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PRODUCTION OF CHROMIUM-ALLOYED CORROSION-RESISTANT METAL POWDERS AND RELATED PRODUCTS

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FIG. 1.

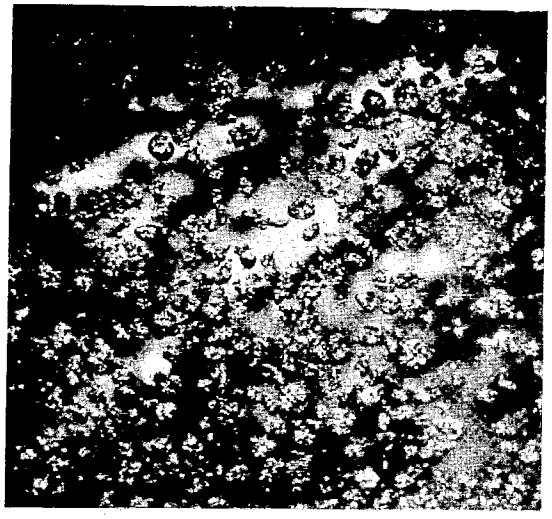
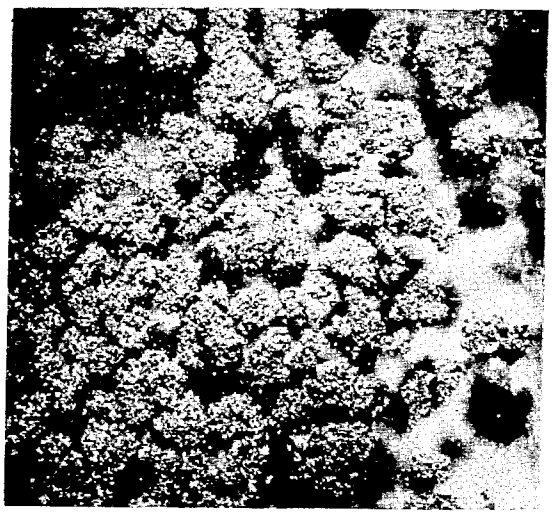


FIG. 2.



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PRODUCTION OF CHROMIUM-ALLOYED CORROSION-RESISTANT METAL POWDERS AND RELATED PRODUCTS

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8 Claims. (Cl. 75—0.5)

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This invention relates to readily compactible and moldable metal powders which resist corrosion; shaped bodies of such powders, and methods for producing the same, some aspects of the invention being of a broader scope.

Among the objects of the invention are powders of metal particles which are in a readily deformable plastic condition, and may be compacted into relatively strong metal bodies with relatively low pressures, at least the surface layer of the metal powder particles having alloyed therewith chromium deposited thereon from a gaseous or liquid chromium compound at an elevated temperature.

A particular object of the invention is such readily compactible and moldable metal powder containing essentially powder particles of at least one metal of the group consisting of iron, nickel, and cobalt, and of mixtures and alloys of said metals, which particles are in a readily deformable, relatively soft plastic condition, at least the surface layer of said particles having alloyed therewith chromium which has been deposited thereon at an elevated temperature from a gaseous or liquid chromium compound.

Other objects of the invention include compacted bodies made of such surface-alloyed powder particles, and economical production of such powder particles, and economical production of compacted bodies from such powder particles of the invention.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications therof, reference being had to the accompanying drawings, wherein:

Fig. 1 is a greatly enlarged photograph of a sample of powder particles of the invention made of sponge iron powder; and

Fig. 2 shows a similar photograph of powder particles of the invention made from a mixture of iron oxide and nickel oxide powders.

For years past various corrosion-resistant products such as gears, valve parts, bearings, filters, and the like, have been made of stainless steel powders by powder metallurgy techniques. The stainless steel powders generally used for such bodies have been obtained from previously prepared stainless steel ingots, for instance, by subjecting a stainless steel ingot to grain boundary corrosion followed by disintegration; or by melting a stainless steel ingot and atomizing it in the molten state. The so-produced particles of such stainless steel powders are of high density and hardness, and require high-molding pressure of at least 40 to 45 t. s. i. (tons per square inch), which is much too high for economical production of molded products, and results in rapid wear and frequent brake-down of the molding dies. As a result, the production of molded products from stainless steel powders has found only limited use.

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What has been said above about stainless steel powder, which is an alloy of iron, nickel and chromium, applies also to various other generally similar commercially available alloys, such as alloys of iron, cobalt and chromium, of iron, nickel, molybdenum, tungsten and chromium, and of generally similar alloys which are used in heat-resisting bodies, electric heaters, magnetic bodies and in corrosion-resistant hot-strength bodies.

According to the basic concept of the invention, the foregoing difficulties which were encountered in the production of corrosion-resistant ferrous metal bodies by powder metallurgy techniques are overcome by the provision of a readily compactible and moldable metal powder of ductile and relatively soft ferrous powder particles, at least the surface layer of the powder particles having combined therewith chromium, which has been deposited thereon from a gaseous or liquid compound at an elevated temperature, the particles being sufficiently soft and plastic as to make it possible to compact them with a relatively low pressure, for instance, only 25 to 30 t. s. i. into bodies of even greater strength than molded bodies made of prior stainless steel powder.

Various commercially available soft, plastically readily deformable iron powders are suitable for producing corrosion-resistant soft moldable metal powders of the invention. Among such available and suitable soft iron powders is sponge iron powder having a carbon content of .1 to .2% (unless otherwise specifically stated, all proportions are given herein by weight) electrolytically produced iron powder, carbonyl iron powder, eddy mill iron powder, and atomized molten iron powder of similar carbon content. The following impurities present in such available powders, to wit, .3% Mo, .2% Si, and other minor impurities usually present therein, do not impair their usefulness for practicing the invention.

In addition, many relatively hard and difficult to compact fine iron powders containing up to about .2% carbon will, in general, when subjected to the chromium-alloying process of the invention herein described, become softened and

acquire characteristics which render them readily moldable.

In accordance with a phase of the invention—based on the original concept of producing chromium-alloyed soft iron powder—relatively soft powder particles of different metals, to wit, one or more metals of the group including iron, nickel and cobalt, are combined in a proper proportion, and a proper proportion of chromium from a gaseous or liquid chromium compound is deposited on and diffused in such powder particles of the different metals so as to yield a soft powder body with chromium in the proportions required for producing alloy bodies of the desired characteristics.

Any of the known methods for depositing chromium from a gaseous or liquid compound on the surface of a metal body heated to an elevated temperature below the melting temperature of the body, and of chromium, may be used for depositing on and diffusing chromium into metallic powder particles in accordance with the principles of the invention.

Among such known chromium-alloying processes, one that was found particularly suitable for practicing the invention, involves an exchange or displacement reaction of the metal of the treated body with the chromium constituent of a gaseous or vapor phase of a chromium halide, such as chromous chloride gas, at an elevated temperature in the range between about 900° to 1200° C. in accordance with the equation:

$$CrCl_2 + M \rightarrow Cr + MCl_2 \quad (1)$$

wherein M represents the metal of the chromium-alloyed body.

In such process, the chromium of the chromous chloride gas replaces the metal on the surface of the treated body causing the chromium deposited on the surface of the body to alloy therewith and to diffuse into its interior while the gaseous chloride compound of the displaced metal escapes.

Instead of chromous chloride, other chromium halides may be used for effectively carrying out the chromium-alloying process in accordance with the principles of the invention.

In accordance with one phase of the invention, the soft iron particles are first sintered into sinter cake lumps within a reducing atmosphere, such as dry hydrogen, or dry cracked ammonia at an elevated temperature so as to produce a porous sinter cake of low density not higher than about 4 g./cc., and of low strength, not higher than a modulus of rupture of about 6500 p. s. i. The powder particles of such sinter cake may be readily surface-alloyed with chromium. To this end, the sinter cake may be broken up into lumps which are then packed into a chromium-alloying pack and heated to elevated temperature, so as to cause chromium from chromous chloride gas to be deposited on the surface of the powder particles, and diffused into the interior of the particles.

Any of a variety of known chromium-surface-alloying processes may be used for this purpose. By way of example, the sinter cake lumps may be packed in a pack containing ferro-chromium and a stream of a gaseous mixture of hydrogen and HCl is passed through the pack in which case the chromizing agent, that is chromous chloride gas, is produced within the pack. Alternatively, the pack may be impregnated with separately prepared chromous chloride, in which case the hydrogen chloride gas may be at least partially omitted from the gaseous stream and only hydrogen gas passed through the pack. As another alternative procedure, the sinter cake lumps are packed in a pack of porcelain powder, ferro-chromium powder, and a chromium chloride compound, and enclosed within a sealed envelope which is heated to produce the desired chromium-surface-alloying action.

As a still further alternative procedure, the sinter cake lumps may be immersed in a molten salt bath containing chromous chloride and subjected therein to a chromium-surface-alloying treatment at an elevated temperature. By way of example, a suitable bath composition for the latter treatment may consist of 30% $CrCl_2$, 50% $BaCa_2$, and 20% NaCl. By keeping the bath heated to a temperature in the range from about 900° to 1500° C., from about 3 to 10 hours, the desired chromium-surface-alloying action will be produced. The $CrCl_2$ content of such bath may be replaced by elements which generally are $CrCl_2$, in which case an equivalent amount of $CrCl_3$ and chromium metal is included in the bath. In all the foregoing chromium-surface-alloying treatments, the chromium-alloying reaction is represented by the Equation 1 given above.

The chromium-alloying process does not materially increase the density and strength of the sinter cake lumps. As a result, the chromium-alloyed sinter cake lumps may be readily broken up into powder particles of the required size range, and high degree of softness which makes it possible to compact such chromium-surface-alloyed powders under a compacting pressure of only 50,000 p. s. i., into strong green compacts having a modulus of rupture of 400 p. s. i., and higher.

In accordance with another phase of the invention, powder particles of the oxides of either iron, nickel and cobalt, or mixtures of such oxides, or of metals and oxides of this metal group, with or without an additional mixture of powders of molybdenum or tungsten or both—either as free metals or in the form of oxides—are sintered into porous sinter cake lumps within a reducing atmosphere such as dry hydrogen or dry cracked ammonia at an elevated temperature so as to reduce the oxides and produce a sinter cake of low density not higher than about 5 g./cc., and low strength not higher than a modulus of rupture of about 7,000 p. s. i. A convenient way for producing such sinter cake lumps is to mix the powders of the metal oxides with a lubricant and binder and pellet the mixture into pellets which are then reduced and sintered to produce sinter cake pellets or lumps of the required low density and low strength. The sinter cake pellets or lumps so obtained are then packed into a chromium-alloying pack, and their powder particles are surface-chromium-alloyed in a manner similar to the chromium-alloying of the sinter cakes of soft iron powder. The resulting chromium-alloyed sinter cake pellets have the required low degree of density and strength. As a result, they may be broken up into minute surface-chromium-alloyed powder particles of the required degree of range of sizes and low degree of softness for making it possible to compact them into strong green bodies having a modulus of rupture of at least 400 p. s. i. at a pressure of only 50,000 p. s. i. The surface-chromium-alloyed powders produced in accordance with the invention from a mixture of oxides

of the different metals will yield a surface-alloyed powder body, the individual particles of which are alloys of the different metals corresponding to the different metal oxides and the proportion of chromium deposited on the sinter cake pieces.

Without thereby limiting the scope of the invention, and in order to enable those skilled in the art to readily practice the invention, there will now be described one practice of the invention, there will now be described one example of a satisfactory procedure for producing a corrosion-resistant soft iron powder of the invention from commercially available sponge iron powder having a carbon content of about .15%. A typical commercial powder of this type used in the process contained a mixture of minute powder particles having the following particle-size distribution typical of moldable metal powders: 21% —100, +150 mesh; 30% —150, +200 mesh= 13% —200, +250 mesh; 14% —250, +325 mesh, and the balance —325 mesh powder.

The powder is treated to sinter it into a porous cake mass of low density, and thereby facilitate surface-alloying of the powder particles with chromium. This may be done by depositing a layer of powder of about ⅛ to ¼ inch thick into sinter boats of suitable metal such as a heat-resistant iron-chromium sheet metal without in any way compacting the powder. The interior surface of each sinter boat is coated with a stick-suppressing or release medium such as a water suspension of magnesium hydroxide to permit ready separation of the sintered powder body from the boat after the sintering operation. The powder within the boats is then treated within a furnace in a reducing atmosphere of dry hydrogen or purified cracked ammonia at a temperature of about 800° to 1050° C. for one-half to three hours, and then permitted to cool to room temperature. In general, such treatment in the range of about 900° to 1000° C., such as 950° C., for one hour is sufficient for sintering the powder into a sinter cake having a density of 1.7 to 4 g./cc., which is readily frangible into lumps or pieces suitable for packing into a chromium-alloying mass. A good way for carrying on the foregoing sintering treatment is to push the powder containing boats through a tunnel furnace from one end to the other, the heat treatment being followed by cooling which is carried out as a part of a continuous treatment as the boats are moved from one end to the other end of the furnace.

After completion of the sintering treatment, the sinter cakes are removed from the boat, and broken into fragments of a size suitable for packing in a chromium-alloying pack. The sinter cake pieces or lumps are thereupon packed within a chromous chloride producing pack mass, and placed within baskets of suitable heat-resistant metal such as a chromium-nickel-iron alloy. The pack may consist, for instance, of 50% by volume ceramic lumps, such as porcelain pieces, and the balance a chromium alloy such as ferro-chromium alloy. An alternative chromium-alloying pack which was found highly effective consists of a mixture of titanium oxide with ferro-chromium. Good results are obtained with such pack consisting of about 20% titanium oxide, by volume, the balance consisting of ferro-chromium, containing about 70% chromium.

The treating baskets containing the sinter cake lumps packed, for instance, with titanium oxide and ferro-chromium, are placed in a retort and heated to a temperature in the range between 900° and 1250° C., and a stream of hydrogen and hydrogen halide gas, such as hydrogen chloride gas, is passed through the retort for producing reactions causing chromium atoms to be deposited on the powder particles, and to diffuse into the interior of the particles, and alloy therewith.

In such surface-alloying treatment, the hydrogen chloride gas passing through the retort interacts with the ferro-chromium to form chromous chloride gas. The chromium of chromous chloride replaces the metal on the surfaces of the treated powder particles primarily by the exchange reaction. Part of the chromous chloride gas is absorbed by the packing material, such as the ceramic material or the titanium oxide in the pack.

In the particular example herein described, the pack-treatment baskets were of circular shape, and had an outside diameter of 22", and a height of 10". Four such packed baskets were stacked within a closely fitting retort about 60" high. The packing material consisted of TiO_2, 20% by volume, the balance ferro-chromium a closely fitting retort about 60" high. The packing material consisted of TiO_2, 20% by volume, balance ferro-chromium containing 70% chromium. During the initial part of the chromium-surface-alloying treatment, purified dry hydrogen was caused to flow through the enclosed retort space at a rate of 40 cubic feet per hour, while the temperature was raised to about 950° C. The flow of pure hydrogen was thereafter continued at a rate of 20 cubic feet per hour, for four hours at the same temperature of about 950° C. Thereafter, the baskets within the retort were subjected to a succession of five treatment sequences, at about 950° C., each treatment sequence lasting six hours, and consisting of; (*a*) passing through the retort at a rate of 20 cubic feet per hour a mixture of 20 parts of hydrogen and 3 parts of HCl gas for one hour, followed by (*b*) passing pure hydrogen at the same rate for one hour, followed by (*c*) passing the same mixture of hydrogen and HCl gas as in (*a*) for one hour, followed by (*b*) passing pure hydrogen at the same rate for three hours. After a succession of six such treatment sequences of six hours duration each, the treatment was ended by turning off the heat and permitting the retort with its contents to cool while continuing the flow of hydrogen through the retort space until the temperature of its contents was brought down to about room temperature.

Upon completing the foregoing chromium-surface-alloying treatment, the treated metal powder pieces are removed from the baskets, and comminuted by crushing to powder, for instance, in a disc crusher.

Without in any way limiting the scope of the invention, and in order to enable those skilled in the art to readily practice the invention, there are given below the results obtained by subjecting packed iron powder particles to the specific 30-hour chromium-alloying treatment described above.

The resulting chromium-alloyed powder contained 8.5% +100 mesh; 35.5% —100, +150 mesh; 28% —150, +200 mesh; 10% —200, +250 mesh; 9% —250, +325 mesh; and 9% —325 mesh powder. The apparent density of the powder was 2.56 g./cc., and the weight loss due to the hydrogen treatment (hydrogen loss) was .053%, carbon content .045%, titanium content .2%, and chromium content 15%; balance iron. The chro-

mium-alloyed powder was then compacted into test bars and tested for "green strength."

Figure 1 is a photograph of a sample of such powder particles of the invention greatly enlarged on a scale 30 to 1.

The table below gives the modulus of rupture (also called transverse rupture strength) calculated from breaking tests, of chromium-alloyed powders, compacted into test bars under pressures of 25, 35 and 45 t. s. i. designated in the table as C. A. P. The table also shows the comparative modulus of rupture of compacted green bars made from two commercially available stainless steel powders designated in the table as SH 18–8, and SV 18–10 representing stainless steel powders with a chromium and nickel content of 18%–8% and 18%–10%, respectively.

Modulus of rupture of three green test bars pressed at 25, 35 and 45 t. s. i.

Powder	C. A. P. M. R. p./in.²	SH—18–8 M. R. p./in.²	SV—18–10 M. R. p./in.²
25 t. s. i.:			
1	920	61.6	39.2
2	935	94.5	79.3
3	830	84.0	----------
35 t. s. i.:			
1	1,630	145	231
2	1,680	120	405
3	1,630	168	----------
45 t. s. i.:			
1	1,818	294	368
2	1,840	284	605
3	1,615	406	----------

The foregoing test results show the characteristic distinction and the marked superiority in green strength of bodies produced from surface-diffusion chromium-alloyed iron powders of the invention as compared with green bodies produced from available stainless steel powders. The chromium-alloyed powder particles of the invention retain their spongy character, have a tentacle-like shape, and they have a lowered carbon content. Such compacted green bodies produced from soft, moldable chromium-alloyed iron powder of the invention, as well as the powder itself, exhibit excellent corrosion-resistance under prolonged salt-spray tests, and they also resist attacks by 30% HNO_3, cold or hot.

It should be noted that similar results are obtained with other types of soft, plastically deformable iron powders. Furthermore, the invention is not limited to metal powders having the particular size distribution given in the example described above, but may be practiced with soft powders of any particle size distribution of the type used for producing bodies by powder metallurgy techniques.

The results of rupture test given in the foregoing table were obtained by test equipment and test methods described by J. P. Scanlan and R. P. Seelig in Powder Metallurgy Bulletin, vol. 4, p. 128 (1949) with each test bar 1½'' long, $\frac{7}{16}$'' wide, and ¼'' thick.

The tests shown in the table are representative of the characteristic distinguishing chromium-surface-alloyed ferrous powders of the invention over corrosion-resistant prior art powders of similar composition. Thus, soft chromium-surface-alloyed and corrosion-resistant ferrous powders of the invention differ from heretofore available corrosion-resistant powders of generally similar composition by the fact that green compacts made from powder of the invention have a materially greater rupture strength, at least 2 to 4 times greater than similar green powders of similar composition and corrosion-resistance.

A distinguishing characteristic of the corrosion-resistant-chromium-surface-alloyed soft ferrous powders of the invention, is the fact that, when compacted into a green test bar body of the dimensions given above, under pressure of 25 t. s. i., with no lubricant, such compacted green body exhibits a modulus of rupture several times greater than a similar body produced by compacting prior art corrosion-resistant powders of the same composition, under the same pressure. In particular, such green test bar compacts made of powders of the invention have a modulus of rupture of at least 200 pounds per square inch, the modulus of rupture being in fact in all cases at least 400 pounds per square inch, and higher.

In producing surface-alloyed soft, plastically readily deformable ferrous powders of the invention, it is important that at all stages of the processing operations, the powder particles should not be subjected to any material work hardening forces. Thus, for instance, it is essential that in initially sintering the soft iron powder particles into porous sinter cake fragments suitable for packing into the chromium-alloying pack, the powder which is to be subjected to the initial sintering action should not be compacted under any substantial pressure unless special precautions are taken, such as the addition of substantial amounts of volatile material, for example organic lubricant and/or binder material. If a substantial compacting pressure, even as low as 5 t. s. i., is initially applied to such soft ferrous metal powder (Fe, Ni, Co) in preparation for the initial sintering process which precedes the chromium-alloying treatment, such chromium-alloyed sinter fragments will acquire a relatively great density and strength, and large forces will be required for crushing them, and the resulting powder particles will be severely work hardened. Unless the sinter cake fragments which are to be subjected to the chromium-alloying treatment are of low density and strength—obtainable if the powder particles subjected to the preliminary sintering action have not been initially compacted under substantial pressure—the crushing energy required for pulverizing the chromium-alloyed sinter cake fragments would be so large that the resulting chromium-alloyed powder particles would be distorted in shape and work hardened, making it necessary to apply undesirably large pressure for compacting them into bodies of the required final shape.

In other words, when producing surface-chromium-alloyed soft ferrous powders of the invention, it is essential that the sintered powder cake fragments or lumps— produced in preparation for the chromium-alloying treatment—should have a low density, and correspondingly low strength, so as to minimize any work hardening imparted to the powder particles when pulverizing the sintered powder cake fragments or lumps following the chromium-alloying treatment, thus resulting in powder particles exhibiting only minimized work hardening. Furthermore, it is also essential that the sintered powder cake fragments or lumps—produced in preparation for the chromium-alloying treatment—should have high porosity so that they are permeable to the chromium halide gases, by means of which the chromium-alloying treatment is carried on.

As explained above, the proper range of the density of the sinter cake lumps—produced in preparation for chromium-alloying treatment—is about 1.5 to 4.0 g./cc. The modulus of rupture of such sinter cake lumps is correlated to their density, being about 50 p. s. i. for sinter cake lumps having a density of 1.7 f./cc. and increasing to about 6500 p. s. i. for sinter cake lumps having a density of 4.0 g./cc.

Furthermore, as long as the sinter cake lumps, produced in preparation for the chromium-alloying treatment—are of low density and have a low modulus of rupture in the ranges set forth above—they will also have the same density and the same modulus of rupture after being subjected to the chromium-alloying treatment whereby chromium is surface-alloyed with the individual powder particles of such sinter cakes.

Accordingly, to obtain chromium-alloyed powders of the invention, it is sufficient to control the density and/or modulus of rupture of the sinter cakes or sinter cake lumps produced in preparation for the chromium-alloyed treatment. As long as the density of such sinter cake lumps is not more than about 4.0 g./cc., and their modulus of rupture is not more than about 6500 p. s. i. they will, after the chromium-alloying treatment, remain of sufficiently small density and strength as to permit their pulverization without material work hardening of the powder particles. As a result, the chromium-alloyed powder obtained from such sinter cakes will have the desired high degree of softness and plastic deformability as to make it possible to compact such powders into green compacts having a modulus of rupture of at least 200 p. s. i. and higher.

By sintering such green compacted bodies of chromium-alloyed soft iron powder of the invention, compacted with only a relatively small pressure, there are obtained bodies having the same strength as those produced by compacting and sintering prior-art stainless steel powders of similar composition which have been compacted with much higher pressure. Good results are obtained by sintering green compacted bodies of such chromium-alloyed powder at a temperature in the range of 1200° to 1400° C. within a protective atmosphere, such as dry hydrogen, or of purified cracked ammonia. It is also desirable to maintain the protective atmosphere at a dew point of about —50° C. or below. Such low dew point asmosphere may be obtained by a suitable getter such as pure chromium powder or ferrochrome powder (70% chrome) mixed with aluminum oxide (Al_2O_3).

By way of example, a green test bar of the specific chromium-alloyed iron powder of the invention, having properties set forth above, was compacted under pressure of 25 t. s. i. and then sintered at 1300° C. for one hour within a protective atmosphere in the manner described above. The so-sintered bar exhibited a shrinkage of 8.23%, and had a density of 6.68 g./cc. It had Rockwell hardness F 37.5, yield point 21,600 p. s. i., ultimate tensile strength 26,450 p. s. i., elongation 8.5%, reduction in area 4.06%.

The test bar, sintered in the above manner, repressed or coined at a pressure of 35 t. s. i., and resintered for another hour under the same sintering conditions, exhibited a shrinkage of 1.73%. The resintered bar had Rockwell hardness F 25.5, yield point 26,900 p. s. i., ultimate tensile strength 45,000 p. s. i. elongation 20.5%, reduction in area 19.0%. Each such sintered body exhibited excellent resistance to corrosion under prolonged exposure to salt-spray as well as to hot and cold 30% HNO_3.

Green compacted bars made from soft chromium-alloyed iron powder of the invention may be utilized as a very effective electric contact material, as bearing material or the like, by infiltrating the green compacted bar with silver, copper and alloys thereof. By way of example, a green bar produced by compacting the specific chromium-alloyed iron powder of the invention having the specific properties set forth above, and compacted under a pressure of 25 t. s. i., and having a density of 5.47 g./cc., was infiltrated with pure fine silver at 1220° C. for one hour in a protective atmosphere of dry hydrogen. Such silver-infiltrated bat exhibited an infiltration shrinkage of 4.42%, a density of 7.59 g./cc., a resistance of 17.9 microhms—cm. It had Rockwell hardness F. 63, yield point 22,800 p. s. i., ultimate tensile strength 37,000 p. s. i., elongation 9.3% and reduction in area 10.5%.

A similar body compacted under a pressure of 35 t. s. i., and infiltrated with silver in the same manner, had a Rockwell hardness F 75.5, infiltration shrinkage 7.9%, yield point 27,—p. s. i., ultimate tensile strength 39,600 p. s. i., elongation 10.5%, reduction in area 9.9%. It is thus seen that such silver-infiltrated green compacted powder bodies of the invention exhibit excellent physical properties, and the infiltration may be effected at relatively low temperature in generally available furnaces and atmospheres. Such silver-infiltrated bodies have also the desired dimensional stability and exhibit excellent corrosion-resistance under prolonged salt-spray.

Chromium-alloyed iron powders of the invention of the type described above, are also very useful for producing corrosion-resistant bodies of relatively high hot-strength suitable for applications requiring corrosion-resistance at elevated oxidizing temperatures, as well as high strength. To this end, the shaped sintered compacts of chromium-alloyed readily moldable powders of the invention of the type described herein are infiltrated at an elevated temperature, such as 1100°–1250° C. with an infiltrant of copper, or a suitable copper alloy.

By way of example, a green bar of the specific chromium-alloy iron powder of the invention set forth above, compacted under pressure of 35 t. s. i., and having a green density of 5.98 g./cc. was sintered for one hour at a temperature of 1300° C. in a protective atmosphere in a manner specifically described in the previous example. The resulting sintered body having a density 6.68 g./cc. was infiltrated with a copper base alloy containing about 90% copper, 2% iron, 8% manganese, .½% titanium. The infiltration was carried on at a temperature of about 1200° C. for one and one-half hours in an atmosphere of purified cracked ammonia, with a pure chromium getter present to keep the dew point of the atmosphere at the desired low temperature. The resulting infiltrated body had a density 7.95 g./cc., yield point 87,700 p. s. i., ultimate tensile strength 105,250 p. s. i., elongation 6.3%, reduction in area 8.3%. The so-obtained body thus exhibited excellent dimensional stability, and excellent resistance to corrosion under prolonged exposure to salt-spray and relatively hot oxidizing gases.

In other words, sintered compacted bodies of the invention, after infiltration with the copper

alloy, have high strength, and dimensional stability, and they also have excellent resistance to corrosion.

According to a further phase of the invention, surface-diffusion, chromium-alloyed, soft, readily plastically deformable iron powders are produced in a very economical way from iron oxides, such as black mill scale containing principally iron oxides (Fe_3O_4 and FeO) which is formed when rolling and forging iron and steel. The iron-oxide mill scale is treated by subjecting it in a pulverized state to a reduction process, and then sintering the resulting iron powder particles into porous pieces, such as lumps suitable for subjecting them to the subsequent chromium-alloying processes in the manner described above. If it is desired to combine with such iron powder additional elements such as nickel, and/or cobalt, the proper proportions of powders of the oxides of such additional metal are mixed with the iron oxide powder before subjecting the powder mixture to the initial reduction and sintering treatment.

By way of example, there will now be described a satisfactory process for producing a chromium-alloyed powder containing soft moldable iron and nickel alloy powder partially chromium-alloyed by surface-diffusion of chromium in accordance with the process of the invention. Powder particles of iron oxide mill scale containing essentially Fe_2O_3 and FeO are mixed with powdered nickel oxide and lamp black, and ball milled into a powder of —100 mesh. As an example, 200 parts of the mill scale are mixed with 22.6 parts nickel oxide and one part of lamp black. The powder mixture is then ball milled to powder of —100 mesh, and placed in treatment boats of heat-resistant metal coated on the interior with a stick-suppressing medium, and treated in a furnace under reducing atmosphere such as dry hydrogen or cracked ammonia at a temperature in the range between 800° and 1100° C. for one-half to three hours, and then permitted to cool in the same atmosphere. Satisfactory results are obtained by such treatment carried on at a temperature of about 950° C. for one hour. The powder mix may be pelleted into pellets before subjecting it to the foregoing treatment, or it may be placed into the treatment boat as a thin powder layer about ⅛ to ¼'' deep, in which case the resulting sinter cake produced by the reducing heat treatment is broken up into lumps. The powder is formed into pellets by mixing it with a lubricant and binder so that the resultant mixed powder may be readily made up into small porous pellets, for instance, of cylindrical shape, having a diameter of about ¼ to ½ inch, and the same height, with a pellet density of 3 to 4 grams per cubic centimeter. Any suitable lubricant and binder which decomposes and/or volatilizes at elevated temperatures of about 800° to 900° and above, may be used as a lubricant and binder in making such pellets. For instance, high fatty acids such as stearic acid, and salts of stearic acid such as zinc stearate and the like are suitable for use as a lubricant. Carbohydrates such as dextrose dissolved in water, or camphor dissolved in alcohol may be used as a binder in making such pellets.

The reducing and sintering treatment carried out at an elevated temperature in the manner described above causes the different metal constituents of the different powder particles, i. e. of nickel and iron powder to mutually diffuse with each other, and the individual powder particles become actually alloyed.

In the particular example referred to herein, the reducing and sintering treatment was performed at a temperature of about 1050° C. for one hour, resulting in sinter cake pellets having a density about 2.3 g./cc., with a weight loss of about .5%. The reduced sintered powder pellets were then packed in baskets within a chromous chloride producing mass, and subjected to a chromium-alloying diffusion treatment in a manner similar to that described in connection with the fragmented sinter cakes of sponge iron powder above, except that the contents of each basket was subjected to a continuous chromium-alloying treatment of an overall duration of about 52 hours as follows: The same initial treatment including the four hours during which hydrogen only was passed through the retort space followed by eight treatment sequences of six hours each, and each sequence being identical with the treatment sequences applied to the sponge iron powder as described above. The foregoing chromium-alloying treatment was carried on at a temperature of 900° C., and the baskets were then cooled in an atmosphere of flowing hydrogen.

The so-chromium-alloyed sinter cake fragments were then crushed into powder which had the following physical properties: Apparent density 1.90 g./cc., flow 43.6 second per 50 grams, hydrogen loss .012%, iron content 74.85%, nickel 8.6%, chromium 16.5%, titanium .2%, carbon .05%. The so-chromium-alloyed powders when compacted into green test bars under a pressure of 25 t. s. i. had a calculated modulus of rupture of 960 p. s. i.; when compacted under a pressure of 35 t. s. i., a modulus of rupture of 1800 p. s. i.; and when compacted under a pressure of 45 t. s. i., a modulus of rupture of 2580 p. s. i.

The iron nickel alloyed powder particles which have been subjected to the chromium-alloying treatment in the manner described above, when compacted into shaped bodies and then sintered and/or infiltrated, exhibited superior physical characteristics in a manner analogous to the sintered and/or infiltrated compacted bodies from sponge iron powder described above.

Bodies similar in properties to those exhibited by known alloys containing one or more of the metals of the group including iron, nickel, cobalt, with or without modifying additions, such as molybdenum, tungsten, in combination with chromium, may be produced in a manner analogous to that described in connection with the mixed iron and nickel powders. To this end, powders of the different selected metals other than chromium, are mixed in proper proportion and the mixed powders are subjected successively to the reducing and chromium-alloying treatment in a manner similar to the treatments described above as applied to the mixture of powders of the oxides and nickel.

By prolonging the chromium-alloying treatment, or by subjecting the chromium-alloyed sinter cake pieces, such as pellets or cake fragments, to a suitably long additional heat or sintering treatment, the chromium content of the outer layers of the powder particles of such bodies may be caused to diffuse to any desired degree toward the interior of the individual powder particles, and thus cause such powder particles to be substantially uniformly alloyed with chromium. Furthermore, such prolonged

diffusion treatment causes the different metals of the individual powder particles, as well as their chromium content, to mutually diffuse, thereby giving the resulting body the characteristics of the desired metal alloy composition.

The invention thus makes it possible to produce in an economical way from readily moldable powders of the different metals, such as iron, nickel, cobalt, molybdenum, tungsten, and the like, bodies of desired complicated shape having properties heretofore obtainable only by making such shaped bodies out of ingots produced by alloying the different metals in a molten state. In contrast therewith, in order to make similar shaped bodies by prior-art practice, the alloy metal ingot combining the different metals had to be shaped by machining operations, or in the alternative, the alloy ingot had to be first pulverized and the hard powder particles of such alloy ingot used for making the desired shaped body by a more difficult powder metallurgy process.

There will now be described by way of example, one satisfactory procedure for producing a chromium-alloy powder body containing in desired proportions iron, nickel, tungsten, molybdenum, from the powder oxides of these different metals by subjecting the mixtures of the different oxide powders to a combined reducing and sintering treatment which also causes alloying of their different metallic constituents, followed by a chromium-alloying treatment in a manner analogous to the treatment described above as applied to powder mixtures of iron and nickel oxide powders.

Powders of nickel oxide, iron oxide (mill scale), molybdenum oxide (MoO_3) are mixed in proper proportions so that after the reducing and chromium-alloying treatments, the resulting chromium-alloy powder will contain the different metals in proportions corresponding to the desired end product. The powders of the different metal oxides are ball milled to bring them down to a proper size, such as —100 mesh, and then subjected to a reducing and sintering treatment in a manner similar to that described in connection with the reducing and sintering treatment applied to the mixture of mill scale powder with nickel oxide powder. The ball-milled mixture of the powders of iron oxide, nickel oxide, molybdenum oxide, and lamp black is thereupon first subjected to a reducing treatment at about 600° C. for one hour in a protective atmosphere of dry hydrogen for partially reducing the iron oxide, nickel oxide, and for reducing MoO_3 to MoO_2. The treatment temperature is then raised to about 1000°–1150° C., and the treatment continued for another hour to reduce all remaining oxides to a metallic state and at least partially alloy them. Where tungsten content is desired, the proper proportion of tungsten oxide powder is added to the original oxide powder mix, and similar heat treatments are applied; however, both these treatment temperatures are raised by about 50° to 70° C.

The broken sinter cake lumps or pellets of the reduced metal powder alloy are then subjected to a chromium-alloying treatment carried on in a manner similar to that described above in connection with the chromium-alloying treatments applied to the alloy powders of iron and nickel powder, resulting in alloy powder particles containing the proper proportions of the metals iron, nickel, molybdenum, and/or tungsten, combined with the proper proportions of chromium so that the resulting powder contains the different metals in proportions corresponding to the desired alloy. Such chromium-alloyed powder particles may be readily compacted or coined into bodies of desired shape, whereupon the so-compacted bodies may be subjected to a sintering operation with or without an infiltrating treatment, whereby the shaped body is given the desired great strength. The sintering operation may be carried on for a sufficient length of time to cause the different metal constituents of the different powder particles to alloy with each other, and with chromium to any desired extent. It is thus possible to produce in a highly economical way strong bodies exhibiting hot strength and corrosion-resistance out of oxide particles of the different metals which heretofore had to be alloyed in molten state at high temperatures in order to obtain bodies of comparable strength.

It should be noted that when producing chromium-surface-alloyed soft metal powders of the invention from oxides of the desired metals, such as oxides of iron, nickel, cobalt, molybdenum, and tungsten, and mixtures thereof, the oxide powders may be pelleted into pellets for the preliminary reducing and sintering treatment. When such pellets are subjected to the combined reducing and sintering treatment of the type described above, the admixed lubricant and binder is decomposed, and driven off. As a result, the reduced pellets have the required low density and small strength, comparable to the strength of the sinter cake fragments produced by sintering sponge iron powder deposited in a layer of about ¼ of an inch within the treatment boats in the preliminary treatment of sponge iron powder described hereinbefore. As long as the sinter cake pellets resulting from the preliminary reducing and sintering treatment have a density not exceeding about 5 g./cc., and a modulus of rupture not exceeding about 6500 p. s. i., the sinter cake pellets will yield chromium-alloyed powders having the desired high degree of softness and plastic deformability as to make it possible to compact such powders into green compact bodies having a modulus of rupture of at least 400 p. s. i. and higher with a pressure of only 50,000 p. s. i.

As used in the specification and claims, the expression "sinter cake body" include both sinter cake lumps and sinter cake pellets of sufficiently low density and strength that upon comminution of such chromium-alloyed sinter cake body into minute chromium-alloyed powder particles having the desired high degree of softness and plastic deformability which make it possible to compact such powders into green compacted bodies having a modulus of rupture of at least 400 p. s. i., and higher with a pressure of only 50,000 p. s. i.

The principles of the invention described above in connection with specific exemplifications thereof, will suggest various other modifications and applications of the same. It is accordingly desired that the present invention shall not be limited to the specific exemplifications shown or described therein.

We claim:

1. The method of providing a readily compactible and moldable metal powder comprising first producing readily frangible porous sinter cake pieces composed essentially of sintered metal powder particles of at least one metal of the group consisting of iron containing at most about

.2% carbon, of nickel, and of cobalt, and mixtures and alloys of at least two of said metals so that said cake pieces have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a chromium compound is deposited on the powder particles of said cake pieces and caused to diffuse into said powder particles so that said powder particles contain at least about 3% chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable metal powder particles having the deposited chromium alloyed therewith so that when said chromium-alloyed particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

2. The method of providing a readily compactible and moldable metal powder comprising first producing readily frangible porous sinter cake pieces of sintered metal powder particles composed essentially of at least one metal of the group consisting of iron containing at most about .2% carbon, of nickel, and of cobalt, together with up to at least one metal of the group consisting of molybdenum and tungsten, and of mixtures and alloys of said metals: so that said sinter cake pieces have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a chromium compound is deposited on the powder particles of said cake pieces and caused to diffuse into said powder particles so that the said powder particles contain at least about 3% chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable metal powder particles having the deposited chromium alloyed therewith so that when said chromium-alloyed particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch, said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

3. The method of providing a readily compactible and moldable metal powder comprising first producing readily frangible porous sinter cake pieces composed essentially of sintered metal powder particles of at most about .2% carbon, of nickel, and of cobalt, and mixtures and alloys of at least two of said metals so that said cake pieces have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a gaseous chromium compound is deposited on the powder particles of said cake pieces and cause to diffuse into said powder particles so that said powder particles contain at least about 3% chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable metal powder particles having the deposited chromium alloyed therewith so that when said chromium-alloyed particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch, said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

4. The method of providing a readily compactible and moldable metal powder comprising first producing readily frangible porous sinter cake pieces composed essentially of sintered metal powder particles of at least one metal of the group consisting of iron containing at most about .2% carbon, of nickel, and of cobalt, together with up to about 30% of at least one metal of the group consisting of molybdenum and tungsten, and of mixtures and alloys of said metals so that said sinter cake pieces have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a gaseous chromium compound is deposited on the powder particles of said cake pieces and cause to diffuse into said powder particles so that the said powder particles contain at least about 3% chromium, and thereafter comminuting said cake pieces into minute plastically deformable metal powder particles having the deposited chromium alloy therewith so that when said chromium-alloyed particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

5. The method of providing a readily compactible and moldable metal powder comprising preparing a powder mass of powder particles composed essentially of at least one metal of the group consisting of iron containing at most about .2% carbon, of nickel, and of cobalt, and mixtures and alloys of at least two of said metals, at least some of said powder particles containing the metal in the form of an oxide, producing readily frangible porous metallic sinter cake pieces by heating the powder mass in a reducing atmosphere at a temperature of at least about 700° C. so that said cakes have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a chromium compound is deposited on the powder particles of said cake pieces and caused to diffuse into said powder particles so that the said powder particles contain at least about 3% of chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable powder particles of said metals having the deposited chromium alloyed therewith so that when said chromium-alloyed metal particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

6. The method of providing a readily compactible and moldable metal powder comprising first preparing a powder mass of powder particles composed essentially of at least one metal of the group consisting of iron containing at most about .2% carbon, of nickel, and of cobalt, together with up to about 30% of at least one metal of the group consisting of molybdenum and of tungsten, and of mixtures and alloys of said metals, at least some of said powder particles containing the metal in the form of an oxide, producing readily frangible porous metallic sinter cake pieces by heating the powder mass in a reducing atmosphere at a temperature of at least about 700% C. so that said cakes have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a chromium compound is deposited on the powder particles of said cake pieces and caused to diffuse into said powder particles so that the said powder particles contain at least about 3% chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable powder particles of said metals having the deposited chromium alloyed therewith so that when said

chromium-alloyed metal particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

7. The method of providing a readily compactible and moldable metal powder comprising first preparing a powder mass of powder particles composed essentially of at least one metal of the group consisting of iron containing at least one metal of the group consisting of iron containing at most about .2% carbon, of nickel, and of cobalt, and mixtures and alloys of at least two of said metals, at least some of said powder particles containing the metal in the form of an oxide, producing readily fragible porous metallic sinter cake pieces by heating the powder mass in a reducing atmosphere at a temperature of at least about 700° C. so that said cakes have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a gaseous chromium compound is deposited on the powder particles of said cake pieces and caused to diffuse into said powder particles so that the said powder particles contain at least about 3% of chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable powder particles of said metals having the deposited chromium alloyed therewith so that when said chromium-alloyed metal particles are compacted in the absence of a binder into a green body having a pressure of about 50,000 pounds per square inch said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

8. The method of providing a readily compactible and moldable metal powder comprising first preparing a powder mass of powder particles composed essentially of at least one metal of the group consisting of iron containing at most about .2% carbon, of nickel, and of cobalt, together with up to about 30% of at least one metal of the group consisting of molybdenum and of tungsten, and of mixtures and of alloys of said metals, at least some of said powder particles containing the metal in the form of an oxide, producing readily frangible porous metallic sinter cake pieces by heating the powder mass in a reducing atmosphere at a temperature of at least about 700° C. so that said cakes have at most a density of about 4 grams per cubic centimeter, and thereafter subjecting said cake pieces to a chromium-alloying treatment in which chromium from a gaseous chromium compound is deposited on the powder particles of said cake pieces and caused to diffuse into said powder particles so that the said powder particles contain at least about 3% of chromium, and thereafter comminuting said cake pieces into minute plastically readily deformable powder particles of said metals having the deposited chromium alloyed therewith so that when said chromium-alloyed metal particles are compacted in the absence of a binder into a green body under a pressure of about 50,000 pounds per square inch said green body exhibits a modulus of rupture of at least about 200 pounds per square inch.

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