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METHOD OF PRODUCING METAL POWDERS

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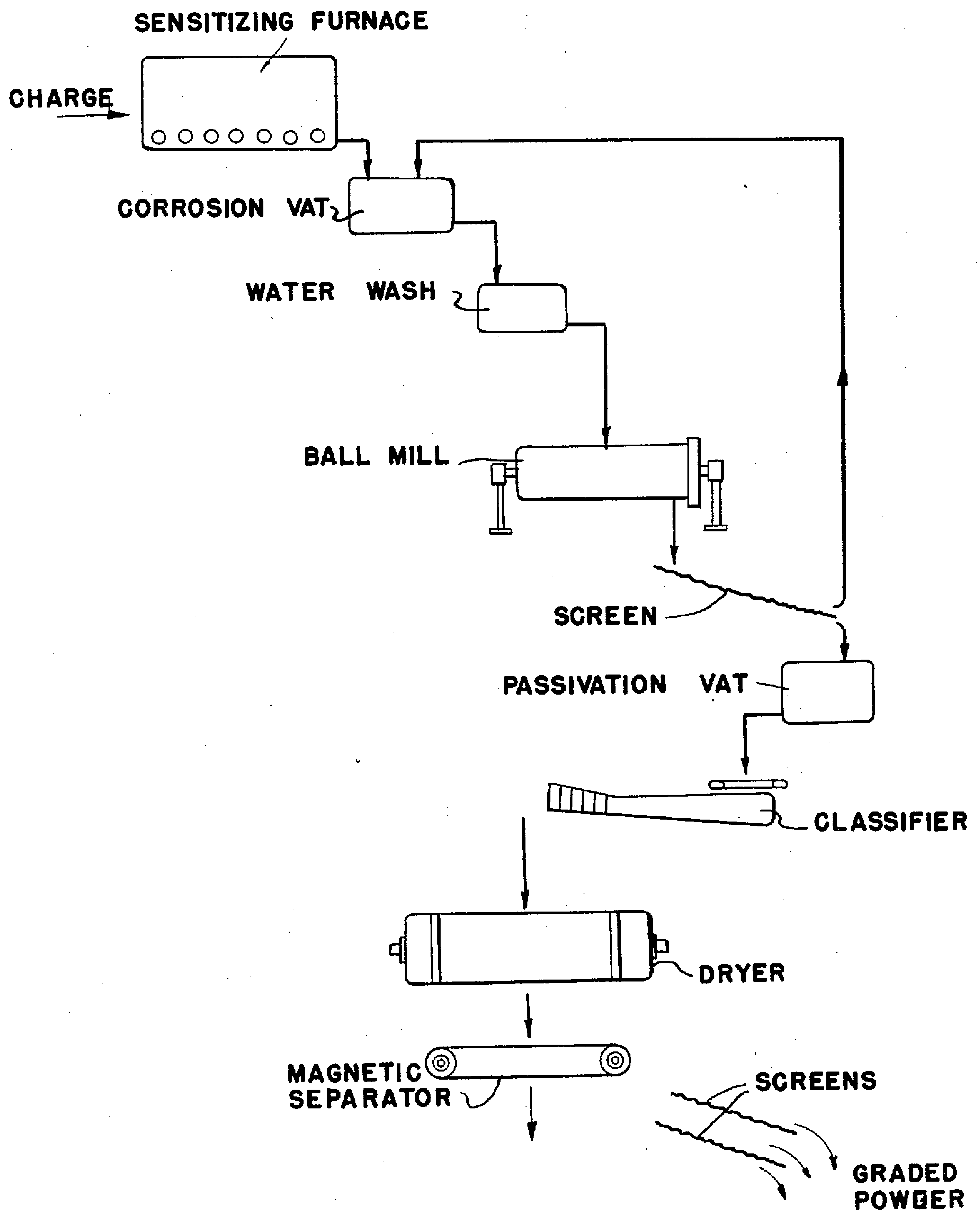

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METHOD OF PRODUCING METAL POWDERS

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5 Claims. (Cl. 75—.5)

This invention relates to an improved method of producing metal powders. This application is a division of prior application, Serial No. 479,436, filed March 17, 1943, now Patent No. 2,462,659.

In the field of ferrous powder metallurgy there is an increasing demand for products of improved physical and chemical characteristics, such as increased tensile strength, corrosion resistance and the like. Such improvements are difficult to attain when utilizing relatively pure iron powder as a starting material, for any improvement in properties which is achieved is secured by expensive treatments, such as hot pressing and diffusion of secondary constituents, such as carbon and the like, into the iron matrix.

It is well known in the field of fusion metallurgy that the most effective and economical method of modifying the physical and physicochemical characteristics of ferrous base products is to combine predetermined alloy constituents with the base metal in the melt so as to secure an ultimate alloy of the desired analysis and corresponding physical characteristics. In the field of powder metallurgy the desirability of utilizing alloy powders has been recognized and attempts have been made to produce such products. The suggested methods however have been so expensive as to preclude commercial production. This high expense has been largely due to the fact that the production of the alloy has been based on a special treatment of the prefabricated iron powder, as for example by effecting diffusion of one or more solid phase alloying constituents into the solid phase iron powder or powder compact.

The present invention relates to the production of special alloy powders by utilizing cheap, readily available scrap material containing the desired alloy constituents and reducing this material to the powder form by utilizing what, for the sake of a term, may be called an inherent weakness in the starting material. Because of the desirable characteristics of stainless steel as a superior metal for the production of high strength, corrosion and heat resistant products this material will be chosen as a medium to illustrate the fundamental concept of the invention. It will be understood, however, that the invention may be availed of for the production of powder from any alloys, whether ferrous or non-ferrous, which exhibit the special metallurgical characteristics which are utilized as herein described.

It is known that one of the major shortcomings of austenitic steels of the stainless type containing approximately 18 to 25% chromium and 8 to 20% nickel and above .02% carbon is their susceptibility to intergranular corrosion when heated to a temperature between about 500° C. and 900° C. for an appreciable period of time. In these circumstances the carbon which existed in metastable solid solution is rejected in the form of a chromium-rich carbide in the grain boundaries. The steel which is thus sensitized is susceptible to preferential corrosion by a number of different corrodents. When subjected to such preferential boundaries become weak and the erstwhile massive material is readily crushed to a powder.

The present invention utilizes this intergranular corrosion susceptibility of such steels to produce an alloy steel powder of desirably low carbon content.

Utilizing such a concept it will be appreciated that powders may be produced utilizing cheap equipment and with simple technique. In order more effectively to explain the invention, a diagrammatic illustration, in flow sheet form is shown in the accompanying drawing.

The essential operations involved in the improved process is a heat treatment or sensitization of cheap starting material such as sheet or shot and a preferential disintegration of the boundary areas, preferably by chemical corrodents, to produce particles corresponding to the grain size of the material treated.

With these major steps there are employed other steps, such as mechanical disintegration, classification, brightening and/or passivation, which improves the product for certain uses. As will be appreciated, the products produced under the principles of the invention may be widely utilized. The classified or graded powder may be utilized either alone or in a blend with iron powder to produce powder metal compacts. As will be seen more fully hereinafter, chromium-nickel in alloy powders of extremely low carbon content may readily be produced by the new method. Such powders may be compacted or briquetted with any suitable bonding agents and may be employed as an addition agent to an iron-chromium or iron-nickel chromium melt of a relatively high carbon content to secure an ultimate alloy of a desirably low carbon content.

The low carbon content of the products producible under the invention renders them exceptionally useful for welding rods. The powders may be compacted to the desired shape and coated with suitable fluxing agents to produce welding metal or very low carbon analysis.

The iron-chromium powders described herein with peculiar advantage may be mixed or blended with predetermined percentages of silver powder and then compacted to produce excellent electrical contact material. Since an alloy of 18% of chromium and 8% of nickel has the same electrochemical potential as silver such contact materials present the advantages of high corrosion resistance and excellent electrical conductivity.

In carrying out the invention cheap source material may be utilized. Because of its adequate supply, ready availability and low cost stainless steel scrap is preferred. This may be utilized in the form of borings and turnings, shotted material or sheet trim scrap. While not necessary in operating the process it is preferable, when sheet trim is used, to employ a relatively thin gauge scrap since the use of the thin section material insures a more rapid and uniform corrosion treatment. It is also desirable to utilize the cold rolled scrap. When hot rolled scrap is employed and scale may be removed in a manner well known to those skilled in the art after the heat treatment, subsequently to be described, or at any other suitable stage in the process. It is also desirable, although not essentially necessary, to classify the scrap to the extent that stabilized stainless scrap, i. e., columbium and titanium bearing stainless is culled from the charge. If such preliminary classification is not desirable the mixed scrap may be employed since the stabilized scrap is readily separable from the sensitized material during the course of the treatment. With the certain scrap materials intergranular corrosion may be accelerated by heating in a carburizing atmosphere, as for example in an atmosphere of illuminating gas.

As is well known, the grain size of the alloy which is utilized as a source material will vary depending upon the thermal and mechanical history of the scrap. A typical charge of scrap may consist only of hot rolled material or cold rolled material or a mixture of these two. The cold rolled material may also be of different degrees of reduction. The particle size and particle size distribution required in the ultimate powder may, if desired, definitely be established in the charge by making this up of predetermined mixtures of hot and cold rolled material which latter may itself comprise scrap or different degrees of cold reduction. Where circumstances so dictate the charge may be standardized as to the eventual particle size by heat treating the mixed scrap prior to the heat sensitizing treatment. This step, as will be appreciated, may be carried out in the furnace employed for the sesitizing treatment as a preliminary step in the process. As will thus be appreciated the process is operable with run-of-mill scrap which varies widely in length and cross-section as well as with smaller scrap, such as borings, turnings and the like.

The process may be carried out with simple standard equipment and chemicals and with a modicum of labor and control. As shown in the drawing the scrap to be treated is charged to the furnace 1. If desired prior to such charging the scrap may be treated for the purpose of cleaning it of hot scale or for any other purpose. To facilitate handling the scrap it preferably is first pressed into a relatively loose bale and is charged to the furnace in the form of such units. When borings and turnings are employed it may be charged to a furnace in a suitable container.

The furnace 1 may be of any suitable type, such as a gas or oil fired furnace. Typical annealing furnaces serve effectively. The only essential requirement of the furnace is that it shall be capable of attaining and holding a temperature in the carbide precipitation range, i. e., from about 500° C. to 900° C. or above.

In the furnace 1 the charge of scrap is heated up to the carbide precipitation range and held within that range, preferably with cyclic variations, for a period of time sufficient to insure complete sensitizing of the stock.

The time of the sensitizing treatment, as will be appreciated, will depend upon the characteristics of the material undergoing treatment. If the charge is comprised largely of stainless of approximately .08% carbon which has an average cold reduction of 50% the heat treatment may be continued 8 or 10 hours or less. With this type of stock the furnace may be charged and brought up to a temperature of the order of 1050° C. and held at this temperature for a period of about one-half hour after which the temperature may be dropped to about 800° C. and cooled slowly from 800° C. to 400° C. for a period over about two hours.

In the event that the scrap is less severely cold worked the heating cycle should be prolonged to about 24 hours more or less. For this type of charge the furnace preferably is raised to a temperature of between about 400° C. and 760° C. and held at this temperature for about 12 hours. The temperature is then preferably slowly dropped to about 400° C. within the next 12 hour period. In each case, as will be appreciated, the material is sensitized in the carbide precipitation range for a period of time adequate to insure thorough orientated carbide precipitation. Cyclic heatings are preferred over the maintenance of a steady heat. Cyclic heatings between approximately 400° C. and 900° C. are advantageous and slow cooling from this upper temperature down to 400° C. similarly accelerates the desired action.

It will be understood that the heat treatment or sensitizing will also be governed in part by the carbon content. In the preceding examples a steel scrap of about .08% carbon constituted the charge. When the carbon content is higher the heating cycle may be shortened and when the carbon content is lower the heating cycle should be commensurately prolonged. For very low carbon scrap, for example 0.5% C, the heating time must be increased to from about two to about five times to that given in the first examples When the carbon content of the scrap is low, i. e., less than .06% C, it is preferable to sensitize in a carburizing atmosphere.

After the scrap has been sensitized in the manner described it is then given a chemical disintegration treatment. If desired prior to such chemical disintegration the material may be pickled by any suitable agent to remove oxide. As shown in the drawing such chemical disintegration is accomplished by charging the treated scrap to the vat 2. This vat may be of any suitable material, such as a ceramic or wooden vat lined with stabilized stainless steel or any other material which is resistant to the action of the corrodent and which does not contaminate the powdered product. In the vat the sensitized scrap is digested in a chemical solution which preferentially attacks or corrodes the grain boundaries of the sensitized metal. For this purpose a modified Strauss solution may be employed. This solution, for example, may comprise 47 cc. H_2SO_4 (sp. g. 1.84) and 13 grams $CuSO_4.5H_2O$ per liter. The solution preferably is held at an elevated temperature of from about 80° C. to 100° C, and the scrap is held in the vat for about 2 to 24 hours. In these circumstances the steel is well corroded along the grain boundaries. In the course of this corrosion particles of steel varying from fine powder up to relatively large section detach themselves from the scrap sheet stock and fall to the bottom of the tank. When smaller material, such as borings and turnings are employed this is substantially all reduced to a powder in the vat. When sheet stock is used the quantity of the disintegrated detached material may be increased by occasionally pounding the scrap during the latter stages of the chemical corrosion. It will be appreciated that chemical solutions other than that mentioned may be utilized for this intergranular corrosion. Thus, in lieu of the solution mentioned there may be employed such corrodents as dilute sulphuric acid, ammonium sulphate and sulphuric acid, ferric chloride, copper chloride, potassium hypochlorite, trichlorethylene, hot salt solutions and the like. As indicated previously, any solution which preferentially attacks the carbide-rich grains may be utilized.

After the corrosion treatment is completed the corroded material may be removed from the vat **2** by any suitable means and thoroughly washed in the container **3**. The washed material from which adherent corrodent has been removed may then be passed to the ball mill **4** and milled therein to reduce the larger particles to a powder. It will be appreciated that in lieu of the ball mill shown in the drawings any other disintegrating mechanism, such as a hammer, stamp mill or tumbling mill, may be employed. The time of treatment in the ball mill will, of course, depend upon the type of material treated and the degree to which the sensitized product has been corroded. Reduction in a tumbling mill tends to preserve the powder as single crystals. Other types of milling tend to make the powder polycrystalline. As will be appreciated, if the material is cold worked during the disintegrating operation it tends to make the resulting powder magnetic.

After thorough disintegration in the ball mill a charge of powder is discharged from the mill to the screen **5**. The material which has not been powdered or pulverized is returned, as shown by line **6**, to the corrosion vat for further treatment. The material passing through the screen **5**, which preferably is less than 150 mesh, is charged to a suitable container **7** in which it is treated with a suitable solution, such as nitric acid which serves to dissolve the copper which plates out from the Strauss solution and brighten the powder as well as to passivate the stainless steel particles. For this treatment a 10% commercial nitric acid solution may be employed. Preferably, the temperature of the liquid in the vat **7** is maintained between about 54° C. and 60° C.

In some circumstances where the charge of scrap employed is contaminated with inorganic materials it may be desirable to treat the product to insure their removal. For this purpose the material from vat **7** may be washed and then passed to a suitable classifier **8** which may, for example be a Wilfley table. In this classification treatment extraneous inorganic material is removed. The classified metallic powder may then be discharged to the drier **9**. This preferably comprises a rotary drier in which the material is dried down at temperatures maintained at 215° C. more or less.

The product which is discharged from the drier comprises metallic particles of stainless steel intermixed with metal carbides. In order to fractionate this material and to procure a metal powder free from the carbides the product may be treated in the magnetic separator **10**. In typical operation the carbides contained in the mass exist in the fines, i. e., the material of minus 325 mesh. When the product discharged from the drier is at a temperature of 215° C., which is substantially the Curie point of the carbides, magnetic separation is greatly facilitated. The carbide material is discharged from the separator at **11** and then the metallic powder may be passed to the screen system **12** from which powder of differential particle size is recovered. It will be appreciated that the above described process presents an eminently simple method of producing metallic powder of predetermined particle size for powder metallurgy uses. Stainless steel powder so produced is singularly free from metal carbides and oxides, these having been removed during the course of the treatment. By reason of the freedom from oxides and carbides the material is extremely plastic and lends itself most readily to compacting and sintering. In the event that the powder is cold worked to a considerable extent, as for example by reason of a long ball milling operation, plasticity may be restored by annealing at temperatures not higher than 900° C. for about an hour more or less and then slowly cooled. Preferably, this annealing is effected in dry hydrogen or a vacuum in order to avoid undue oxidation or carburization.

Stainless steel powder has been produced in accordance with the preceding process with eminently satisfactory results. A charge comprised of stainless steel sheet trimmings was annealed in a sensitizing furnace for a period of 24 hours during about 8 hours of which the product was held within the temperature of the carbide precipitation range. This product was then corroded for about 24 hours in the Strauss solution previously described. Upon disintegration and classification, i. e., the separation of the powder produced in the corrosion treatment from the larger sections and removal of oxides and the like an eminently satisfactory product was produced. Upon a screen analysis this product was found to comprise 30% of powder between 100 and 200 mesh, 54% between 200 and 325 mesh and 16% below 325 mesh. This particle size dispersion is thus practically ideal for compacting. A cold compact made up of the powder thus produced withstood a pressure of 50 tons per square inch without cracking. This, as will be appreciated, compares most favorably with typical iron powder compacts which display a tendency to crack under a pressure of 40 to 50 tons per square inch.

In the preferred method of producing articles from the stainless steel powder the cold pressed compact is preferably sintered in a hydrogen atmosphere. When sintering at a temperature between 900° C. and 1250° C. for 120 minutes, products have been produced which possess a tensile strength in excess of 60,000 pounds per square inch with a reduction of more than 10% in area. It will be appreciated that with these improved physical characteristics combined with the excellent chemical characteristics of stainless steel, sintered products possess a very wide permissive field of use. The stainless steel powder so produced may, of course, be mixed or blended with other metal powder, such as iron powder, or any desired type silver powder, nickel powder and the like so as to produce products of variant physical, physiochemical and/or electrical characteristics.

As will be appreciated, the physicals of the compacts produced under the present invention are such as to permit subsequent processing so as to more effectively conform the compacts to an intended use. These compacts, for example may be forged and hot rolled to produce articles of physical characteristics comparable to products produced by typical fusion metallurgy methods.

It will be understood that the process of producing the stainless steel powder herein described and as illustrated by the flow sheet is susceptible of many modifications. As previously explained, the process is available for use with different types of scrap, i. e., hot and cold rolled scrap. Where hot rolled scrap is used it is desirable to pickle the material at some suitable stage to remove oxides. Where oxide removal is complete prior to passivation or drying physical classification or separation as illustrated at stage **8** may be dispensed with. Obviously in lieu of the particular apparatus shown other similarly functioning apparatus may be employed. Again since, as pointed out, the carbides occurring in the material are largely included in the fines the classification in a mechanical classifier may be sufficiently effective so as to preclude the necessity of magnetic separation. Again, the sensitizing treatment may be carried out in a rotary kiln in which a corrosive gaseous atmosphere is maintained.

The stainless steel powder produced as described herein may be classified as desired so as to give any predetermined particle size distribution. For high pressure pressing, i. e., over 30 tons per square inch, a powder is preferred containing about 66⅔% of between 100 and 200 mesh material, 16⅓% more or less of between 200 and 325 mesh material and 16% below 325 mesh. For lower pressure pressing a preferred product comprises about 42% of material between 100 and 200 mesh, about 42% of material between 200 and 325 mesh and about 16% of material below 325 mesh. As is understood by those skilled in the art, in making up the powder mixture for compact lubricants, such as graphite, may be introduced. Similarly, silver powder may be utilized for its lubrication. As noted above, the particular analysis of the powder employed for the compacting will be predetermined upon the desired use. Thus, for bearing material the stainless steel powder may be admixed with copper or silver phosphide or low melting silver solders so as to improve the bearing surface. These and other modifications and ramifications will occur to those skilled in the art of utilizing the improved product.

It is clearly to be understood, as explained earlier, that the present invention comprehends the broad concept of producing metal powders from cheap source material by invoking and utilizing an inherent characteristic of such source material for powder production. Stainless steel has been chosen herein as illustrative of a classical material of this type. The invention, however, comprehends the production of metal powders or metal alloy powders from any source material which, by reason of a heat treatment, is embrittled and/or rendered corrodable in the boundary areas. The invention is, therefore, applicable to any alloy whether of the solid solution type or not which through heat and/or mechanical treatment develops grain boundary weakness which thus permits disintegration of such boundary areas. For certain products like stainless steel separation into powder is facilitated by chemically corroding this differential boundary phase. In certain other alloys a liquid corrodent need not be employed and particularly where the grain boundary phase is of a brittle character. In such circumstances powdering of the material after the heat sensitizing treatment may be effected by any suitable type of trituration or grinding. Whenever desired this grinding may be in a liquid menstruum which serves as a lubricant and/or as a protective material to preclude oxidation and the like. Typical of such products which may be treated in accordance with the invention are aluminum-magnesium alloys, aluminum silicon alloys and similar non-ferrous products which upon heat sensitizing or mechanical working develop an intergranular embrittled phase which may readily be mechanically reduced or corroded so as to produce a powder of a particle size corresponding to the grain size of the matrix after the heat treatment. Thus, magnesium-aluminum alloys containing up to 10% of aluminum may be employed. For example, brass may be heat treated and cold worked after which the product may be milled in the presence of a suitable corrodent, such as a mercurous nitrate solution of suitable strength. Again, Armco iron may be heated to about 1315° C., slowly cooled and then milled in the presence of ammonium nitrate to produce a powdered product. Other alloys amenable to the treatment to produce metallic powders are: magnesium-bismuth alloys containing up to 10% bismuth; magnesium-copper alloys containing up to 5% copper; magnesium-lead alloys containing up to 10% lead; magnesium-zinc alloys containing up to 8.4% zinc; and magnesium-silicon containing up to about 1.4% silicon. The above-mentioned alloys, of course, are not exclusive or extensive but are merely illustrative of the general type comprehended herein.

While preferred embodiments of the invention have been described it is to be understood that these are given didactically to illustrate the underlying principles involved and not as limiting the invention to the chosen examples.

I claim:

1. A method of producing a magnesium-enriched metal powder from magnesium base alloy which contains a second metallic component whose solubility in the alloy matrix varies to a marked degree with temperature and which, upon heat treatment, largely precipitates as an intergranular phase, enriched in the second component and which intergranular phase is relatively more brittle than the granular phase of the alloy which comprises, heat treating the alloy in solid phase, at a selected temperature sufficiently high to establish such embrittled intergranular phase, disintegrating the heat treated material and separating the granular from the intergranular material.

2. A method of producing a magnesium-enriched metal powder from magnesium base alloys which contain a second component whose solubility in the alloy matrix varies to a marked degree with temperature and which, upon heat treatment, largely precipitates as an intergranular relatively corrodable phase, enriched in the said second component, which comprises, heat treating the alloy, in solid form, at a selected temperature sufficiently high to establish such intergranular phase, selectively corroding the intergranular material and separating and recovering the granular alloy phase.

3. A method of producing a magnesium-rich alloy powder which comprises, heat treating a

magnesium-aluminum alloy containing up to 10% aluminum at a temperature which insures the formation of an embrittled intergranular phase, disintegrating the heat treated material and separating a granular matrix phase enriched in magnesium from the intergranular phase enriched in aluminum.

4. A method of producing magnesium powder which comprises, heat treating a magnesium base copper alloy containing up to about 5% copper at a temperature sufficiently high to insure the formation of an embrittled intergranular phase relatively enriched in copper, disintegrating the heat treated material and separating the alloy grains from the disintegrated intergranular material.

5. A method of producing magnesium powder which comprises, heat treating a magnesium base zinc alloy containing up to about 8.4% zinc at a temperature sufficiently high to insure the formation of a relatively embrittled intergranular phase of different composition from the granular phase, disintegrating the heat treated material and separating the disintegrated intergranular material from the grains of the alloy.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
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