

Dec. 12, 1967

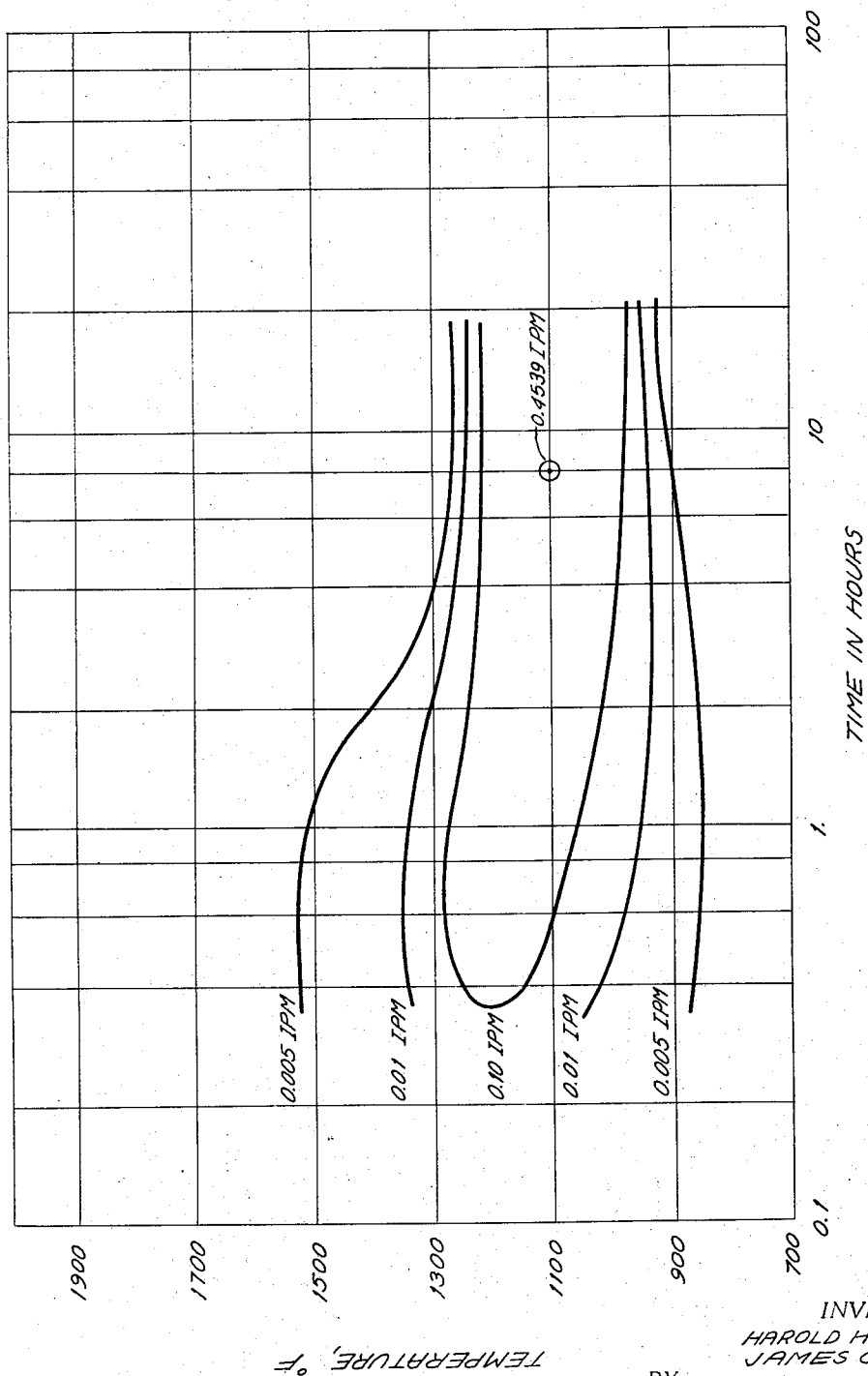
H. H. HONAKER ET AL

3,357,826

POWDER METALLURGICAL PRODUCTION OF CHROMIUM-CONTAINING ALLOYS

Filed Nov. 14, 1966

2 Sheets-Sheet 1



TIME IN HOURS

Fig. 1

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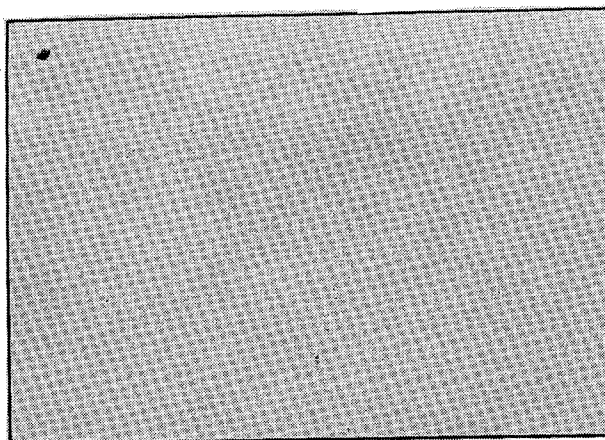


**FIG. 2**



**FIG. 3**

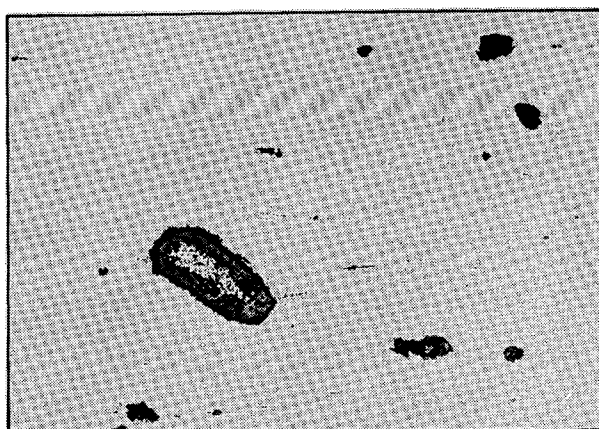


**FIG. 4**

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## POWDER METALLURGICAL PRODUCTION OF CHROMIUM-CONTAINING ALLOYS

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15 Claims. (Cl. 75-206)

### ABSTRACT OF THE DISCLOSURE

Directed to a process for producing wrought chromium-containing metal articles, including usual mill forms such as strip, tubing, plate, bar, etc., essentially devoid of chromium oxide inclusions wherein an initial powder mixture is prepared containing about 5% to about 60% of chromium powder, contaminated with chromium oxide along with up to about 20% molybdenum, up to about 10% tungsten, up to about 5% columbium, up to about 4% copper, at least about 0.1% up to about 0.8% carbon, at least about 0.01% to about 0.5% of a spacing agent and the remainder substantially an iron-group metal, pressing the mixture into a billet, heating the billet to sintering temperature under nonoxidizing conditions, sintering the billet at a temperature of at least about 1900° F. in a flowing gas atmosphere reducing to chromium oxide and thereafter working, e.g., hot working, the sintered billet to consolidated alloy shape.

The present invention is directed to the production of chromium-containing alloy products by powder metallurgy and, more particularly, to the production of wrought chromium-containing alloy products using powders as the starting materials.

Industrial experience has demonstrated the advantages of providing wrought products such as strip, tubing, plate, bar, etc., made of metals such as nickel and iron, nickel-iron alloys, etc., by pressing metal powders or mixtures of metal powders to the form of a billet, sintering the billet, and hot working the sintered billet into mill forms of common configuration. In this way, it is possible to produce useful mill products having exceptional and controllable properties and chemical composition. Metal powders of controlled composition are readily available. Thus, for example, nickel and iron powders may readily be obtained commercially. It would be desirable to produce chromium-containing alloys by the aforementioned method also since alloys such as nickel-chromium alloys and nickel-chromium-iron alloys have properties which are in industrial demand. However, commercially available chromium powders are invariably contaminated with chromium oxide on the surface thereof and attempts to produce chromium-containing alloys from pressed and sintered blends of such oxide-contaminated chromium powders with other metal powders such as nickel powder have resulted in the production of final compacted metal articles which were still contaminated with chromium oxide from the oxide in or on the initial chromium powder. It was also found that unacceptably long sintering times attributable to such oxide contamination were required in order to secure necessary diffusion amongst the powder particles so as to obtain a homogeneous alloy composition. Furthermore, it was found that the oxide contamination of the consolidated wrought chromium-containing alloy article reduced the mechanical properties and corrosion resistance of the article.

It has been considered that solution of this vexing problem would enable the production from initial oxide-contaminated chromium-containing metal powder blends of

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useful products which would have properties superior to those obtainable in wrought products of the same nominal composition made by conventional procedures from an ingot of solidified molten metal.

We have now discovered a method for producing wrought products made from initial compressed metal powder blends containing chromium powder contaminated with chromium oxide, which products are essentially devoid of harmful oxide contamination and have improved properties. The method which we have discovered is applicable in conventional equipment and can be practiced on a commercial scale.

It is an object of the present invention to provide a method applicable on a commercial scale for the production of homogeneous chromium-containing alloy wrought mill products from initial powder mixtures containing chromium powder contaminated with chromium oxide.

It is a further object of the invention to provide powder metallurgy articles made from initial powder mixtures containing chromium powder contaminated with chromium oxide, which articles are substantially devoid of oxygen.

It is another object of the invention to enable the substantially complete elimination of chromium oxide from pressed metal powder compacts containing chromium powder contaminated with chromium oxide.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawing in which:

FIGURE 1 depicts the time-temperature-sensitization relation determined from corrosion rates in boiling nitric acid of a wrought nickel-chromium-iron alloy produced according to the invention;

FIGURE 2 is a photomicrograph taken at 100 diameters depicting the unetched microstructure of a wrought nickel-chromium-iron alloy produced in accordance with the invention from an initial metal powder mixture containing oxide-contaminated chromium powder; and

FIGURES 3 and 4 are photomicrographs taken at 100 diameters depicting the unetched microstructures of wrought nickel-chromium-iron alloys produced from initial metal powder mixtures containing oxide-contaminated chromium powder but in which ingredients required in accordance with the invention to be present in the initial powder mixture were omitted.

Broadly stated, the invention is directed to a method for producing wrought metal products made of a chromium-containing alloy having improved metallurgical properties and characteristics from an initial powder mixture containing chromium powder contaminated with chromium oxide, which comprises providing such a mixture of chromium powder with an iron-group metal powder having a controlled carbon content and containing a small amount of a volatile spacing agent, pressing the resulting mixture, heating the powder pressing to a temperature exceeding the volatilization temperature of the said spacing agent in a protective atmosphere, sintering the powder pressing at a temperature exceeding the reduction temperature of chromium oxide with carbon in a gas reducing atmosphere reducing to chromium oxide, and working, e.g., hot working, the sintered powder mixture to form a consolidated alloy shape substantially devoid of chromium oxide contamination.

In carrying the invention into practice, an initial powder mixture is prepared which contains in weight percent about 5% to about 60% of chromium powder, e.g., about 10% to about 30% or 50% chromium, up to about 90% nickel powder, and up to about 90% iron powder. The initial mixture also contains carbon in controlled amounts of at least about 0.1% up to about 0.8%. The carbon content

of the mixture is controlled within the required range by additions of carbon thereto. Carbon may be introduced into the mixture as carbon or graphite powder or as a heat decomposable carbon compound such as a liquid or solid hydrocarbon, carbohydrate, etc. The initial mixture also contains at least about 0.01% up to about 0.5%, by weight, of a heat volatilizable spacing agent having a volatilization temperature between room temperature and about 1200° F. The spacing agent advantageously is a salt such as an ammonium halide, e.g., ammonium chloride, although other salts which decompose at a temperature below about 1200° F., such as ammonium carbonate, may be employed in the place of the ammonium halide. The ammonium halides are particularly advantageous spacing agents for purposes of the present invention, since they volatilize at temperatures below about 1200° F. to yield gaseous products which are not found in the sintered metal. The amount of heat volatilizable spacing agent is at least about 0.01% by weight of the initial powder mixture to obtain the minimum required pore formation during sintering but does not exceed about 0.5% by weight because cracking of the billet may then be encountered during sintering. Advantageously the amount of spacing agent is about 0.05% to about 0.2% by weight of the initial mixture.

Chromium powders, including ferrochromium powders, employed in accordance with the invention have a particle size of about 1 to about 60 microns, although from the standpoint of diffusion, the particle size desirably does not exceed about 40 microns, and generally contain about 0.4% to about 0.8% oxygen as a chromium oxide contaminant which is generally present on the surface of the powders. The chromium powder should not contain more than about 0.025% sulfur, more than about 0.05% magnesium, more than about 0.3% silicon or more than about 0.1% aluminum. Magnesium, silicon and aluminum should be as low as possible since the oxides of these elements form difficultly-reducible spinels with chromium oxide. Thus, electrolytic chromium powder, which is very low in silicon, aluminum and magnesium, is very satisfactory for purposes of the invention. If desired for special purposes in the final sintered and consolidated metal article, other ingredients may be included in the initial powder mixture. Thus, the initial powder mixtures may contain up to about 5% columbium, up to about 4% copper, up to about 20% molybdenum, up to about 10% tungsten, and up to about 20% cobalt. Powdered materials such as aluminum, titanium, silicon and manganese desirably are not present in the initial mixtures since these metals and/or their oxides interfere with the reduction of chromium oxide as contemplated in accordance with the invention. If such materials are desired in the product for special purposes, the powders thereof can be initially coated with nickel, iron or cobalt as, for example, by decomposition of a corresponding metal carbonyl to reduce the interfering effect of the metals during sintering. However, any oxides present on the metal powder surface prior to coating will not be reduced and will remain in the final product with detrimental results in regard to corrosion resistance, etc. For purposes of the invention, it is advantageous to employ carbonyl nickel powders and carbonyl iron powders generally having particle sizes in the range of about 3 to about 10 microns, although other commercial types of iron and nickel powders may be used. Certain powders, e.g., carbonyl iron powder and carbonyl nickel powder, containing carbon in amounts up to about 1% may be employed and the carbon content of the powders is effective in contributing the required carbon content in the initial powder mixture. Chromium-containing alloy powders, e.g., stainless steel powders, and other alloy powders may be employed in the initial mixture. The initial powder mixture contains at least about 0.1% or about 0.15% by weight of carbon to effect reduction of chromium oxide but does not contain more than about 0.8% by weight of carbon because residual carbon in the

wrought products would then be excessive in many instances. Advantageously, the initial powder mixture contains about 0.15% to about 0.25% by weight of carbon because such amounts are normally sufficient to reduce the chromium oxide and provide the desired final carbon content. Carbon is included in the initial powder mixture in an amount sufficient to combine stoichiometrically with the oxygen present in the mixture as chromium oxide. Necessary carbon additions are most advantageously made by means of fine carbon powder, e.g., carbon black, or graphite powder having a particle size of about 0.5 to about 50 microns. Those skilled in the art will appreciate that, in addition to this amount of carbon, a sufficient amount of carbon must also be present to compensate for carbon losses by mechanisms such as methanation, combination with chemisorbed gases present in certain powders, e.g., carbon dioxide, etc. Accordingly, the amount of carbon in the initial mixture is generally about 20% to about 70% or 100% or more in excess of the aforesaid stoichiometric amount. Advantageously, the other metal powders employed in the initial powder mixture have particle sizes of about 2 to about 50 microns. More advantageously, the particle size of the powders does not exceed about 40 microns in order to facilitate diffusion during sintering so as to yield the homogeneous consolidated metal article.

After the initial powder mixture has been thoroughly blended, it is pressed at ambient temperatures into a form such as a billet. Hydrostatic pressing is advantageously employed for this operation. Sufficient pressure is employed to provide a green strength in the pressed powder article of an order such as to permit handling of the pressed powder billet. Pressures in the range of about 10,000 to about 50,000 pounds per square inch (p.s.i.), e.g., about 30,000 p.s.i., are sufficient. The green billet has a porosity of about 45% to about 25%. The green billet is then transferred to an atmosphere-controlled furnace. The pressed powder billet is heated to the sintering temperature at a rapid rate while maintaining thereabout a protective atmosphere nonoxidizing to the constituents thereof. Sintering is accomplished by holding the pressed power shape, e.g., billet, in the temperature range of about 1900° F. or about 2000° F. to about 2300° F. for about 4 to about 12 hours, or more, while maintaining a gas flow, e.g., dry hydrogen, past the billet of about 1/3 to about 1 standard cubic foot per hour per pound of metal being treated. It is found that in order to secure carbon reduction of the chromium oxide content of the powder mixture in a dry hydrogen (i.e., hydrogen having a dew point not exceeding about minus 90° F.) atmosphere, temperatures of at least about 1900° F. are required. Heating in the temperature range about 2000° F. is conducted at a slow rate, e.g., approximately 50° F. per hour. At the completion of sintering, the sintered shape has a porosity of about 25% to about 15%. The hot sintered billet may be taken directly to a hot working operation such as a hot rolling mill or may be hot extruded in a conventional extrusion press for the formation of fully dense mill forms, including rod, bar, plate, tube, etc. Hot extrusion is the preferred method for consolidating sintered billets made of high chromium alloys such as an alloy containing 50% chromium, balance nickel. Alternatively, the sintered shape may be cooled to a temperature below about 300° F. in a protective atmosphere. It is to be understood that heating of the billet up to the sintering temperature, e.g., up to temperatures in the range of about 1000° F. to about 1900° F., may be conducted in an essentially oxygen-free atmosphere such as 90% nitrogen-10% hydrogen, argon, dry hydrogen, etc. Sintering at temperatures of 1900° F. and above is conducted in dry hydrogen, dry dissociated ammonia or other atmosphere reducing to chromium oxide at the sintering temperature.

It is found in accordance with the invention that even large sintered metal shapes such as a billet 4 inches by

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5 inches in cross section and weighing about 30 to about 200 pounds is essentially devoid of oxide content throughout the cross section thereof.

In order to give those skilled in the art a better understanding of the invention and a better appreciation of the advantages of the invention, the following illustrative examples are given.

#### Example I

A billet containing about 76% nickel, about 16% chromium and about 7% iron was prepared by mixing carbonyl nickel powder having a particle size of about 5 microns, carbonyl iron powder having a particle size of about 5 microns, and electrolytic chromium powder containing about 0.7% oxygen and having a minus 325 mesh particle size together with about 0.1% ammonium chloride and sufficient carbon powder to provide in the mixture about 0.18% carbon. The billet was hydrostatically pressed at about 30,000 p.s.i. pressure. A similar billet was prepared with the exception that no carbon addition was made thereto. The second billet contained about 0.05% carbon. Each billet was 2½ inches square and weighed 40 pounds. Each billet was cut into four sections weighing 10 pounds each and pairs of billet portions from each initial billet were sintered at 1400° F.; 1800° F.; 2000° F. and 2200° F. for 8 hours in flowing dry hydrogen. In each case, heating to the sintering temperature was conducted as rapidly as possible. The oxygen and carbon contents of the resulting sintered products are given in the following Table I:

TABLE I

| Sintering Temperature, ° F. | Initial Carbon, 0.05%   |                         | Initial Carbon, 0.18%   |                         |
|-----------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|                             | Oxygen Content, Percent | Carbon Content, Percent | Oxygen Content, Percent | Carbon Content, Percent |
| 1,400.....                  | 0.17                    | 0.03                    | 0.16                    | 0.14                    |
| 1,800.....                  | 0.13                    | 0.012                   | 0.09                    | 0.10                    |
| 2,000.....                  | 0.08                    | 0.005                   | 0.013                   | 0.03                    |
| 2,200.....                  | 0.09                    | 0.003                   | 0.012                   | 0.04                    |

The sintered products produced from the initial mixture containing 0.18% carbon were essentially free from oxide inclusions after the sintering treatment at 2000° F. and 2200° F. as reflected by the materially lower oxygen contents obtained therein.

#### Example II

A 2½ inch by 2½ inch billet weighing 20 pounds and containing about 77% nickel, 16% chromium, 7% iron, 0.18% total carbon, and 0.05% ammonium chloride was pressed, sintered at 2300° F. for about 9 hours, with total time at temperature above 2000° F. being 14 hours, and hot worked to full density using the procedure and starting materials set forth in Example I. The microsection of the hot worked material at the center of the wrought product showed no oxide inclusions and the oxygen content was about 0.016%. The procedure was repeated using similar initial mixtures containing 0.1% and 0.2% ammonium chloride, respectively, and identical results were obtained.

#### Example III

Using the procedure described in connection with Example I, a 4 inch by 5 inch billet was prepared from an initial powder mixture containing about 0.1% ammonium chloride, about 0.18% carbon, about 76% nickel, about 16% chromium, and about 7% iron. The mixture was hydrostatically pressed to size at about 10,000 p.s.i. and was rapidly heated to 2000° F. and sintered at 2250° F. for about 12 hours. An atmosphere comprising 90% nitrogen and 10% hydrogen was employed during heating to 1150° F. at which point dry flowing hydrogen was introduced and maintained as the atmosphere up to 2200° F. About the last six hours of sintering was conducted in a flowing atmosphere generated from the dis-

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sociation of ammonia. A sintered billet was hot worked to flat bar about ½ inch by 3 inches. The worked material contained about 0.001% oxygen and about 0.05% carbon. The material was subjected to room temperature and elevated temperature short-time tensile tests and to corrosion tests comprising immersion for 24 hours in a boiling solution of 65% nitric acid. The results of these tests are shown in the following Tables II and III. In Table III, comparison results obtained upon wrought metal of similar composition produced from an ingot prepared from molten metal are also given.

TABLE II.—SHORT-TIME TENSILE TEST DATA

| Test Temperature, ° F.     | 0.2% Yield Strength, k.s.i. <sup>1</sup> | Tensile Strength, k.s.i. | Elongation, percent | Reduction in Area, percent |
|----------------------------|------------------------------------------|--------------------------|---------------------|----------------------------|
| 15 R.T. <sup>2</sup> ..... | 51.4                                     | 99.0                     | 38.0                | 64.0                       |
| 1,000.....                 | 43.7                                     | 91.5                     | 36.0                | 35.5                       |
| 1,200.....                 | 41.7                                     | 75.0                     | 26.0                | 27.8                       |
| 1,400.....                 | 40.0                                     | 42.6                     | 20.0                | 25.6                       |
| 1,600.....                 | 24.3                                     | 25.0                     | 9.0                 | 13.0                       |
| 1,800.....                 | 13.8                                     | 14.9                     | 8.5                 | 12.5                       |

<sup>1</sup> k.s.i. = thousands of pounds per square inch.

<sup>2</sup> R.T. = room temperature.

TABLE III.—CORROSION RATE—24 HOURS SUBMERSION IN BOILING 65% NITRIC ACID

| Condition                                                            | Corrosion rate, inches per month | Corrosion rate, inches per month comparison melted alloy |
|----------------------------------------------------------------------|----------------------------------|----------------------------------------------------------|
| 2,200° F., 1 hour water quench.....                                  | 0.00072                          | 0.0213                                                   |
| 2,200° F., 1 hour water quench plus 1,100° F., 8 hours water quench. | 0.1047                           | 2.138                                                    |

Further corrosion testing of alloy materials having a composition similar to and produced in a manner similar to that set forth in the foregoing examples was conducted. The corrosion test again consisted of immersion in boiling 65% nitric acid for 24 hours. The alloy specimens tested were subjected to a heat treating cycle comprising heating at 2200° F. for 1 hour, water quenching and reheating at 900° F.; 1000° F.; 1100° F.; 1200° F.; 1300° F.; 1400° F.; 1500° F. and 1700° F. for time periods ranging between ½ and 8 hours followed by a water quench. The corrosion rate upon the specimens was determined in terms of inches per month and the diagram shown in the accompanying FIGURE 1 was constructed on the basis of the data. The data demonstrated that the breadth of the sensitization range for the wrought powder metallurgy product is substantially less than that of a melted alloy product having the same nominal composition tested in wrought form and that the peak corrosion rate is substantially lower than that of the melted alloy product. The wrought powder metallurgy product is of the order of 5 times to 500 times more resistant to corrosion in the severe boiling nitric acid test than is the corresponding melted product.

Other compositions which may be produced as consolidated wrought products in accordance with the method of the present invention include alloys containing 50% nickel and 50% chromium; 40% nickel and 60% chromium; 32% nickel, 20% chromium, balance iron; 80% nickel and 20% chromium; 42% nickel, 6% chromium, balance iron; 74% nickel, 16% chromium, 2% columbium, balance iron; austenitic stainless steels such as the 18% chromium, 8% nickel grade; martensitic and ferritic stainless steels represented by the AISI Type 403 and Type 430 designations, respectively, etc.

In contradistinction to the properties provided in the material produced in accordance with the invention as reflected by short-time testing, a billet of similar size to that prepared in accordance with Example I was prepared with the exception that no carbon addition was made to the initial powder mix. Wrought material produced from the

sintered billet had a room temperature yield strength (0.2% offset) of about 45.7 k.s.i., a tensile strength of about 91.2 k.s.i., an elongation of about 28% and a reduction in area of about 24%. The microstructure of this material is shown in the accompanying FIGURE 3. Oxide inclusions are readily evident therein.

Another material prepared in accordance with the procedure of Example II except that neither ammonium chloride nor carbon was added in the initial powder mixture was prepared in wrought form. The microstructure of this material is shown in the accompanying FIGURE 4 and again undesirable oxide inclusions are clearly evident therein. In contrast to these unsatisfactory results, simultaneously processed material produced with both carbon and ammonium chloride in accordance with Example I had a yield strength (0.2% offset) of 49.7 k.s.i., a tensile strength of 97.6 k.s.i., an elongation of 47% and a reduction in area of 67.7%. The microstructure of this material is shown in the accompanying FIGURE 2 and it is significantly cleaner than those of FIGURES 3 and 4. The traces of inclusion material in FIGURE 2 are well distributed and are not harmful. In another instance, billets having a cross-section of about four inches by five inches were prepared by the procedure of Example II with one of the billets being made from an initial mixture containing 0.10% by weight of ammonium chloride spacing agent and the other from a mixture containing no such spacing agent. In each case, the initial mixture contained about 0.18% carbon. In the forged condition, the billet made without the initial ammonium chloride addition contained about 0.03% oxygen and displayed many oxide inclusions in the microstructure while the forged billet made with the initial spacing agent addition contained only about 0.005% oxygen and had a clean microstructure. The forged material produced using the spacing agent had an elongation of 41% and a reduction in area of 66% whereas the forged material produced without the spacing agent had an elongation of 33% and a reduction in area of 47%. The test demonstrated that the presence of the spacing agent in the initial powder mixture, which preferably is an ammonium halide, i.e., ammonium fluoride, ammonium chloride, ammonium bromide or ammonium iodide, or ammonium carbonate, is essential for purposes of the invention.

While the theory underlying the present invention is not exactly understood, it is, nevertheless, a fact that the invention makes possible the production of chromium-containing alloys which are essentially devoid of oxide traceable to the oxide contamination initially present in the chromium powder. It appears that in the sintering of pressed billets in accordance with the invention, volatilization of the spacing agent affords channels through the pressed billet which enable permeation of the hydrogen atmosphere and through flushing of gaseous products therefrom. In any event, the process of the invention provides metallurgically clean chromium-containing alloy products from starting materials including oxide-contaminated chromium powder.

The present invention is not to be confused with the process described in the literature which has been called "activated sintering." In this different process, the operators have sought to maintain halide atmospheres about pressed compacts during the sintering thereof. The process does not employ a stream of flowing hydrogen in contact with the material being treated. The requirements of this process in relation to the operation thereof are severe and the process has not been widely employed, although good results have been reported in the literature. The process suffers from difficulties such as attack on furnace interiors from the use of reactive chemicals, corrosion of the metal compacts being treated, increased costs traceable to the preoxidizing step employed in treating the powder, and the requirement that the compacts be placed in retorts or boxes during the sintering operation. In addition, control difficulties apparently have been experienced in insuring that each of the pressed compacts in the retort receives the

same dosage of halide. Furthermore, carbon in the pressed compacts has been identified as a "poison" with respect to the achievement of the desired effects.

The process provided in accordance with the present invention is free of the serious commercial difficulties which have been encountered with the so-called activated sintering process and may be carried out in conjunction with the treatment of large, heavy billets from powder compacts which may be converted to usual mill forms such as tubing, bar, rod, strip, wire, etc., with high metal recovery and with the potential of providing unusual properties in the products, particularly from the viewpoints of close control of composition, improved corrosion resistance, etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. The process for producing wrought chromium-containing metal articles essentially devoid of chromium oxide inclusions which consists essentially of preparing an initial powder mixture contaminated with chromium oxide and consists essentially of, by weight, about 5% to about 60% of chromium, up to about 20% molybdenum, up to about 10% tungsten, up to about 5% columbium, up to about 4% copper, at least 0.1% up to about 0.8% carbon, at least about 0.01% to about 0.5% of a spacing agent, and the balance substantially an iron-group metal, pressing said mixture into a billet, heating said billet to sintering temperature under nonoxidizing conditions, sintering said billet at a temperature of at least about 1900° F. in a flowing gas atmosphere reducing to chromium oxide to provide a sintered billet substantially devoid of chromium oxide inclusions and thereafter working said sintered billet to a consolidated alloy shape substantially devoid of chromium oxide inclusions.

2. The process according to claim 1 wherein the initial powder mixture consists essentially of, by weight, about 5% to about 60% chromium, and at least one metal powder from the group consisting of up to about 90% nickel, up to about 90% iron, and up to about 20% cobalt.

3. The process according to claim 2 wherein the nickel powder is carbonyl powder.

4. The process according to claim 1 wherein the carbon content of the initial powder mixture is about 0.15% to about 0.25%.

5. The process according to claim 1 wherein the spacing agent is present in the initial powder mixture in the amount of about 0.05% to about 0.2%.

6. The process according to claim 1 wherein the spacing agent is selected from the group consisting of ammonium halides and ammonium carbonate.

7. The process according to claim 1 wherein the spacing agent is ammonium chloride.

8. The process according to claim 1 wherein the powder ingredients have particle sizes not exceeding about 40 microns.

9. The process according to claim 1 wherein the chromium content in the powder mixture is about 10% to about 50%.

10. The process according to claim 1 wherein sintering is conducted at a temperature of about 2000° F. to about 2300° F. for at least about 4 hours.

11. The process according to claim 1 wherein the sintering is conducted in a gas atmosphere from the group consisting of dry hydrogen and dry dissociated ammonia flowing at a rate of about 1/3 to about 1 standard cubic foot per hour.

12. The process according to claim 1 wherein the pressing operation is an isostatic pressing.

13. The process according to claim 1 wherein the

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sintered billet is hot worked to substantially full density.

14. The process according to claim 13 wherein the sintered billet is directly hot worked from the sintering operation.

15. The process according to claim 1 wherein the initial powder mixture consists essentially of, on the basis of metal powder ingredients, about 6% to about 60% chromium, at least about 8% and up to about 80% nickel, and the balance essentially iron.

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