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METHOD OF MAKING METAL BODIES INCORPORATED WITH NON-METALLIC REFRACTORY MATERIAL AND PRODUCT THEREOF

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The present invention deals with a method of incorporating non-metallic refractory material into metal bodies and more particularly with a powder metallurgy method of making composites of this sort.

It is known that high temperature strength properties of various metals can be improved by the incorporation into the metals of non-metallic substances such as metal oxides, which increases resistance of the metals to deformation and enables the metals to sustain high stress at elevated temperatures for prolonged periods of time. The incorporation of the non-metallic substances into a matrix metal is generally accomplished by conventional powder metallurgy methods whereby powders of, for example, metal oxides are mixed with a matrix metal powder and the mixture is subsequently compressed and sintered to form the composite compact or product. Such conventional powder metallurgy methods have the disadvantage that the non-metallic substances can be incorporated into the matrix only in very limited amounts where malleable sintered compacts are desired. When the compact made by the conventional methods contains more than a critical maximum amount of the non-metallic substance, the continuity of the matrix metal is disrupted, and the material lacks sufficient ductility for satisfactory fabrication into wires or sheets. For example, in the application of such methods to the manufacture of a platinum-thorium oxide compact, about 0.5 percent thorium oxide is about the largest amount which will yield a readily workable metal containing such oxide. Prior art platinum-thorium oxide compositions have a slight degree of workability up to a thorium oxide concentration of about 1 percent.

Another disadvantage of the conventional powder metallurgy methods with non-metallic additives, especially in the manufacture of shaped articles, is that excessive shrinkage and shape distortion of the compacted article is apt to occur on sintering of the article primarily because of the presence of an excessive occurrence of pores or voids free from the non-metallic substance.

The present invention concerns a method of making metal bodies incorporated with non-metallic refractory material by impregnating a porous body of compacted powder metal in a "green" condition with a liquid providing, after drying and subsequent heat treatment up to metal sintering temperatures, metal incorporated with such non-metallic refractory material. Such liquid may itself be decomposable to non-metallic refractory material or, more usually be a volatile solvent with a solute producing the non-metallic refractory material or a volatile liquid dispersing a suspension such as a colloidal suspension. The term "green" refers to the condition of the metal powder prior to the heat treatment thereof or prior to the sintering of the compressed powder. In accordance with this invention increased amounts of non-metallic refractory material may be incorporated into the body than possible by conventional mixing methods while still maintaining the metal body in a ductile condition amenable to working of the metal to form shaped products therefrom. In the case of the thorium oxide addition to platinum previously mentioned, a slightly workable bar is possible with around 2 percent ThO_2 in contrast to the previous limit of about 1 percent. A readily workable bar producing 20-mil wire is possible in accordance with this invention containing 1.1 percent ThO_2 in the Pt as compared to the previous limit of about 0.5 percent ThO_2.

It is an object of the invention to provide an improved method for incorporating non-metallic refractory material in a porous metal matrix.

It is another object of the invention to provide a method for an improved dispersion of a refractory oxide throughout a metal matrix.

It is a further object of the invention to provide a method for incorporating controlled amounts of refractory crystalline oxides in a compressed powder metal matrix, whereby the shrinkage of the matrix can be controlled during subsequent sintering operations.

It is a still further object of the invention to provide a method for incorporating oxides in a malleable powder metal matrix in amounts greater than heretofore considerd possible, in order to control shrinkage of the composition during sintering operations while still maintaining the composition in a substantially ductile condition.

It is a still further object of the invention to provide a workable oxide impregnated metal composition capable of sustaining high stress at elevated temperatures for prolonged periods of time.

Another object of the invention is to provide a method for improved dispersion of graphite throughout a metal matrix, such metal being substantially unreactive chemically with said graphite.

Other objects and advantages of the invention will become apparent from the description hereinafter following.

The invention deals with a method for improved dispersion of non-metallic refractory material in a "green" porous compacted powder metal body by impregnating the body with a liquid which yields on heat treating a non-metallic refractory material, heat treating the impregnated body to a temperature sufficient for the liquid to leave a solid residue, further heating the body to convert such residue to non-metallic refractory material and to sinter the body at elevated temperatures, and thereafter working the compacted and sintered body to a desired shape and form.

Forming of metals by powder metallurgy has the particular problem that excessive shrinkage and shape distortion may occur on sintering. Shape distortion may be particularly serious following linear compaction because of pressure cones and high void areas resulting from this type of pressing. Shrinkage is particularly to be expected as a result of isostatic pressing since a lower pressure is required and used for pressing of "green" pieces in order to avoid screen effects of surface compaction greater than the compaction of the interior of the piece. However, with isostatic compaction the porosity of the "green" compact and in consequence the subsequent macrodispersion of non-metallic refractory material therein can be very evenly distributed throughout the entire compact in contrast to the less homogeneous porosity and distribution resulting when linear compaction is employed.

It should be noted that in accordance with the method of this invention, whereby metal powder is compacted prior to addition of the impregnating liquid, the "green" compact provides continuous metal-to-metal contact, so that every grain of metal is pressed against one, and usually more than one, other grain of metal. Thus, in contrast to the prior art method of wetting all surfaces of metal powders with impregnating liquid, only surfaces in contact with the pores of the "green" compact are wetted by the method of the present invention. The continuous metal-to-metal bonds remaining in the sintered compact, despite a large content of non-metallic refractory additive evenly dispersed through the pores of the material, are believed to account for the combination of improved ductility and improved strength made possible by the method of this invention.

By the method of the present invention, a "green" compact porous metal shape is impregnated with a solution yielding a non-metallic refractory material whereby much larger amounts of the refractory may be combined with the metal and in a more favorable distribution so that greater strength and ductility for the composition results. With a prior art method whereby thorium oxide is mixed with platinum powder, the incorporation of the thorium oxide in an amount up to about 0.5 percent thorium oxide is about the largest amount which yields a readily workable bar. In comparison, the method of the present invention provides for the incorporation of up to about 1.1 percent thorium oxide into a compressed platinum powder matrix and whereby the composition is readily workable. Consequently, it is now possible to add a sufficient amount of a refractory oxide to a porous metal matrix so that serious shrinkage does not occur on sintering the oxide-containing material. Powder products containing a small amount of an oxide additive, like those with no additive, may shrink seriously on sintering, and if larger amounts of additive oxide are provided in accordance with the conventional procedure, the products lack adequate physical strength and ductility. When such larger amounts of refractory metal oxide are added to a porous metal compact by impregnation according to this invention, the physical strength and ductility of the composition are preserved and shrinkage or sintering may be essentially prevented primarily because of the incorporation of a large amount of oxide.

It is desirable that the liquid impregnating the porous matrix penetrates the pores of the compressed powder as much as possible. Such increased penetration may be accomplished by evacuating the gases in the compressed body under vacuum and thereafter contacting the evacuated compressed body with the impregnating liquid. Wetting of the metal by the liquid also assists in the penetration of the liquid into the small pores, and to improve the wetting, a wetting agent may be used in the liquid provided objectional impurities are not thereby introduced into the compact.

It has been found as was discussed that a slightly workable Pt bar with as much as 2 percent of ThO_2 or Al_2O_3 may be formed by the process of this invention. Such materials may be shaped, for example by coining. The upper limit of ThO_2 or Al_2O_3 which may be added to Pt workable by coining was not determined. It will be apparent that with less dense metals than Pt in "green" compacts higher weight percents of additives may be impregnated by the method of this invention, the quantities depending on the pore volumes of the "green" compacts as well as on the metal density. Workability of the composite sintered bars will depend in part on the ductility of the metals.

Compacting of bars in accordance with this invention is favorably carried out by isostatic pressing such as exerting pressure on a flexible sack containing the "green" metal powder through a liquid medium. Certain limits are set as to suitable isostatic pressure, and in the case of a −200 mesh platinum powder, from about 5 to 30 tons per sq. inch pressure may be employed. If the pressure is much less than 5 tons per sq. inch, it is difficult to handle the compact without its breaking up. If more than about 20 tons sq. inch pressure is employed, a skin of a more compacted surface is formed on the compact and tends to retard the removal of gases from the pores and the subsequent admission of the liquids into the pores. Preferably, the pressure should not be over 20 tons per sq. inch in the case of platinum powder compacts, but with other metallic powders, a somewhat lower compacting pressure may be employed with a softer metal and also a somewhat higher pressure may be employed with a harder metal. Impregnating solutions for incorporating oxides into compacted powders according to this invention are solutions such as saturated solutions of thorium-nitrate, aluminum-nitrate and yttrium-nitrate, but other oxide-forming salts such as metal formates may also be employed so long as they are capable of decomposition under heat to form a substantially pure oxide. By varying the percentage of the saturated solution mixed, e.g. with distilled water, one can vary the weight percentage of oxide in the finished bar and up to 2 percent oxide has been readily incorporated into the bar by this method. It has been noted that by incorporating oxides into metals by the method of this invention that equivalent amounts of oxide incorporation in comparison with conventional incorporation by mixing has resulted in a superior product with much less tendency for shrinkage. While this is not particularly understood, it is believed that the impregnation method of this invention provides for the incorporation of pure oxides in the form of crystals which are believed to bridge the pores or voids, and thereby provide for increased resistance to shrinkage. The following examples illustrate methods of preparing the material of this invention:

EXAMPLE I

A wire bar of platinum was pressed from −200 mesh platinum powder in an isostatic mold under a load of 7 t.s.i. About 6 ounces of Pt were used to fill a rubber sack of about ½" diameter and 9" length. The bar was weighed and then placed in a chamber where the air in the voids was evacuated. After two hours of vacuum, the chamber was flooded with a 17 percent solution of thorium nitrate while the chamber was under vacuum condition and the solution rapidly penetrated throughout the compressed bar. The bar was removed and air dried and heated from room temperature to 800° C. in air. Heating from the room temperature to 200° C. took a half hour, from 200° C. to 600° C. another half hour, and from 600° C. to 800° C. an additional half hour. Evolution of gas occurred largely successively from free water, hydrate water and nitrogen oxides. The heating was carefully controlled at a slow rate to prevent blowing of powder out of the pores by the evolved gases. After the decomposition, the bar was transferred to a sintering furnace and sintered at 1400° C. for one hour. The bar was subsequently removed, cooled and weighed, and a percentage oxide was calculated at 0.2 percent thorium oxide. The bar was then cold swaged and drawn to finished wire with appropriate anneals.

In accordance with the procedure of the above example, various other concentrations of thorium nitrate solution were employed and provided thorium oxide contents of 0.5 percent, 0.6 percent, 0.77 percent, 0.8 percent, 1.0 percent, 1.23 percent and 2 percent in a similarly compressed and sintered platinum bar. A similar series of bars was prepared by impregnating $Al(NO_3)_3$ solution into "green" Pt compacts, workable Pt–Al_2O_3 composites being successfully made with up to 2 percent Al_2O_3.

EXAMPLE II

Six troy ounces of relatively soft platinum sponge of about 99.999 percent purity was ground with a plastic ball in a plastic bottle until a sample was found to pass through a 200 mesh sieve. A portion of the powder was placed in a rubber sack of ½" diameter and 9" length. The sack was closed by a rubber stopper and placed in a water-filled container. Isostatic pressure was transferred to the powder by advancing a plunger into the container and building up the pressure to 6700 lbs. in approximately three minutes. Thus, the pressure on the powder reached about 7 tons per square inch. The bar was then removed, sintered, cold swaged with appropriate anneals, and drawn to 20 mil wire. At 1200° C. its E.M.F. was determined to be −6 microvolts, and its temperature co-efficient of resistance was 0.003906 ohm per ohm per degree centigrade.

EXAMPLE III

Two troy ounces of identical powder described in Example II was compressed in the manner described in Example II. After removal from the isostatic press, the compact was placed in a stainless steel pipe equipped with threaded end caps connected to stainless steel needle valves. The interior of the pipe including the voids of the powder compact was evacuated to a pressure of less than 1 mm. of Hg by drawing gas out through one of the needle valves. A 17 percent solution of thorium nitrate was placed in a tube connected to the other needle valve so that the solution could be admitted to the evacuated tube and to cover the porous compact. The thorium nitrate was thus transferred to the pores of the compact. The compact was removed from the steel pipe and heat treated in air according to the following schedule:

	Hr.
Room temperature to 200° C.	½
200–600° C.	½
600–800° C.	½

The compact was next transferred to a sintering furnace and sintered at 1400° C. for one hour, whereafter it was cooled and weighed and found to contain 0.2 percent thorium oxide. The compact was in the form of a bar having a diameter of ⅜". The bar was swaged at about 8 percent cross-sectional reduction per pass through a swaging machine with 1200° C. anneals after each pass until it was reduced in cross section to about 3/16". Swaging was continued to a 64 mil size with about 50 percent cross-sectional reduction between anneals. After an anneal at 64 mils, the resultant wire was drawn to a 20 mil diameter with one annealing at the 32 mil size. At 1200° C. this wire had an E.M.F. of +3 microvolts and a temperature co-efficient of resistance of 0.003910. It will be observed that the platinum powders used were of thermocouple purity and that the wire produced by Example III, in addition to its improved high temperature stability because of the incorporation of the oxide, compared favorably as a thermocouple grade material in comparison with the wire produced by Example II. The lack of effect on the temperature co-efficient of resistance resulting from thoria addition to platinum is attributed, first to the fact that thoria is substantially unreactive chemically with the platinum, and second to the continuous metal-to-metal contact previously discussed so that a multiple thoria film resistance is not interduced into the wire.

In accordance with the procedure of Example III, various other concentrations of thorium oxide were employed and provided thorium oxide contents of 0.5 percent, 0.6 percent, 0.8 percent, 1.0 percent and 2 percent in a similarly compressed and sintered platinum compact.

As stated above, the material prepared in accordance with this invention is superior for use under high temperature conditions for prolonged periods of time. The favorable distribution of higher amounts of oxide than was previously possible results in an improvement of the high temperature rigidity. It has long been known that platinum-rhodium alloys have greater high temperature rigidity than platinum, and that increases in stress to rupture life going from platinum to 90 percent platinum–10 percent rhodium and then to 60 percent platinum–40 percent rhodium are expected. It has been found that the superiority of platinum–0.5 percent thorium oxide in comparison with the platinum-rhodium alloys for extended periods is remarkable. The following tabulation compares stress for wire failure of a 50 mil wire determined at 100 hrs. with results extrapolated to 1000 hrs.

	100 hrs.	1,000 hrs.
Thermocouple Purity Pt	130	50
60 Pt–40 Rh	700	320
Thermocouple Purity Pt+0.5% ThO_2	640	470

While the above examples deal with platinum powder compacts having incorporated therein the oxides of aluminum and thorium, it has been found that other refractory oxides can be expected to provide the beneficial results of the invention, and that among other such oxides, it has been found that yttrium-oxide incorporated in the same manner as described with respect to aluminum-thorium oxide is especially beneficial. A composition according to the invention was made in accordance with the examples and impregnated with a solution of yttrium nitrate which resulted in the dispersion of 0.15 percent yttrium oxide in a platinum powder matrix. It has been found that the beneficial results of the method of this invention are obtained by the use of various metals and metal alloys. In the case of an alloy, a coprecipitated 90 percent platinum-10 percent rhodium powder was prepared by coprecipitating from $(NH_4)_2PtCl_6$ and

$$(NH_4)_3RhCl_6$$

from a solution thereof, and the coprecipitate was heated to form a sponge of the combined metals. The resultant powder was ground, compacted and impregnated with a solution of yttrium nitrate yielding 0.15 percent yttrium oxide. Further, comparative stress to rupture strength results were obtained as follows:

100 hour stress to rupture test at 1450° C.

	P.s.i.
Pt	140
90 Pt–10 Rh	600
80 Pt–20 Rh	660
60 Pt–40 Rh	700
Pt+.77% ThO_2	900
90 Pt–10 Rh+.15% Y_2O_3	940

The invention contemplates the substitution for platinum and platinum alloys of other metals such as the metals silver, nickel, copper, etc. and alloys thereof. The following example illustrates the method of incorporating oxides in accordance with this invention into a steel matrix.

EXAMPLE IV

A powder to produce a nickel steel is supplied at −200 mesh size in the following proportions: 96 percent of Fe containing 0.2 percent C, 3.5 percent of Ni, and 0.5 percent of Mn. This powder after thorough mixing is placed in a rubber mold blank for a 6" cam. The mold with the powder is placed in a chamber filled with light mineral oil which is then closed except for a pump connection. A compression pump is used to deliver pressure to the oil, and the build-up of pressure is continued slowly until a pressure of 10 tons per sq. inch is exerted against the powder contained in a rubber mold immersed in the oil. It was necessary for good subsequent penetration of the impregnating liquid into the matrix that the rate of compression be slow enough that the porosity is distributed uniformly through the matrix and that a skin of lower porosity is not formed on the outer surface of the matrix. The porous cam blank is removed from the mold and placed in a chamber which is thoroughly evacuated. Aluminum nitrate solution is admitted to cover the piece and left to stand in contact with it for one-half hour. The concentration of the aluminum nitrate is determined in terms of comparative weights of the "green" compact and of the product after impregnation and sintering so that the desired amount of aluminum-oxide precursor is admitted to the pores of the compact. In this case, aluminum nitrate proportional to 0.5 percent aluminum oxide is introduced into the pores. The cam blank is removed from the solution and then heated slowly in air from 200° C. to 300° C. until water and N-oxides are largely removed from the cam. The cam is then further carefully heated up to a temperature of 600° C. in an additional hour to remove the balance of the N-oxides. The cam blank was then taken rapidly to 1100° C. for five hours and sintered at this temperature in a neutral atmosphere (argon). The resultant cam products are characterized by excellent strength and tenacity and require less machining to dimensions than a product gear made by other prior methods previously described. As hereinbefore stated, various oxides forming salts may be employed in lieu of the salts specifically recited in the examples and including various metal formates, an example of a metal formate solution being 20 percent of aluminum formate trihydrate dissolved in de-ionized water at 90° C.

In accordance with the invention, it has been discovered that impregnated and sintered metal containing more than about 0.5 percent oxide does not seriously swell, distort or shrink on sintering; that when a chemically pure salt which does not react with the sintered metal is used there is no change or substantially no changes in the thermoelectric properties of the metal while its stress to rupture characteristics are advantageously improved, that the percentage of voids in a worked powder bar containing the impregnated oxide is very much lower than that of a standard worked powder bar where the oxide is mixed with the powder before pressing; that the method of this invention provides a product which is extremely well stabilized against deleterious grain growth; that there is a decrease in surface wear of products formed by this invention; that there is high strength characteristics evident in products made according to the invention; and that the method of the invention is eminently suited for making articles where close tolerances must be held. Examples of articles which may be advantageously fabricated from materials made in accordance with this invention are resistance thermometer wires, furnace windings, various forms of gears, cams, turbine and jet engines and metal structures, etc.

In addition to oxide additives other non-metallic refractories may be impregnated in accordance with the present invention. For example, carbon-forming materials may be impregnated into the "green" compacts. Composites of metal and graphite are formed with noble metals which do not form carbides when heated with graphite. Additional examples of additions of material forming non-metallic refractories are now given:

EXAMPLE V

A "green" silver compact pressed isostatically in a rubber sack as has been described for Pt compacts is heated to 60° C., evacuated and impregnated with a sucrose solution saturated at 50° C. Drying by slow heating, caramelizing of the sugar, and slow heating until carbonizing is complete is carried out. The composite is then heated at sintering temperature. The product has usefulness as an electrical contact with decreased sticking.

EXAMPLE VI

Another method for a high graphite silver contact prepared according to this invention involves impregnating the evacuated "green" compact with styrene containing a very slight amount of dibenzoyl peroxide. The compact is slowly heated but not raised above the normal boiling point of the styrene (146° C.) until a solid polymer is formed. It is then heated slowly until carbonization is complete after which it is sintered and formed into a contact shape as in Example V.

EXAMPLE VII

A "green" copper compact is prepared and evacuated. Titanium nitride (TiN) prepared by a reaction of titanium powder and nitrogen gas is wet ground in water to form a colloidal suspension, which is adsorbed in the copper compact. The water is removed by slow heating and the Cu–TiN composite is sintered and drawn to wire. Such wire is conductive and may be used where stiff copper wire is desired.

Various modifications are contemplated within the scope of the appended claims.

What is claimed is:

1. The method of making a workable oxide incorporated metal body comprising isostatically compacting a metal powder to form a porous compact thereof, of a substantially uniform porosity impregnating the compact with a solution of an oxide-yieldable impregnant substantially uniformly throughout its mass, heat treating the impregnated compact to convert the liquid impregnant to an oxide deposited in the pores of the compact, sintering the compact at sintering temperatures, and thereafter working the sintered compact into desired form.

2. The method of making a workable oxide impregnated metal body comprising isostatically compacting a metal powder to form a porous compact thereof, of a substantially uniform porosity impregnating the compact with a solution of an oxide-yieldable impregnant substantially uniformly throughout its mass, heat treating the impregnated compact to remove the liquid leaving an oxide-yieldable residue in the pores of the compact, further heat treating the compact to convert the residue to a substantially pure oxide, sintering the compact at sintering temperatures, and thereafter working the sintered compact into desired form.

3. The method according to claim 2, wherein the impregnant is an oxide-yieldable metal salt solution.

4. The method of making a workable oxide impregnated metal body comprising isostatically compacting a metal powder to form a porous compact of substantially uniform porosity, impregnating the compact with a metal salt solution substantially uniformly throughout its mass, heat treating the impregnated compact to convert the solution to a metal salt thereof uniformly distributed throughout the pores of the compact, further heat treating the compact to decompose the metal salt to a substantially pure metal oxide, sintering the compact at elevated temperatures and thereafter working the compact into desired form.

5. The method of making a workable oxide impregnated metal body comprising isostatically compacting a metal powder to form a porous compact of substantially uniform poroisty, evacuating the pores of the compact, impregnating the evacuated compact with an aqueous metal salt solution throughout its mass, heat treating the impregnated compact to evaporate the water leaving the metal salt uniformly distributed throughout the pores of the compact, further heat treating the compact to decompose the metal salt to a substantially pure oxide, sintering the compact at elevated temperatures and thereafter working the compact to desired form.

6. The method of claim 5, wherein the aqueous metal salt solution is a saturated solution of a salt selected from the group consisting of thorium nitrate, aluminum nitrate and yttrium nitrate.

7. The method of making a workable metal body incorporated with non-metallic refractory material comprising isostatically compacting a metal powder to form

a porous compact thereof of a substantially uniform porosity, impregnating the compact substantially uniformly throughout its mass with a liquid yielding the non-metallic refractory material, heat treating the impregnated compact to convert the liquid to the non-metallic refractory material, sintering the compact at sintering temperatures, and thereafter working the sintered compact into desired form.

8. The method of claim 7 in which the non-metallic refractory material is graphite.

9. The method of claim 7 in which the non-metallic refractory material is a nitride.

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