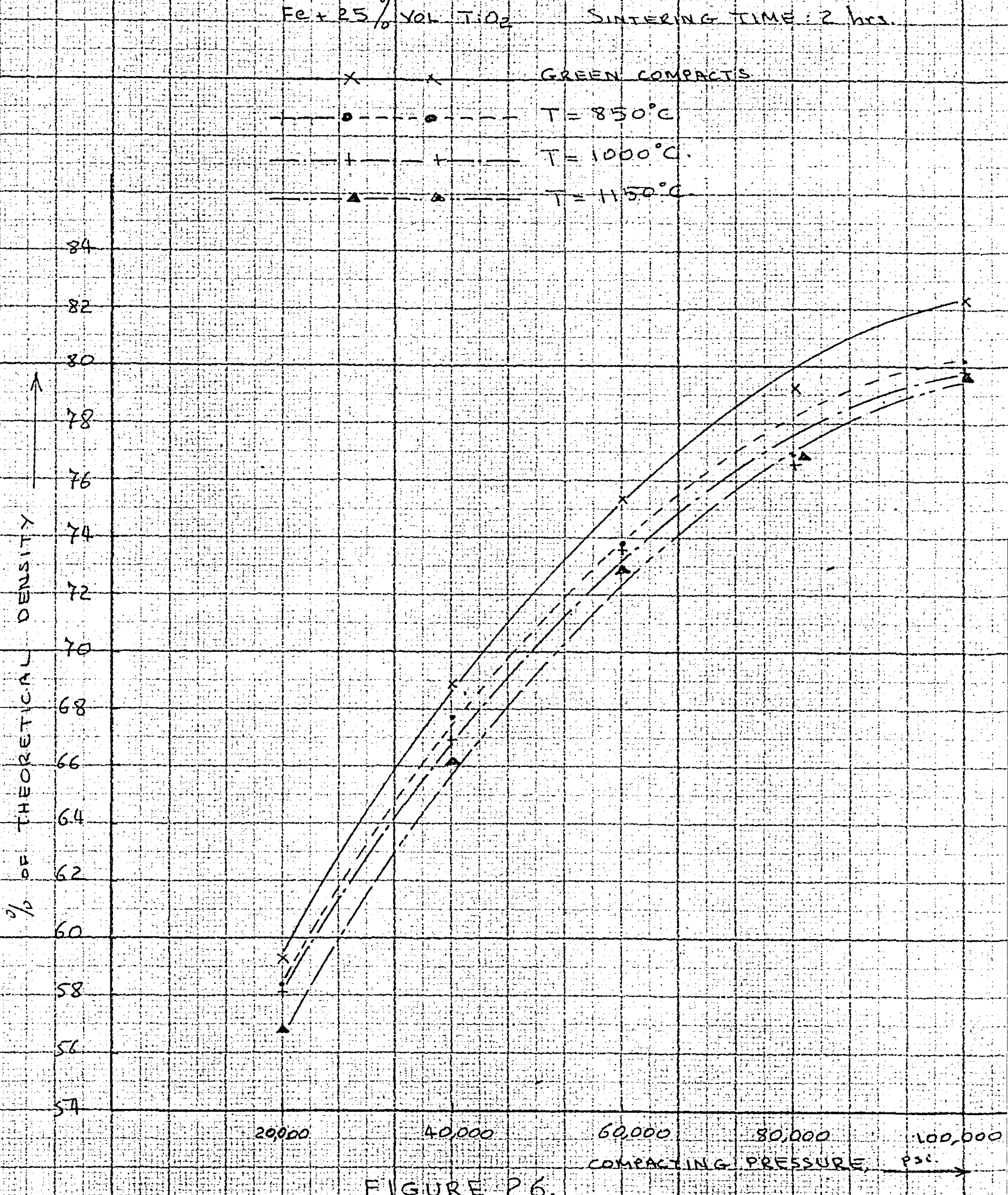


FIGURE 26.

EFFECT OF SINTERING TEMPERATURE AND COMPACTING PRESSURE ON THE DENSITY OF Fe + 25 Vol.% TiO$_2$ COMPACTS.

Fe + 25 Vol. % TiO_2

T = 850 °C , t = 2 hrs. ROCKWELL H

COMPACTING PRESSURE psi.	AVERAGE			ABSOLUTE	
	HIGH	CENTER	LOW	HIGH	LOW
20,000	—	—	—	—	—
40,000	35	28	4	35	2
60,000	62	57	41	62	40
80,000	70	65	54	70	53
100,000	80	76	65	80	64

TABLE XVIII

T = 1000 °C , t = 2 hrs. ROCKWELL H

COMPACTING PRESSURE psi.	AVERAGE			ABSOLUTE	
	HIGH	CENTER	LOW	HIGH	LOW
20,000	—	—	—	—	—
40,000	66	55	42	67	41
60,000	72	67	53	73	48
80,000	87	81	76	88	73
100,000	86	82	76	91	70

TABLE XIX

T = 1150 °C, t = 2 hrs. ROCKWELL H.

COMPACTING PRESSURE psi.	AVERAGE			ABSOLUTE	
	HIGH	CENTER	LOW	HIGH	LOW
20,000	53	10	—	—	—
40,000	85	74	67	89	64
60,000	83	81	77	85	72
80,000	98	95	92	100	89
100,000	95	97	93	99	86

TABLE XX

Fe
$p = 60{,}000$ psi.
$T = 900\,^{\circ}C$

SINTERING TIME hrs.	% OF THEORETICAL DENSITY
2	73.4
4	73.6
8	73.8
12	73.95
16	74.0

TABLE XXI

SINTERING TIME VS. DENSITY OF IRON COMPACTS.

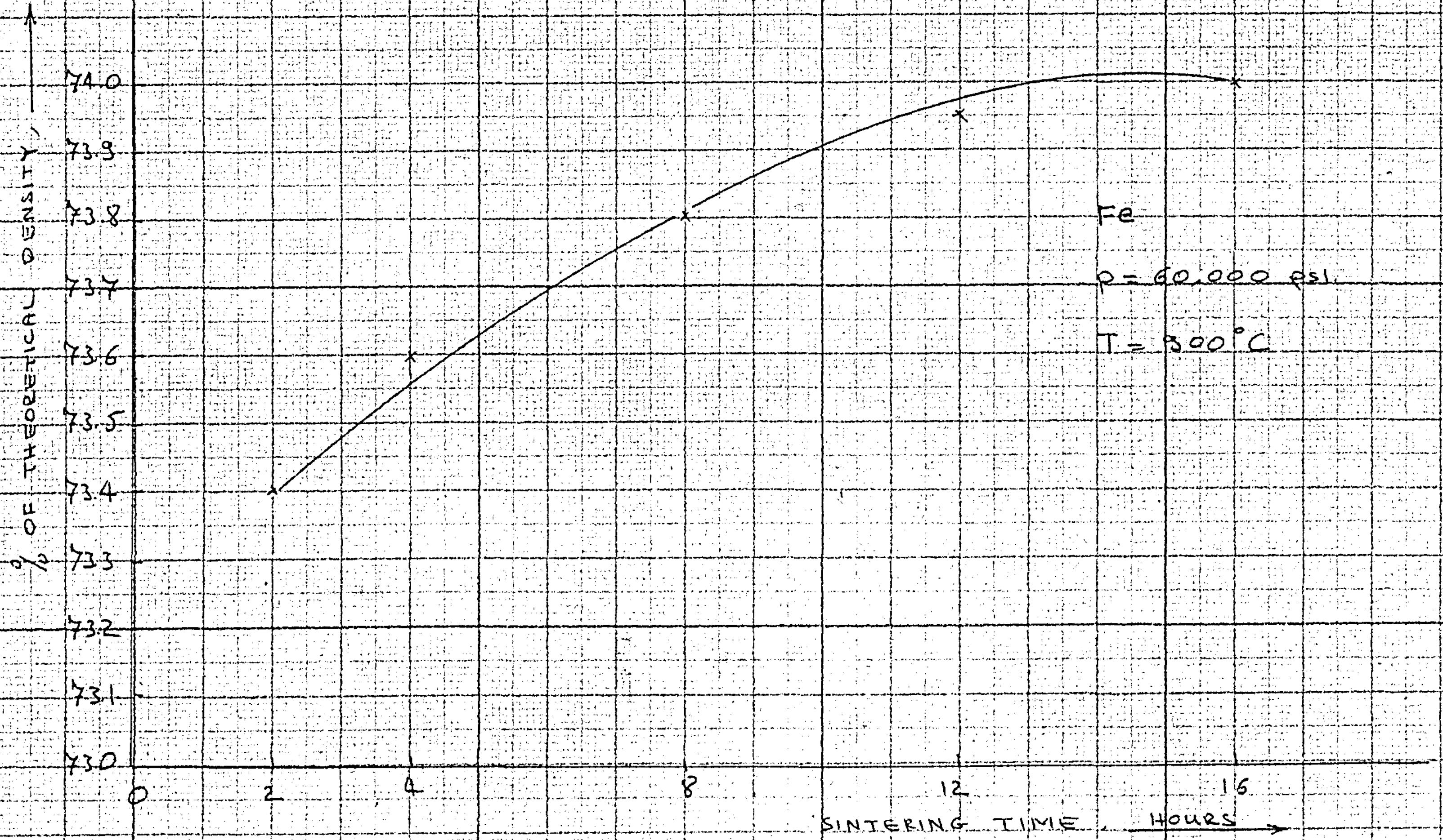


FIGURE 27.

EFFECT OF SINTERING TIME ON THE DENSITY OF IRON POWDERS.

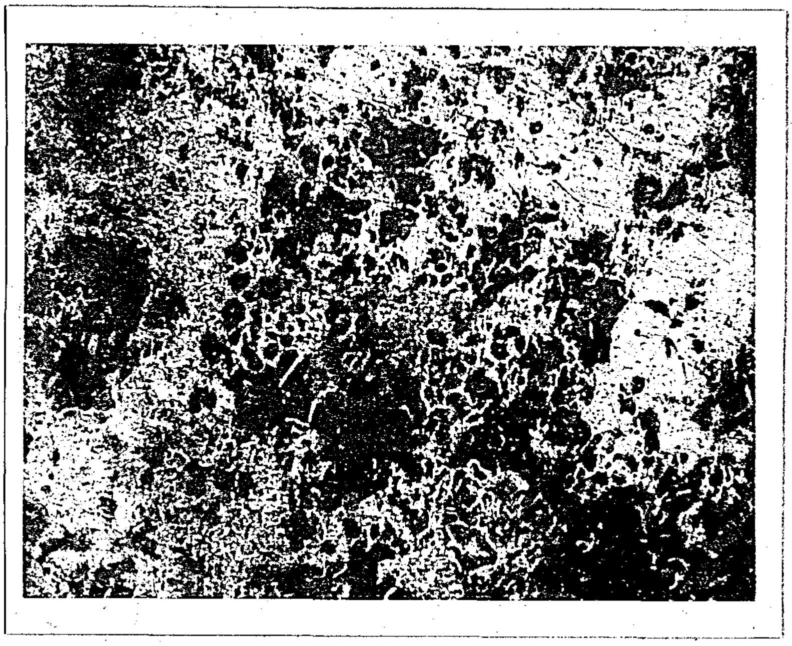


FIGURE 28-a

GREEN COMPACTS OF IRON PRESSED AT 40,000 psi. X 133

$$\% \text{ TOTAL POROSITY} = \frac{\text{true density} - \text{bulk density}}{\text{true density}} = 35\%$$

FIGURE 28-b

IRON COMPACTS PRESSED AT 40,000 psi. AND SINTERED 4 hrs. IN CO AT 1200°C. X 133

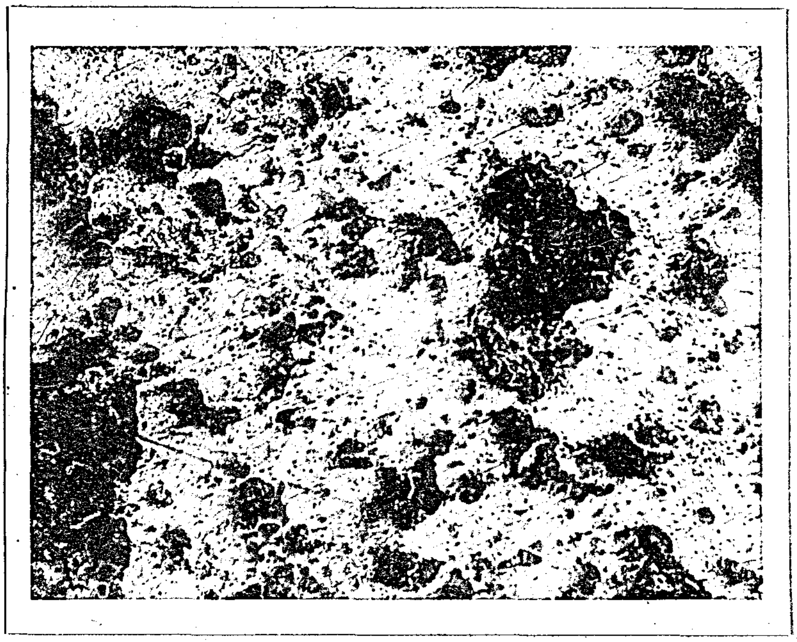


FIGURE 29-a

GREEN COMPACTS OF IRON PRESSED AT 100,000 psi. X 133

% TOTAL POROSITY = 19.2 %

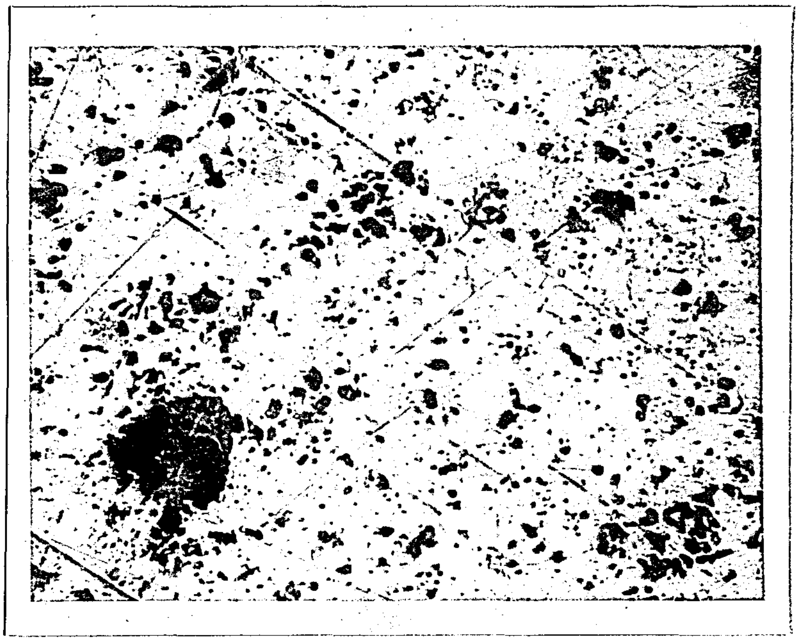


FIGURE 29-b

IRON COMPACTS PRESSED AT 100,000 psi AND SINTERED 4 hrs. IN CO AT 1200°C. X 133.

1. INFLUENCE OF COMPACTING CONDITIONS

a. COMPACTING PRESSURE

Results:

1. Green density increases with increasing compacting pressures. (Table IV, Figure 14.)
2. The rate of density increase decreases with increasing compacting pressures. (Table IV, Figures 15 and 16.)
3. Sintered density increases with increasing compacting pressures. (Table VIII, Figure 17.)
4. Hardness of sintered products increases with increasing compacting pressures, Tables V, VI and VII.
5. Shrinkage during sintering is greater in compacts formed at low pressures. Shrinkage decreases with increasing pressures. High pressures may even produce growth instead of shrinkage. (Table VIII and Figure 17.)

b. DWELL TIME (Time of application of maximum pressure)

Results:

1. The green and the sintered densities of the compacts decrease during the early stages of maximum pressure application followed by an increase with increasing time. The rate of this increase decreases with increasing dwell time. (Table IX, Figure 18.)

c. TYPE OF PRESSURE APPLICATION (Thickness effect.)

RESULTS: Soft Powder

1. Green density increases to a maximum as the thickness of the compact in the direction of applied pressure decreases (critical thickness). For very thin compacts green density drops again. (Table X, Figure 19.)

2. Sintered density increases slowly as the compact thickness decreases to the critical value and increases rather markedly for thinner compacts (Table X, Figure 19.)

Hard Powder

3. Green density increases as compact thickness decreases (Table XI, Figure 20).

4. As the compact thickness is decreased in the direction of compression, sintered density increases first, with decreasing rate of increase, then decreases again for thinner compacts (Table XI, Figure 20.)

Common for all powders

5. Density of the product decreases with increasing distance from the moving punch. (Table XII, Figure 21 and Table XIII, Figure 22)

6. 100% theoretical density is produced for the top layer of the product which is in contact with the moving punch. (Table XIII, Figure 22.)

d. COMPACTING IN VACUUM

Results:

1. Compacting in vacuum increases shrinkage and results higher sintered densities. (Table XIV, Figure 23 and Table XV, Fig. 24.)

2. SINTERING CONDITIONS

a. SINTERING TEMPERATURE

Results:

1. Final density of one-metal compacts increases with increasing sintering temperatures (Table XVI, Figure 25).

2. Harness of one-metal compacts increases with increasing sintering temperatures (Tables V and VI).

3. Final density of Fe - 25% (Vol) TiO_2 compacts decreases with increasing sintering temperatures. (Table XVII, Figure 26)

4. Hardness of Fe - 25% (Vol) TiO_2 compacts increases with

increasing sintering temperatures. (Tables XVIII, XIV and XX.)

b. SINTERING TIME

Results:

1. Density increases with increasing sintering time. (Table XXI, Figure 27.)

2. The rate of increase of density decreases with increasing sintering time. (Table XXI, Figure 27.)

DISCUSSION OF RESULTS

1. COMPACTING CONDITIONS

a. COMPACTING PRESSURE :

1. With increasing compacting pressures an increase in green density is expected, because, application of pressure forces the powder particles to come closer, decreasing the porosity and thus increasing the density.

2. The fact that the rate of increase of density decreases with increasing pressures, i.e. the pressure vs. density curve flatten out, is due to the fact that pressure can force loose powder more easily. With increasing pressures powder particles take closer positions, the number of points of contact between particles increases Pressure is expended in overcoming friction and to create particle deformations (work hardening effect). Therefore, greater pressure increments are necessary to produce the same increase in density at higher pressures. (Fig. 15 and 16.)

The maximum green density attainable by cold pressing however, depends not only on the applied pressure but also on the rate of pressure application as well as on other factors such as the susceptibility of the metal to plastic deformation and its work hardening properties and powder characteristics, particularly particle shape.

We have found that other variables being the same a compacting pressure of 100,000 psi. produces different percentages of theoretical densities for the green compacts of copper and iron. (Table IV, Fig.14)

i.e. pressure = 100,000 psi.
Copper .....91% of theoretical density
Iron .....81% " " "

We conclude the copper powder we have is more favourable for producing higher densities. It is understood that the susceptibility to plastic deformation is lower for Fe, and greater pressures are required to produce compacts of higher densities. (See Susceptibility to plastic Deformation.) This conclusion is in accordance with Fig.2.

The hardness of the Fe powder may be due to its crystal structure, particle shape or its method of preparation. Some powder production methods create work-hardening effects (mechanical methods), or hardness may also be due to the presence of hard surface oxides. These effects together with the methods to avoid them are given in Fig. 3, Fig. 4 and Table II.

The fact that Co particles are coarser than the Fe particles (Table , Appendix A) creates an effect in the opposite direction i.e. lowers the density of Cu and increases of Fe (Fig. 3).

3. Sintered density also shows the effects discussed above for results 1 and 2 for the same reasons (Fig. 17).

4. Hardness of sintered compacts increase with increasing pressures, due to better cohesion and stronger work hardening effects produced at higher pressures. This result checks with Fig. 1 and justifies our selection of density as a base for other physical properties.

5. In result 3, we saw that the density of the sintered part increases with increasing pressures. However, it is not possibl to generalize this relationship. The shrinkage during sintering has a marked effect on the final densities.

Shrinkage during the sintering process is, to a large extent, due to the increased attraction and consequent closer contact between the metal particles. Surface tension, chemical reactions, and recrystallization processes are other determining factors (see Theoretical Principles). Another very important factor effecting the size changes that occur during sintering is the effect of occlude gas.

When heat is applied during sintering these gases expand and try to escape through the pores in the compact. A lightly pressed compact leaves relatively large pores, and the gas may escape without deforming the channels left after pressing. On the other hand, a compact which has been subjected to high pressures contains no passag ways large enough for the gas to escape through, and the expanding gas pushes the particles apart in its effort to escape. This interna pressure naturally expands the compact and causes a larger and more porous product then that originally formed, thus lowering the sinter density.

These two factors, namely the increased attraction due to high temperatures and the escaping efforts of occluded gases work in opposite directions, and the degree of shrinkage or growth is the resultant of these effects.

b. DWELL TIME

1. Experiments carried out to determine the effects of dwell time indicate that density decreases as dwell time increases, during the early stages of dwell time. However, higher densities are obtained on further increase of dwell time. This is probably due to the following reason: The force was applied to the press by hand and when maximum pressure is reached it is observed that additional force must be maintained to keep the pressure on the powder constant, otherwise pressure decreases about 200-500 psi. This is due to the action of elastically deformed particles.

Since the force is maintained by hand high degree of constancy can not be expected and the maximum pressure is maintained by increasing the force slightly as soon as any decrease in pressure is observed on the gage. This process in turn, might have two effects First of all this procedure may provide some time necessary to shift the particles to the most favorable position for packing, and second it may cause additional plastic deformations on the contact points of powder particles (Table IX, Figure 18).

C. TYPE OF PRESSURE APPLICATION (Thickness effect)

Soft Powder

1. The change of density with the change of compact thickness is due to the fact that powders do not follow the hydrodynamic laws and thus nonuniform pressure distribution during compacting and nonuniform density of the product is produced. In the case of compression from one side only the density of the compact will decreas with increasing distance from the advancing punch as indicated in Result 5 (Table XII, Figure 21 and Table XIII, Figure 22). This is a consequence of the friction occuring between the particles themselves and at the walls of the die. Therefore, the density is lower the higher the compact. This necessitates the application of compression from two directions, when the thickness of the part exceeds a maximum value determined by factors such as the over-all design of the compact, the required strength of the finished part and particularly the powder characteristics.

Density decrease observed in compacts thinner than the critical one is attributed to the higher effective pressing speed for these very thin compacts. (Speed and time of pressing is kept constant.)

2. Table X and Figure 19 indicate the effect of lowering the compact thickness on green and sintered densities and provides a picture to compare the differences. It is observed that shrinkage

takes place when the compacts are sintered. This shrinkage decreases as the compact thickness decreases because higher green densities and thus lower porosities and smaller pores are obtained with shorter compacts. For such cases we know that the effects of occluded gases, which oppose shrinkage and cause growth, start to be strong enough to lower the amount of shrinkage if it does not cause growth.

Increased sintered density, i.e. increased shrinkage in compacts thinner than the critical value is surprising. This might be the effect of higher effective pressing speeds for thinner compacts as suggested by Balshin. Either fragmentation occurs or the elimination of surface oxides which decrease the clean surface areas is improved. Both of these increase the amount of available clean surface areas which promote shrinkage by creating adhesive forces upon the application of heat during sintering.

3. A slight density increase in the green compacts were observed as the thickness of compacts pressed from hard iron powder is decreased. Thicknesses were reduced by filling the die with less and less powder. Thicknesses of less than 2 mm. could not be obtained without damaging the die walls. If these thicknesses are produced a more explicit interpretation can be offered: (Table XI, Figure 20).

4. This result indicates the effect of thickness on the rate of growth during sintering. The initial decrease of growth and the decreasing rate for thinner compacts as well as the increased

growth for very thin compacts could not be interpreted satisfactoril nevertheles this data is included to illustrate the importance of powder characteristics on the behaviour of compacts and their resultant properties (Table XI, Figure 20).

5. This result was discussed above together with the first result.

6. This result indicating the fact that 100% theoretical density can be obtained in that layer of the compact closest to the moving punch is very important. Experiments carried out at first with sintered iron products. A thin layer of the compact is remove on lathe and by measuring the length and weight of the compact befo and after this operation the density of the removed layer is calculated. The results for iron compacts pressed at 40,000 psi, and sintered 4 hours at 1200°C are given in Table XII and Figure 21. T density of the top layer (74% of theoretical) was found to be about 7% greater than the overall density of the compact. We know howeve from our previous work that our iron powder is not very favorable a experiments were done on more favorable copper powder this time als increasing the compacting pressure to 100,000 psi. (Table XIII, Figure 22). The density of the layer adjacent to the moving punch was found to be almost 100% of the theoretical density. This is th combined result of the infinite pressure on this layer and the absence of factors that deviates the behaviour of powder under pressure from hydrodynamic laws.

The importance of this result lies in the fact that, our greatest difficulty in the course of this investigation was the impossibility of obtaining high densities (97-98% of theoretical) due to the limited capacity of our experimental facilities. These difficulties disappear if we focus our attention on the properties of this layer only.

d. COMPACTING IN VACUUM

1. A number of pilot tests were made to create high vacuum during compacting process. It was possible at the end to obtain a vacuum of 1.5 cm. of Hg. (For details see Apparatus and Appendix B.) A number of experiments were carried out with different powders to determine the effect of this vacuum.

We know that growth phenomena - that is, decrease in apparent density during the sintering process - are mainly caused by the gas content of the compacts. (See theoretical Principles.) In addition to the gasses dissolved by the metal, the following sources for gases can be distinguished (3):

1. adsorbed gas films;
2. gases entrapped during compacting;
3. gases originating from chemical reactions during the sintering process.

It was our intention to eliminate the first 2 of these 3 main sources. However, we were not successful in eliminating the adsorbed gas films due to unsufficient vacuum, gases entrapped during compacting are largely eliminated. The effect of this partial vacuum on the densities of copper compacts pressed at 80,000 psi and 100,000 psi and sintered 2 hours at 750°C are illustrated in Tables XIV and XV and Figures 23 and 24, together with the effects of compact thickness.

Similar tests were run with powders of other metals such as Fe and Fe+TiO_2 and no net results were obtained. However, it is thought that compacting in higher vacuum would create the same effect (increased shrinkage or decreased growth).

Ruer and Kuschmann (40) have shown that one hour's exposure to air of copper and iron powders prepared by reduction of oxides in hydrogen followed by evacuation results in weight increases amounting 5.44 mg. and 20.43 mg. per 100 g. of powder respectively.

This shows the importance of adsorbed gases and explains why the above result (increased shrinkage or decreased growth) is not revealed by Fe powders, since our vacuum was not sufficient enough to eliminate the adsorbed gases. This insufficient vacuum is caused by the leakage between the die walls and the plungers.

2. INFLUENCE OF SINTERING CONDITIONS

a. SINTERING TEMPERATURE

1. Density of one-metal compacts increase with increasing sintering temperatures. At higher temperatures the increased mobilit

of atoms creates additional adhesive effects, resulting in shrinkage. However, the above result is not independent of compacting pressure, since we know that compacts might exhibit growth as well as shrinkage during sintering at different compacting pressures.

2. The hardness of the one-metal compacts increases with increasing sintering temperatures due to two main factors;

a. the recovery from plastic deformation
b. the increase of hardness with increasing density.

This result also justifies our selection of density as the base of all other physical properties, 3 and 4. In the case of powders composed of more than one component, it is necessary to take additional factors into account in order to explain the effects of sintering temperature. Schwarzkopf (3) states that the most important of these is the homogenization by diffusion. The extent of diffusion during sintering determines the properties of the compact.

b. SINTERING TIME

1 and 2. These results indicate that the effects of sintering time and temperature on the physical properties of compacts are in the same direction. Sintering time permits the occurance of slow processes which are accelerated at higher sintering temperatures. Therefore, it seems that it is possible to obtain similar effects with short sintering periods at high temperatures and with long sintering periods at low temperatures.

SUMMARY AND CONCLUSIONS

The library research made and the laboratory experiments performed to determine the influence of processing variables and the physical properties of powder metallurgy products are presented on this report. The originality of this work can be summarized by listing 2 of our experimental results.

1. Compacting in vacuum results in higher densities by increasing shrinkage or decreasing growth.

2. Even with compacting pressures unsufficient to produce maximum green density it is possible to obtain 100% theoretical density in the layer adjacent to the advancing punch.

The importance of these results are understood when the limitations of our experimentation are considered. For example, our vacuum was enough only to eliminate a part of the gases entrapped during compacting. Under high vacuum such as 10^{-3} - 10^{-4} Torr it will be possible to eliminate the adsorbed gas films and if in addition, proper sintering atmospheres are used to minimize the gases originating from chemical reactions during sintering, spectacular results can be expected with properly treated powders.

Throughout our work we were aware of our limitations and no spectacular results were expected. However, the discovery of 100% theoretical density in the layer adhacent to the moving punch eliminates these limitations for the coming investigators having limited facilities.

"RECOMMENDATIONS"

It is understood that experimental work on "Powder Metallurgy" in Robert College will be continued by graduate students. The student, therefore, wishes to state the difficulties encountered and some possible solutions thinking that they might give some help to the coming investigators.

1. The time available for this work is very short, the student must lose no time to start library research and pilot tests with the available materials and apparatus.

2. Every effort must be made to obtain the powders with favorable characteristics for the intended work, if it is not possible to import them possibilities of treating the available powders must be sought.

3. A press capable of producing pressures of about 150,000 - 200,000 psi and also with means of controlling the pressing speed and dwell time should be obtained.

4. For better results and wider areas of experimentation controlled atmosphere furnaces are necessary, and of experiments with iron powders are continued higher temperature furnaces must be available.

5. If double or multiple action presses are not available, floating dies (Ref. 3., pp. 57) must be used for double action compression on simpler presses.

6. If the effects of vacuum are studied, higher vacuums must be obtained by either using vacuum seal or something like between the punch and die walls or compression through bellows must be tried by evacuating the air of the whole system.

7. Tensile tests can be performed on products by using specially shaped dies to produce small test pieces. (Ref. 13., pp. 248) If small pieces of 2 mm. in diameter are produced a "micro-test" machine is available at I.T.Ü.

8. Excellent microscope facilities are available in the College to study the variation of porosity and distribution of phases in heterogeneous compacts.

9. Attention must be given to the effects of powder characteristics, such as origin, particle size etc. and also to the methods of mixing powders.

10. If high theoretical densities cannot be produced with the available materials and equipment the attention might be focused on the properties of that layer of the compact which is adjacent to the moving punch.

APPENDICES

APPENDIX A

DETERMINATION OF SPECIFIC GRAVITIES OF POWDERS (*)

PROCEDURE: In the computation of the specific gravity of the metal powders from laboratory data, the weight of the pycnometer filled with distilled water at the test temperature will be needed. This value is usually taken from a plot of temperature versus weight of bottle plus water. The plot, or calibration curve, can be determined experimentally.

PYCNOMETER CALIBRATION: This procedure consists of obtaining at least three sets of concurrent temperature and weight measurements about 4°C apart and within the temperature range of 20° to 30°C. Each set, representing the coordinates for a point on the calibration curve is obtained as follows:

1. To a clean pycnometer add, deaired, distilled water at room temperature until it is full, and insert the plug in its place, wipe off the excess water.

2. Check whether the water column is level with the top of the plug and carefully dry the outside of the bottle.

3. Weigh the bottle plus water to 0.01 g.

4. Measure the water temperature to 0.1°C. Hold the tip of the thermometer at different elevations within the water to see if

the temperature is uniform.

5. If the temperature is nonuniform, place the thumb over the open end of the bottle and turn it upside down and back to mix the water thoroughly for a temperature observation.

6. Heat the bottle of water slightly by placing it in a warm water bath and repeat the above steps. Repeat this procedure until enough points are obtained to plot the calibration curve.

SPECIFIC GRAVITY DETERMINATION:

1. Put approximately 10 g. of oven-dry powder, weighed to 0.01 g. into a calibrated pycnometer which is already half full of dearied, distilled water. Be sure that no powder grains are lost when they are put into the pycnometer.

2. Remove all of the air which is entrapped in the powder by 10 minutes of boiling: (the presence of entrapped air can be detected by the movement of the surface of the suspension upon the application a release of vacuum), accompany the boiling with continuous agitation. The application of a partial vacuum is desirable to lower the boiling point, then less cooling will have to be done later.

3. Cool the bottle to some temperature within the range of the calibration curve.

4. Add water, insert the plug in its place wipe off the excess water and dry the bottle.

5. Weigh the bottle with water and powder in it to 0.01 g.

6. After checking to be sure that the contents of the bottle are at a uniform temperature, record the temperature (better obtain several sets of temperature and weight observations as the sample cools-the most accurate reading is obtained at room temperature, since a more uniform temperature is likely to exist.)

CALCULATIONS: The specific gravity of the powdered metal, can be obtained from:

$$G_p = \frac{W_p Gr}{W_p - W_1 + W_2}$$

in which,

G_T = specific gravity of distilled water at temperature T.
W_p = dry weight of powder
W_1 = weight of pycnometer, powder and water
W_2 = weight of pycnometer plus water.

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* Soil Testing for Engineers by T. William Lambe
The Massachusetts Institute of Technology.
John Wiley and Sons, Inc. N.Y., 6th printing, May, 1960, pp. 15-21.

TESTED BY: T. AKALIN

DATE OF TEST: 6th of MARCH, 1967

PYCNOMETER CALIBRATION

PYCNOMETER NO: 37

DETERMINATION NO.	1	2	3	4
WT. BOTTLE + WATER, W_2, in g.	132.00	132.11	132.18	132.19
TEMPERATURE, T, in °C.	29	25	22	21

TABLE XXII

PYCNOMETER CALIBRATION TABLE

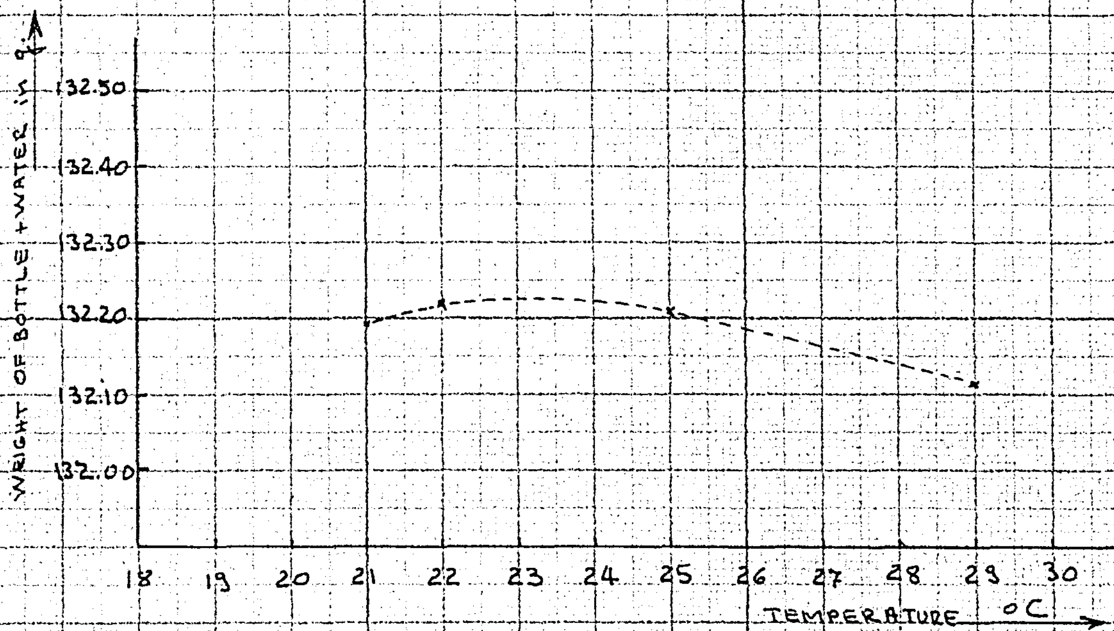

FIGURE 30.

PYCNOMETER CALIBRATION CURVE

IRON POWDER SPECIFIC GRAVITY DETERMINATION

DETERMINATION No.	1	2	3
BOTTLE No.	37	37	37
WT. BOTTLE + WATER + POWDER, W_1 in g.	140.66	140.76	140.87
TEMPERATURE T, in °C	29.0	25.0	21.0
WT. BOTTLE + WATER, W_2 in g.	132.00	132.11	132.19
EVAPORATING DISH NO.	B-12	B-12	B-12
WT. DISH + DRY POWDER, in g.	53.47	53.47	53.47
WT. DISH, in g.	43.47	43.47	43.47
WT. POWDER in g.	10.00	10.00	10.00
γ_{WATER} AT T	0.9960	0.9971	0.9980
γ_{POWDER} (SPECIFIC GRAVITY)	7.43	7.39	7.56

$\boxed{\gamma_{Fe} = 7.46}$

TABLE. XXIII

TITANIUM OXIDE POWDER SPECIFIC GRAVITY DETERMINATION

DETERMINATION No.	1	2	3
BOTTLE No.	37	37	37
WT. BOTTLE + WATER + POWDER, W_1 in g.	139.62	139.71	139.81
TEMPERATURE	29.0	25.0	21.0
WT. BOTTLE + WATER, W_2 in g.	132.00	132.11	132.19
EVAPORATING DISH No.	B-12	B-12	B-12
WT. DISH + DRY POWDER, in g.	53.47	53.47	53.47
WT. DISH, in g.	43.47	43.47	43.47
WT. POWDER in g.	10.00	10.00	10.00
γ_{WATER} AT T	0.9960	0.9971	0.9980
γ_{POWDER} (SPECIFIC GRAVITY)	4.14	4.15	4.19

TABLE XXIV

$\boxed{\gamma_{TiO_2} = 4.16}$

ELECTROLYTIC COPPER POWDER SPECIFIC GRAVITY DETERMINATION

DETERMINATION No.	1	2	3
BOTTLE No.	37	37	37
WT. BOTTLE + WATER + POWDER, W_1 in g.	140.90	141.00	141.07
TEMPERATURE T, in °C	29.0	25.0	21.0
WT. BOTTLE + WATER, W_2 in g.	132.00	132.11	132.19
EVAPORATING DISH NO.	B-12	B-12	B-12
WT. DISH + DRY POWDER, in g.	53.47	53.47	53.47
WT. DISH, in g.	43.47	43.47	43.47
WT. POWDER in g.	10.00	10.00	10.00
γ_{WATER} AT T	0.9960	0.9971	0.9980
γ_{POWDER} (SPECIFIC GRAVITY)	9.05	8.98	8.91

TABLE XXV

$\boxed{\gamma_{Cu} = 8.98}$

FERROMANGANESE POWDER SPECIFIC GRAVITY DETERMINATION

DETERMINATION No.	1	2	3
BOTTLE No.	37	37	37
WT. BOTTLE + WATER + POWDER, W_1 in g.	140.45	140.56	140.64
TEMPERATURE	29.0	25.0	21.0
WT. BOTTLE + WATER, W_2 in g.	132.00	132.11	132.19
EVAPORATING DISH No.	B-12	B-12	B-12
WT. DISH + DRY POWDER, in g.	53.47	53.47	53.47
WT. DISH, in g.	43.47	43.47	43.47
WT. POWDER in g.	10.00	10.00	10.00
γ_{WATER} AT T	0.9960	0.9971	0.9980
γ_{POWDER} (SPECIFIC GRAVITY)	6.43	6.44	6.44

TABLE XXVI

$\boxed{\gamma_{F.m.} = 6.44}$

ZINC POWDER SPECIFIC GRAVITY DETERMINATION

DETERMINATION No.	1	2	3
BOTTLE No.	37	37	37
WT. BOTTLE + WATER + POWDER, W_1 in g.	140.54	140.71	140.78
TEMPERATURE T, in °C	29.0	25.0	21.0
WT. BOTTLE + WATER, W_2 in g.	132.00	132.11	132.19
EVAPORATING DISH No.	B-12	B-12	B-12
WT. DISH + DRY POWDER, in g.	53.45	53.45	53.45
WT. DISH, in g.	43.45	43.45	43.45
WT. POWDER in g.	10.00	10.00	10.00
γ_{WATER} AT T	0.9960	0.9971	0.9980
γ_{POWDER} (SPECIFIC GRAVITY)	~~6.83~~	7.12	7.08

$\boxed{\gamma_{Zn} = 7.10}$

TABLE XXVII

21 st of MARCH, 1964

SIEVE ANALYSIS

IRON POWDER TABLE XXVIII

SIEVE NO	NOMINAL SIEVE OPENING		WEIGHT OF SIEVE gms.	WEIGHT OF SIEVE+POWDER gms.	WEIGHT OF RETAINED POWDER gms.	PERCENT RETAINED	CUMULATIVE PERCENT RETAINED	PERCENT FINER
	mm.	in.						
40	0.420	0.0165	90.4	90.4	0	0	0	100.0
50	0.297	0.0117	88.2	88.2	0	0	0	100.0
70	0.210	0.0083	59.2	59.2	0	0	0	100.0
100	0.149	0.0059	83.2	92.6	9.4	18.8	18.8	81.2
200	0.074	0.0029	83.0	98.0	15.0	30.0	48.8	51.2
325	0.044	0.0017	77.8	98.6	20.8	41.6	90.4	9.6
PAN	—	—	82.3	87.1	4.8	9.6	100.0	—

TITANIUM OXIDE POWDER TABLE XXIX

SIEVE NO	NOMINAL SIEVE OPENING		WEIGHT OF SIEVE gms.	WEIGHT OF SIEVE+POWDER gms.	WEIGHT OF RETAINED POWDER gms.	PERCENT RETAINED	CUMULATIVE PERCENT RETAINED	PERCENT FINER
	mm.	in.						
40	0.420	0.0165	90.4	90.4	0	0	0	100.0
50	0.297	0.0117	88.2	88.2	0	0	0	100.0
70	0.210	0.0083	59.2	60.2	1.0	2.0	2.0	98.0
100	0.149	0.0059	83.2	107.9	24.7	49.4	51.4	48.6
200	0.074	0.0029	83.0	96.4	13.4	26.8	78.2	21.8
325	0.044	0.0017	77.8	88.7	10.9	21.8	100.0	0
PAN	—	—	82.3	82.3	0	0	—	—

21 st of MARCH, 1964.

SIEVE ANALYSIS

ELECTROLYTIC COPPER POWDER

TABLE XXX

SIEVE NO	NOMINAL SIEVE OPENING		WEIGHT OF SIEVE gms.	WEIGHT OF SIEVE + POWDER gms.	WEIGHT OF RETAINED POWDER gms.	PERCENT RETAINED	CUMULATIVE PERCENT RETAINED	PERCENT FINER
	mm.	in.						
40	0.420	0.0165	90.4	90.4	0	0	0	100.0
50	0.297	0.0117	88.2	88.2	0	0	0	100.0
70	0.210	0.0083	59.2	62.5	3.3	6.6	6.6	93.4
100	0.149	0.0059	83.2	105.4	22.2	44.4	51.0	49.0
200	0.074	0.0029	83.0	96.3	13.3	26.6	77.6	22.4
325	0.044	0.0017	77.8	87.3	9.5	19.0	96.6	3.4
PAN	—	—	82.3	84.0	1.7	3.4	100.0	—

FERROMANGANESE POWDER

TABLE XXXI

SIEVE NO	NOMINAL SIEVE OPENING		WEIGHT OF SIEVE gms.	WEIGHT OF SIEVE + POWDER gms.	WEIGHT OF RETAINED POWDER gms.	PERCENT RETAINED	CUMULATIVE PERCENT RETAINED	PERCENT FINER
	mm	in.						
40	0.420	0.0165	90.4	95.8	5.4	10.8	10.8	89.2
50	0.297	0.0117	88.2	97.4	9.2	18.4	29.2	70.8
70	0.210	0.0083	59.2	66.5	7.3	14.6	43.8	56.2
100	0.149	0.0059	83.2	92.2	9.0	18.0	61.8	38.2
200	0.074	0.0029	83.0	91.2	8.2	16.4	78.2	21.8
325	0.044	0.0017	77.8	87.8	10.0	20.0	98.2	1.8
PAN	—	—	82.3	83.2	0.9	1.8	100.0	—

21 st of MARCH, 1964.

SIEVE ANALYSIS

ZINC POWDER

TABLE XXXII

SIEVE NO	NOMINAL SIEVE OPENING		WEIGHT OF SIEVE gms.	WEIGHT OF SIEVE+POWDER gms.	WEIGHT OF RETAINED POWDER gms.	PERCENT RETAINED	CUMULATIVE PERCENT RETAINED	PERCENT FINER
	mm.	in.						
40	0.420	0.0165	90.4	90.4	0	0	0	100.0
50	0.297	0.0117	88.2	88.4	0.2	0.4	0.4	99.6
70	0.210	0.0083	59.2	59.5	0.3	0.6	1.0	99.0
100	0.149	0.0059	83.2	85.1	1.9	3.8	4.8	95.2
200	0.074	0.0029	83.0	86.9	3.9	7.8	12.6	87.4
325	0.044	0.0017	77.8	103.0	25.2	50.4	63.0	37.0
PAN	—	—	82.3	100.8	18.5	37.0	100.0	—

SAMPLE : 50 gms. of powder.

SHAKING TIME : 5 minutes.

SIEVES : U.S. Standard Sieve Series,
Newark Wire Cloth Co., Newark N.J.

SIEVE SHAKER: American Instrument Co.
Silver Spring, Maryland.
Catalog No: 7-120 Serial No: 10014.7

LOCATION: Technical University of Istanbul
Soil Mechanics Laboratory.

CHEMICAL COMPOSITIONS.

IRON POWDER

	MIN	MAX	TYP.
Fe	97.0	—	98.5
Mn	nil	trace	nil
Si	nil	0.10	0.04
Cu	nil	0.10	0.008
C	nil	0.150	0.098
S	nil	0.020	nil
P	nil	0.025	0.008

TABLE XXXIII

TITANIUM OXIDE POWDER

	MIN	MAX	TYP
$TiO_2 + (ZrO_2)$	98	—	99.5
SiO_2	—	1.0	0.26
Fe_2O_3	—	1.0	0.45
C	—	0.05	0.026
S	—	0.02	trace
P	—	nil	—

TABLE XXXIV

FERROMANGANESE

	MIN	MAX	TYP
Mn	80	83	82.5
Si	—	1.5	1.3
Cu	—	0.25	0.06
C	—	1.0	0.782
S	—	trace	trace
P	—	0.2	0.151

TABLE XXXV.

APPENDIX B

LIST OF EQUIPMENT

1 Triple beam balance (0.01g.)
Capacity 311 g. Model 311
Ohaus Scale Corp. Union, N.J. U.S.A.

1 0-25 mm. micrometer
Central Scientific Co. Chicago, Ill., U.S.A.

1 25-50 mm. micrometer
Feinmesszeungfabrik Suhl, Germany.

1 Timer
Eastman Kodac Co. Rochester, N.Y., U.S.A.

1 Press (hand operated)
Buehler Ltd. Evanston Ill., U.S.A.

1 Vacuum pump (Duo-Seal)
Patent No. 2337849
W.M.Welch Manufacturing Co. Chicago 10, U.S.A.

1 Vacuum gage
30 in.-76 cm. vacuum
Marshalltown Gauge Manufacturing, Inc., Iowa, U.S.A.

1 Pycnometer
100 ml. at 20°C.

1 Thermometer
0 - 50°C.

2 Mortar and pestles

4 Spatulas

2 Ring stands

1 Sieve
U.S. Standard Sieve Series Sieve No : 100
Newark Wire Cloth Co., Newark, N.J.

1 Sieve (ordinary)
3/8 in. openings.

1 Sintering oven, Max. temp. 1100°C.
Hevi Duty Electric Co. Milwaukee, Wis.
Pat. 159,215 Type 051-PT Ser. No. 100324
Volts 115 Watts 1150 Cycles 50/60

1 Sintering oven, Max. Temp. 1400°C.
Hevi Duty Electric Co. Milwaukee, Wis., U.S.A.

1 Time switch
Type TSA-47
General Electric, U.S.A.

1 Pair of tongs

1 Pair of asbestos gloves

1 Hot plate
Model HP-1915B 115 Volts AC 700 Watts Type 1900
Thermolyne Corporation, Dubuque, Iowa., U.S.A.

1 Drying oven
Nr. 32810 110/130 Volt 1200 Watt
Carnifix AEG - Fabrikat, Germany.

1 Microscope
Unitron Universal Microscope with polaroid attachment
Unitron instrument Co.
Newton Highlands 61, Mass.

1 Rockwell Hardness Tester
Wilson Mech. Instrument Co., Inc. N.Y., U.S.A.

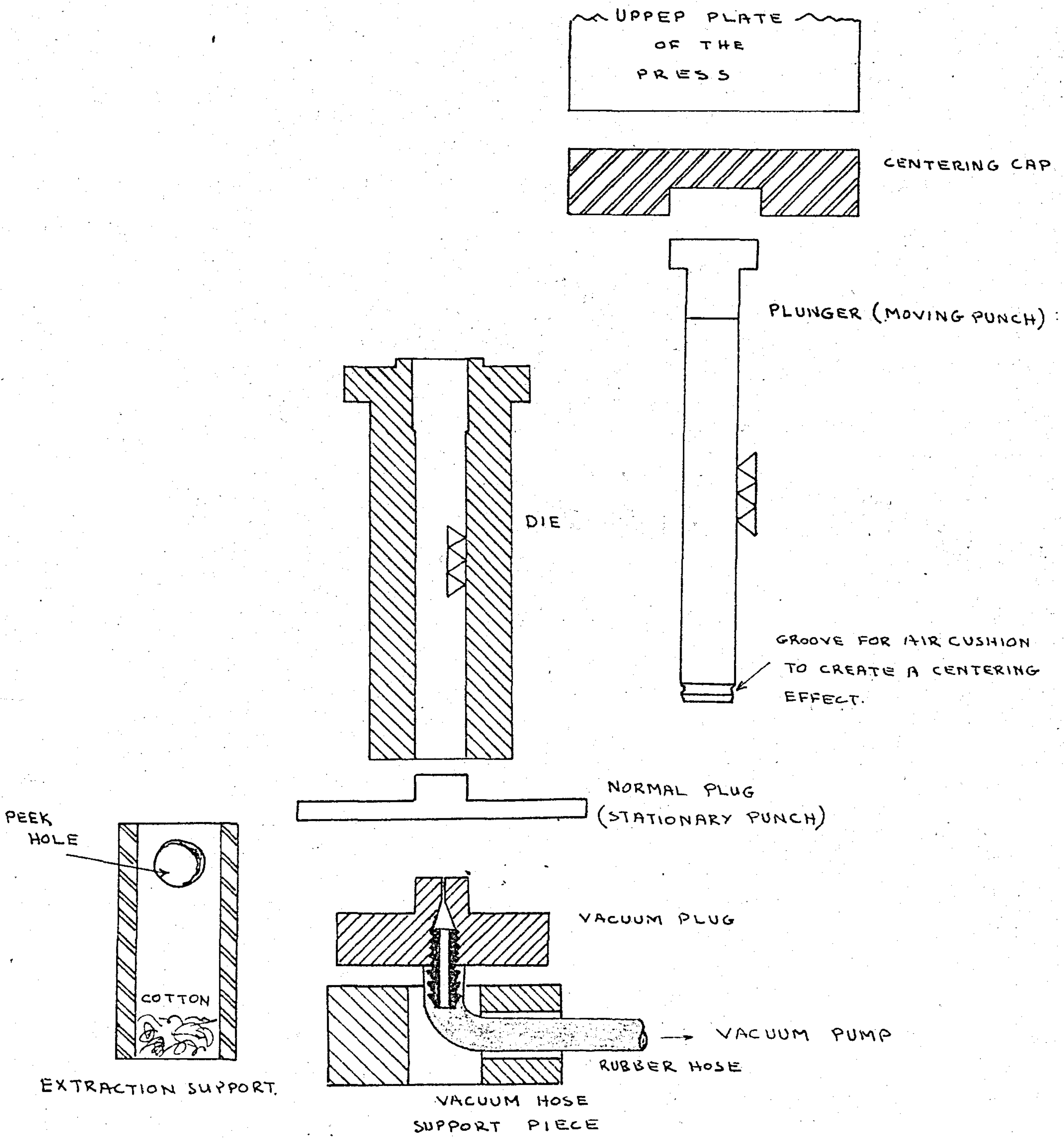

FIGURE 31.

DIE, PLUNGER, CENTERING CAP, NORMAL PLUG, PLUG FOR VACUUM, VACUUM HOSE SUPPORT PIECE, EXTRACTION SUPPORT AND THE "PEEK HOLE". SCALE: 1/1

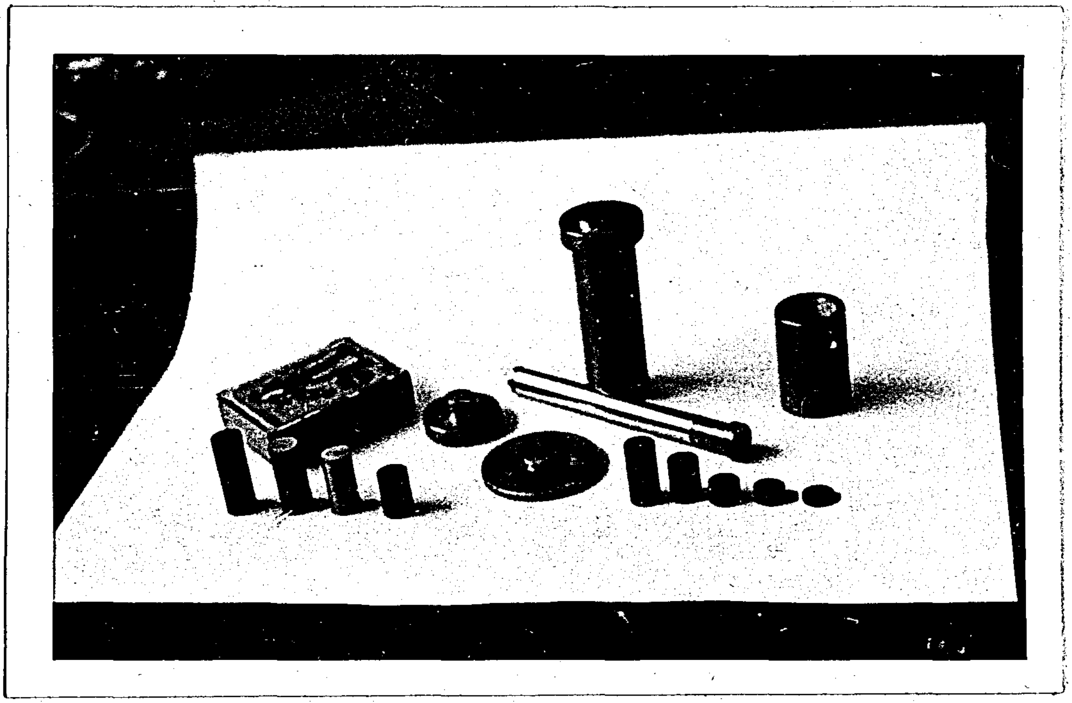

FIGURE 32.

DIE, PLUNGER (PUNCH), NORMAL PLUG, VACUUM PLUG, EXTRACTION SUPPORT (PEEK HOLE) AND VARIOUS COMPACTS. (A MATCH BOX IS INCLUDED TO PROVIDE A CRITERIA FOR THE DIMENSIONS.)

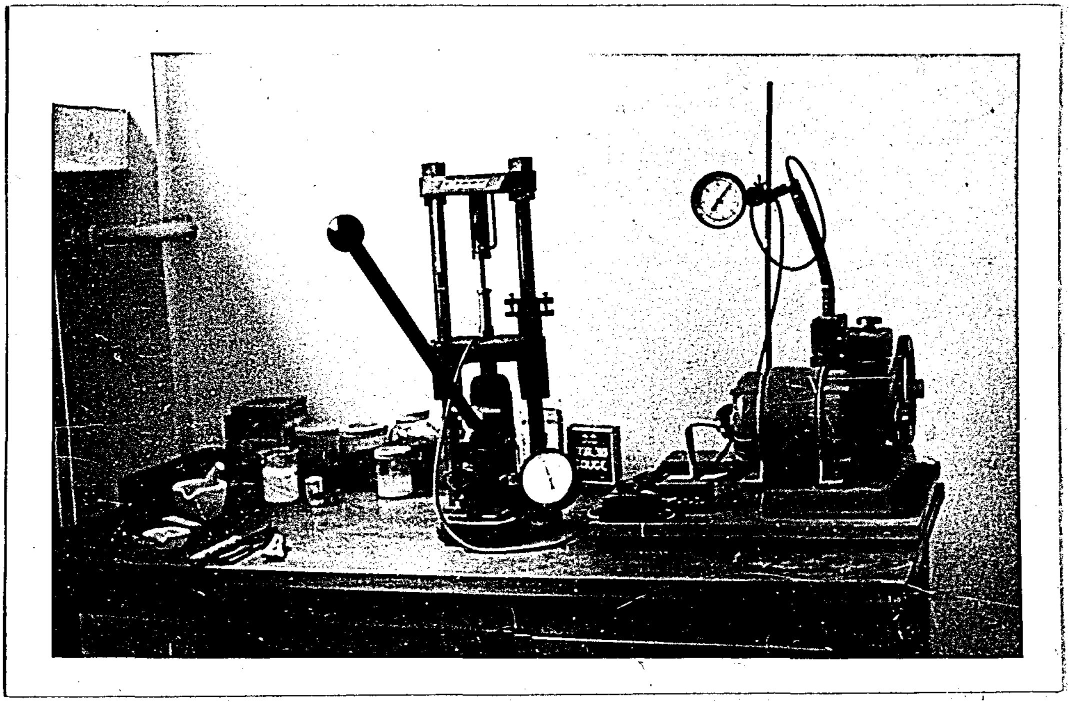

FIGURE 33.

COMPACTING PRESS, DIE, VACUUM PUMP, POWDERS, MIXING, HANDLING AND FILLING EQUIPMENT (PHOTOGRAPH SHOWS COMPRESSION IN VACUUM).

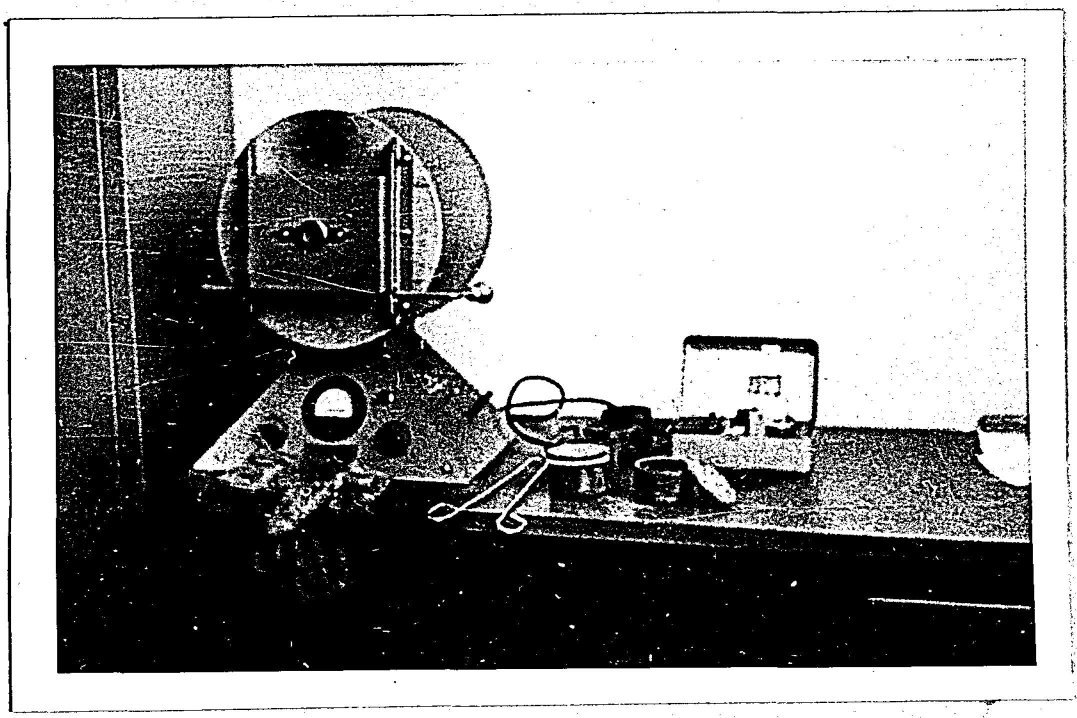

FIGURE 34.

SINTERING OVEN, ASBESTOS GLOVES, TONGS, SINTERING BOXES AND TIME SWITCH.

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