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HIGH-GRADE ALLOY POWDER PRODUCTION

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9 Claims. (Cl. 75—28)

This invention relates to the production of high grade alloy powders.

In the production of high alloy steels such as stainless steel, high chromium and high nickel steels, and particularly in the casting industry, there are produced a considerable amount of borings, turnings and grinding residues. These residues contain high percentages of metallic components which in normal times are very valuable but which in the present circumstances are truly critical metals. These residues are produced, for the most part by machining or grinding castings. The residues produced are usually in finely divided form and are highly contaminated with extraneous and superficial material such as abrasives and bonding material from the grinding wheels. Because of this fine subdivision and high contamination these products, in the past, have not been profitably treated or processed to recover the contained metal values in commercially utilizable form.

A field of use for such products, assuming they could effectively be cleaned, is in powder metallurgy. In this field finely divided powders within a certain range of mesh sizes are positively desired. Such metal powders, in suitable particle size distribution may be compacted under pressure and sintered in a reducing atmosphere to produce formed articles of very satisfactory physical characteristics. In powder metallurgy fabrication one of the difficult and expensive steps in the process is the annealing of the powder. In the case of stainless steel powder compacts this is generally effected by a hydrogen anneal. In order that this be effective, i. e., so that the last traces of oxides be removed from the stainless steel particles, it is necessary to thoroughly dry or dehydrate the hydrogen. This operation is expensive and difficult to control.

It has now been found that these contaminated residues may be very cheaply processed so as to directly produce an annealed powder essentially free from surface oxides. As will be seen more fully hereinafter the present process is characterized by the fact that a plurality of useful functions or results are achieved in a single treating step which step itself is effected with the simplest apparatus and cheap and readily available reagents.

The raw material which is amenable to the new treatment consists of contaminated borings, turnings and grindings of alloys such as 18 chromium 8 nickel or any alloy such as iron-containing, nickel-containing, chromium-containing, copper-containing alloys, which either by heat treatment or by the introduction of a reactive element such as sulphur or the like, establishes an intergranular phase in the alloy which is of different metallurgical characteristics such that this intergranular phase may be disintegrated or corroded to thus liberate the matrix alloy as a powder. The type of material susceptible to treatment thus comprise alloys of the type described in copending application, Serial No. 413,367, filed October 2, 1941.

A salient feature of the improved process is the treatment of preliminarily cleaned scrap in a fused bath of such a character that it is utilized to dissolve or slag off and thus remove from the metal powder undesired contaminants; to impart or transmit heat to the metal within those critical ranges which will effect intergranular precipitation and to anneal the alloy material.

In order to more readily explain the invention its use for the production of stainless steel powder will be described. It is to be understood that this material is chosen to illustrate the principles involved and not as limiting the useful application of the process to this particular alloy.

As noted previously, the raw material treated according to the present process is rather highly contaminated. In the case of grinding residues containing 18–8 stainless steel these contaminants include extraneous and superficial contaminants including components of the grinding wheel such as silicon carbide, silica, alumina, organics and the like. In carrying out the process the crude residues are first treated to preliminarily clean them. This may be done by a variety of methods. For example, the crude material may be deposited in a water vat to float off dirt, wood chips and other such contaminants. The partially cleaned material then preferably is passed through a stamp, ball or hammer mill to reduce the size of the large particles. If desired, prior to the disintegration the crude scrap may be screened to take out the already fine material and thus reduce the load on the mills. The crushed material together with the original screenings are then screened through between a 100 and 200 mesh screen. This simple screening effects a considerable concentration of metal. For example, it is found that a very large percentage of the abrasives and oxides in the original scrap comes out in the —100 or —200 mesh tailings.

The coarse material produced by the above screening then comprises a stainless steel powder which is still contaminated with a certain percentage of oxides, abrasives and the like. This

may be further concentrated by removing additional amounts of the non-metallics as for example, on a Wilfley table. These latter products may be discarded or treated in any desired manner. The metallic concentrate will comprise a powdered material containing from about 90% or less to about 98% stainless steel. While the foregoing treatment is suggested it is to be understood that any other suitable cheap method of removing most of the non-metallics may be employed such as flotation methods, magnetic or electro-static separation and the like. It will be understood that even under the best conditions of preliminary separation the concentrated stainless steel powder will contain a certain amount of impurities or contaminants because certain of these are oxides which are tightly bonded to the steel particles and certain others are silicon carbide, alumina etc., from the grinding wheel which are strongly adhered to the steel particles.

The stainless steel concentrate produced by the above described, or any equivalent concentrating method is then treated in a special bath. In one modification of the invention the steel concentrate is treated in fused caustic soda. The temperature of the fused bath is raised to about 950° C. The bath is cooled slowly so as to hold the temperature within the range 400° C. to 800° C. for a period of a half hour or more. As will be observed the range 400° C.–800° C. is the carbide precipitation range. In this range intergranular precipitation occurs forming a relatively brittle and corrodable intergranular phase. It is found that intergranular precipitation is accelerated if the temperature is cyclically raised and lowered in this range, hence for accelerated intergranular precipitation the temperature of the bath preferably is aperiodically raised and lowered within this range. The stainless steel is held in the bath for a period sufficient to insure the desired degree of intergranular precipitation.

As indicated previously, during treatment in the fused bath other beneficial actions are obtained. Even with very effective preliminary separation the recovered stainless steel does contain a small amount of abrasive. This small amount practically precludes use of the powder for the production of metal compacts because the abrasive causes excessive wear on the dies and tends to weaken the compact. In the improved treatment described herein the fused bath acts as a chemical solvent for certain of these impurities and floats others off as a slag.

After the described heat treatment in the salt bath the steel powder is removed and contacted with a liquor, such as a Strauss solution which dissolves the intergranular phase with the concomitant production of the stainless steel in finely divided powder form.

After such treatment the steel powder may be given an acid pickle, as for example, 10% nitric acid. This serves to dissolve any copper plated out from the Strauss solution as well as to brighten and passivate the stainless steel powder.

It is particularly to be observed that the stainless steel powder thus produced is not only essentially free from abrasive oxides and the like, but also is in annealed condition, in other words, the improved salt bath treatment eliminates the separate hydrogen or similar anneal heretofore found necessary. The product after being washed of adherent acid and dried may then be utilized for the production of powder metal compacts, large remelting briquettes, for use as a metal spray or for any other desired purposes.

It is clearly to be understood that the novel concept of utilizing a salt bath to effect the disintegration of metal particles while concomitantly removing impurities and annealing the powder is of broad applicability and may be used with a number of different types of alloys.

In a modified form of the process a small quantity of sulphur may be added to the bath. Such a bath will not only intergranularly corrode 18-8 stainless steel but also a whole group of higher nickel-chromium-iron, nickel-iron, nickel-copper alloys and the like. Thus a bath composed of fused caustic and up to about 1% of sulphur or a bath composed of the order of 83% barium chloride and about 17% of barium fluoride may be employed. The latter bath which melts at 844° C. may be heated to a temperature of 1010° C. Concentrated high nickel scrap, from which most of the abrasives and other contaminants have previously been removed by wet concentration, dry concentration and the like, is deposited in the bath and kept in the bath at such temperature for a period of a half an hour. Sulphur is then added to the bath in amounts sufficient to produce intergranular embrittlement. In usual circumstances this need not be more than 1% of sulphur. The bath is maintained at a temperature of approximately 900° C. for a few hours and the metal product dumped and quenched in a pickling solution which will dissolve all excess salt, cause intergranular attack and brighten the metal. While after such treatment each particle of the alloy is only partially broken up into its grains it can be pressed with ease.

As will be appreciated the character and composition of the bath may be varied and modified so as to insure optimum conditions for a given scrap which is to be treated. Similarly, the use of sulphur is described herein as representative of any similar addition agent i. e., one which functions to establish and/or accelerate an intergranular phase of differential physico-chemical characteristics as compared to the metal grain itself. While the processes described involve the removal of this formed intergranular phase by means of preferential corrodants it will be understood that the separation may be effected by other methods, as for example, by milling and mechanical separation of the powdered intergranular material from the grains of the alloy.

Thus while preferred modifications of the invention have been described it is to be understood that these are given didactically to illustrate the fundamental principles involved and not as limiting the useful application of the invention to the described embodiments.

I claim:

1. A method of directly producing clean annealed alloy steel powder from contaminated alloy powder which comprises heating the powder in annealing range in a fused salt bath which bath is capable of removing the superficial contaminants.

2. A method of producing clean annealed alloy steel powder from superficially contaminated alloy steel particles which are susceptible to intergranular corrosion or embrittlement which comprises heating the particles in a fused bath and at a temperature which will effect the formation of an embrittled or corrodible intergranular phase in the steel and which bath

removes the contaminants, maintaining the alloy steel in contact with the bath at a temperature sufficiently high to anneal the steel, removing the treated material from the bath and separating the said intergranular phase from the alloy grains.

3. A method of annealing and cleaning nickel-chromium type stainless steel powder which comprises contacting the powder with a fused salt bath maintained at annealing temperatures for a time sufficient to anneal the powder and to dissolve superficial non-metallic contaminants.

4. A method of annealing and cleaning stainless steel powder which comprises contacting the powder with a fused salt bath maintained at annealing temperature for a time sufficient to anneal the powder and to remove superficial non-metallic contaminants, removing the treated powder from the bath and removing excess salt therefrom.

5. A method of disintegrating alloys which are susceptible to intergranular embrittlement by the action of sulphur at elevated temperatures which comprises contacting such alloys with a fused salt bath containing sulphur for a period of time sufficient to establish such intergranular phase, removing the treated material from the bath and separating the granular from the intergranular material.

6. A method of disintegrating and annealing alloys of the stainless steel type which are susceptible to intergranular corrosion which comprises contacting such alloys with a fused salt bath maintained at a temperature which induces intergranular carbide precipitation and for a period of time sufficient to effect substantial carbide precipitation, removing the material from the bath and separating the intergranular phase from the alloy grains.

7. A process according to claim 6, in which the separated alloy grains are treated with a brightening and passivating agent of the type of nitric acid.

8. A method of producing ferrous alloy powders which are susceptible to intergranular embrittlement by the action of sulphur at high temperatures which comprises treating the alloy in a sulphiding fused salt bath.

9. A method of removing superficial contaminants from and annealing stainless steel powder which comprises heating the powder in a fused caustic soda bath at annealing temperatures.

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