Oct. 22, 1968 I. J. HUTKIN 3,407,061

METAL COATING PROCESS

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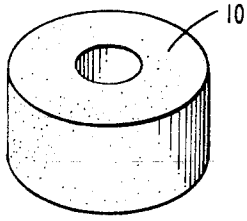


FIG. — 1

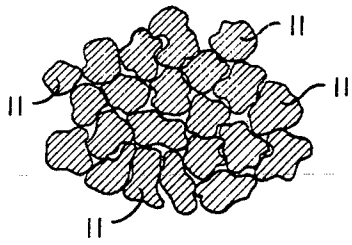


FIG. — 2

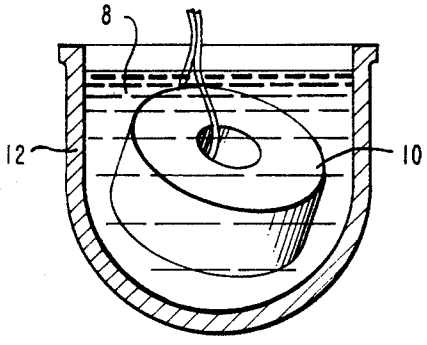


FIG. — 3

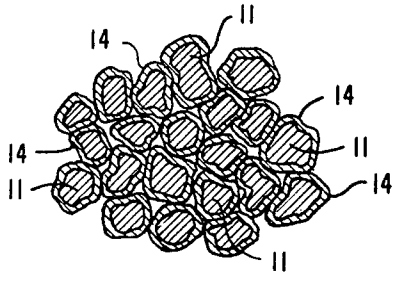


FIG. — 4

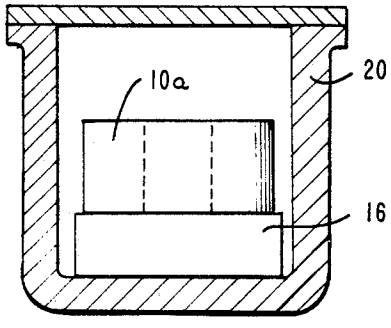


FIG. — 5

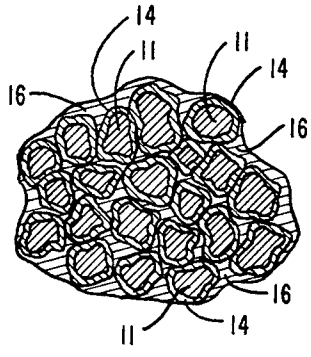


FIG. — 6

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METAL COATING PROCESS

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ABSTRACT OF THE DISCLOSURE

A difficultly wettable compact metal, for example, W, Mo, Zr, Cb, or alloys thereof is coated by forming a thin adherent film of more easily wettable metal, for example, Cu, Ni, Fe, Co, Cr, V, or a Cu-Ag alloy on the compact metal followed by coating the thin metal film with a metal having a lower melting point than the compact metal and which readily wets and bonds to the film-forming metal but which does not readily wet the compact metal, for example, Ga, In, Sn, Ag, or alloys thereof.

The coating and impregnation of metal compacts is well known. Surface coating of compacts is useful in preparing composite products having selected properties. Impregnation of porous metal compacts has been carried out to reduce the porosity of the articles and thereby strengthen them throughout or in selected portions.

However, difficulties have been encountered in coating and/or impregnating metal compacts where the metals of the compacts are normally resistant to wetting by other metals. In such instances, the rate of impregnation is slow, and the impregnation may be incomplete. Moreover, a surface coating of the coating metal may not bond rapidly and easily to the compact surfaces. In many instances, where impregnating is employed and the wettability problem is encountered, it has been necessary to increase the relatively slow rate of speed of impregnation by forcing the molten impregnating metal into the compact under pressure and/or by applying a vacuum to the side of the compact opposite from that contacted by the molten metal.

Specialized, relatively expensive and time consuming techniques have also been resorted to in order to facilitate wetting of the surfaces of the metallic compact with the coating metal so as to speed the impregnation and make it more complete. Such techniques include the use of ultrasonic vibration, roughening of the contact surfaces and pretreating the compact by heating it in a reducing atmosphere to strip off the wetting-inhibiting oxide layers thereof. In the latter instance, if the metal of the compact is refractory, relatively high temperatures may be necessary.

Such techniques are subject to certain deficiencies. If, for example, heating of both the compact and the impregnating metal in a reducing atmosphere to remove oxide films is not carried out, but, instead, pressure and/or vacuum are relied upon to promote impregnation, it has been found that incomplete impregnation may occur, with resulting void areas in the compact. This is particularly the case with large compacts. Moreover, high pressure generally must be employed when the compact pores are small in diameter. If ultrasonic vibration is employed to promote wetting, ultrasonic probes or the like must be used. These, obviously, have limited effectiveness in many instances due to the geometry of the compacts. Moreover, depending on the particular impregnating metal and porous compacts, it is not always practical to treat the impregnating metal and porous compact to a reducing atmosphere at the elevated temperatures required to promote wetting. This type of treatment, in any event, is of limited value when it is applied to massive porous compacts because of the relative inability of the reducing atmosphere to effect complete reduction of all the internal surfaces of the compact.

Accordingly, even the relatively expensive, time consuming and sophisticated techniques currently employed to avoid incomplete impregnation of metal compacts usually provide less than optimal results. A similar situation extends to external coating of difficulty wettable metal compacts. Therefore, it would be advantageous to provide an improved process of surface coating and/or impregnating metallic compacts comprising difficulty wettable metals, with dissimilar metals to provide the desired finished compacts.

Accordingly, the principal object of the present invention is to provide improved metal coated compacts of difficultly wettable metals. It is also an object of the invention to provide an improved process of metal coating difficulty wettable metal compacts. It is a further object of the present invention to provide an improved process of substantially completely impregnating difficulty wettable porous metal compacts with dissimilar metals of lower melting point. It is also an object of the present invention to provide a simple inexpensive process for fully impregnating porous metal compacts comprising difficultly wettable metals with lower melting point metals.

The foregoing and other objects are accomplished in accordance with the present invention by providing the present improved process and the products thereof. The The process comprises coating the difficultly wettable surfaces of compact metal with a thin adherent layer or film of more easily wettable metal and thereafter coating the film with a second metal of lower melting point than that of the compact metal, so as to provide a unitary structure comprising a substrate of the compact metal, the thin adherent film of the first coating metal thereon and the coating of the second lower melting point metal bonded thereto. While the process is adaptable to surface coating of metal compacts, it is also particularly suitable for effecting the essentially complete impregnation of porous metal compacts. Thus, the internal and/or external surfaces of the compact metal can be pretreated with the thin film and then fully coated with the desired lower melting point metal. The pretreating can be carried out either before or after formation of the compact, and utilizing a salt impregnation technique, followed by reduction to the thin film of metal, or utilizing electroless deposition. Accordingly, the process is adaptable to a variety of processing techniques.

Further objects and advantages of the present invention will be apparent from a study of the following detailed description and the accompanying drawings, in which:

FIG. 1 is a schematic perspective view of one embodiment of a compact suitable for treatment in accordance with the present process;

FIG. 2 is an enlarged fragmentary schematic cross section of a sintered granular structure such as comprises the compact of FIG. 1;

FIG. 3 is a schematic side elevation, with portions broken away, illustrating the compact of FIG. 1 suspended in an aqueous solution containing salt of a film-forming metal to be deposited on the interior and external surfaces of the compact;

FIG. 4 is an enlarged fragmentary schematic cross section of the granular structure of the compact of FIG. 3 after deposition of the adherent film of metal thereon;

FIG. 5 is a schematic side elevation, partly broken away, illustrating the compact of FIG. 4 during impregnation thereof with molten coating; and

FIG. 6 is an enlarged schematic fragmentary cross section of the granular structure of the finished composite

compact after full impregnation thereof by the coating metal schematically illustrated in FIG. 5.

Now referring more particularly to the present process difficultly wettable compact metal is pretreated to form thereon a thin adherent film of metal which is more readily wettable than the compact metal. The pretreated compact metal in compact form is then coated and/or impregnated with a coating metal which readily wets and bonds to the film-forming metal but which normally does not readily wet the compact metal. It will be understood that reference hereinafter to metal is intended to include single metals and also alloys of a plurality of metals.

The compact metal may be any suitable metal, for example, tungsten, molybdenum, zirconium, columbium or the like, or any suitable alloy. The metal of the compact is normally difficult to wet by the coating metal and usually has a relatively high melting point, such as, for example, a refractory metal. Its melting point is above that of the metal which is to be used to coat and/or impregnate the compact.

However, the film-forming metal utilized in the present process is more readily wettable by coating metals than is the compact metal. Usually, the film-forming metal also has a lower melting point than that of the compact metal. Moreover, the melting point is equal to or higher than that of the coating metal. The film-forming metal may be any suitable metal or alloy, for example, copper, nickel, iron, cobalt, chromium, vanadium, or a copper and silver alloy. Nickel, copper, cobalt, and iron can be easily applied to the substrate, that is, the compact metal, as water-soluble, heat decomposable salts. Moreover, iron, nickel and cobalt can be electrolessly plated without difficulty directly on the compact metal in the metal form. So also can copper. All such metals, and alloys thereof, are useful for the present purposes as the film-forming metal.

The coating and/or impregnating metal is any metal or alloy which has a melting point below that of the compact and preferably below that of the film-forming metal or alloy, and which normally is difficult to coat on and impregnate into the compact. Moreover, it is a metal or alloy which readily bonds to and wets the film-forming metal. Typical examples of relatively low melting point coating metals which are useful for impregnating and/or coating metal compacts include such metals as gallium, indium, tin and alloys thereof, as well as silver and the like. It wil be understood that selection of the particular compact metal, film-forming metal and coating metal can be made readily in accordance with the foregoing criteria.

The following examples are provided to more clearly show the manner in which the invention is carried out. It is to be understood that the examples are for the purpose of illustration only and the invention is not to be regarded as limited to the specific materials or conditions disclosed therein.

Example I

Referring to the drawings, a formed porous compact **10** shown in FIG. 1 comprising zirconium and having a sintered granular structure **11** as shown in FIG. 2 is immersed in a 5–30 weight percent aqueous copper nitrate solution **8** in container **12** for 5–10 minutes such as shown in FIG. 3. The treated compact **10** is then withdrawn from the solution, dried and heated to about 120° C. whereby the copper nitrate is melted to form a continuous coating on all external and internal surfaces of the compact. The copper nitrate film is then oxidized in air at 200° C. to copper oxide. This copper oxide film is then reduced in hydrogen at 400° C. to form a continuous thin adherent copper film **14** (FIG. 4), on essentially all the external and internal surfaces of the compact. As shown in FIG. 5, the pretreated compact **10***a* is then substantially completely impregnated with indium **16** by heating it in a hydrogen atmosphere at about 410° C. while disposed on a block of the indium within a closed furnace **20**. The structure of the finished composite compact is shown in FIG. 6. As indicated in FIG. 6, the substrate granules of zirconium **11** are completely surrounded with a thin adherent film of the copper **14**. The copper film is in turn bonded to indium **16** which completely fills the voids in the compact and covers the outer surfaces thereof. As indicated in the preceding example, the impregnation is not only complete but also very rapid, so as to provide a very uniform high quality composite compact product.

Example II

Following the general procedure of Example I a compact formed of sintered and pressed tungsten powder is immersed in an aqueous solution containing approximately 20 percent, by weight, of nickel nitrate, $Ni(NO_3)_2$ for about 5 minutes, after which the compact is withdrawn from the solution, drained, then air dried at about 45° C. The dried compact is then placed in a furnace and heated to about 80° C. (60–120° C.) and maintained at that temperature for 10 minutes, during which time the dehydrated nickel nitrate deposited over the external and internal surfaces of the compact melts and flows so as to cover the tungsten surfaces uniformly. The furnace temperature then is raised to 180° C. (140–200° C.) and air is passed through the furnace so that the nickel nitrate film is decomposed to nickel oxide. The 180° C. temperature is held for a period of about 10 minutes, after which time hydrogen is utilized to flush out the oxygen in the furnace, and a hydrogen blanket is established over the compact. The temperature of the compact is then increased to about 300° C. for about 20 minutes, during which time the nickel oxide coating is reduced to nickel. Temperatures of at least 270° C. are suitable for the reduction. Thereafter the compact is cooled to ambient temperature. The tungsten compact now has a thin adherent film of nickel on all internal and external surfaces.

The pretreated compact is then placed on a block of silver disposed in a boat, and the boat is placed in the furnace and heated to 970° C., i.e., slightly above the melting point of silver, in the presence of hydrogen. The compact is held at that temperature until full impregnation of the tungsten compact by the molten silver is complete, i.e., for a period of several minutes. Thereafter, the compact is cooled to ambient temperature, and is withdrawn from the boat. It is now ready for use as a circuit breaker contact, the high temperature refractory metal comprising the tungsten offering good structural strength, while improved electrical conductivity is afforded by the silver. Since the silver has fully impregnated all portions of the tungsten compact, the properties throughout the compact are uniform.

Comparable results can be obtained utilizing suitable heat decomposable soluble salts, such as the nitrates, of the film-forming metals, for example, cobalt nitrate and the like, or selected sulfates, such as cobalt sulfate. The salts of the film-forming metal are selected so as to maintain the salt decomposition temperature and the oxide reducing temperature below that at which reaction between or alloying of the film-forming metal occurs. By carrying out the described procedure, a thin adherent film of the desired metal can be deposited on the surfaces of the porous compact, substantially improving the wettability of the compact while substantially retaining the remaining characteristics of the compact.

Also in accordance with the present process, and as another embodiment thereof, the film-forming metal can be directly deposited on the substrate, that is, the compact metal, by electroless deposition. This can be accomplihed in accordance with well-known techniques, such as those set forth in U.S. Patent Nos. 2,955,959, 2,827,398, 2,532,283, 2,828,227 and 2,827,399. Comparable well-known electrolytic deposition techniques can also be utilized. In such instances, the thin adherent film

of metal deposits out directly on the compact metal so that reduction of the film is not required.

Whether electroless plating, or deposition of a suitable salt, followed by heat decomposition to the oxide and reduction to the thin metal film is employed or a comparable technique is employed, the substrate of compact metal upon which the deposition occurs can either be in the form of the powdered compact metal before compacting and sintering, or in compact form, i.e., after the compact has been formed, as by pressing and sintering. Moreover, where the latter technique is employed and the compact is dense and relatively non-porous, the formation of the thin adherent film can be controlled so as to largely restrict its deposition to the external surfaces of the compact, should only external coating of the compact be desired.

After the thin adherent film of readily wettable metal has been formed on the compact metal, the compact metal, if in powdered form, can then be pressed and sintered into the desired compact configuration. Relatively dense non-porous compacts can be prepared utilizing conventional pressing and sintering techniques well known in the art.

The shaped compact containing the desired more readily wettable metal film on the external and/or internal surfaces thereof is now ready for treatment with the lower melting point coating and/or impregnating metal. This step is carried out at above the melting point of the coating-impregnating metal but below a temperature which would result in reaction or alloying of the coating and/or impregnating metal with the compact metal. Sometimes it is only necessary to heat the coating metal to the temperature required to wet the thin adherent film with the coating metal in a molten condition. For example, silver can be used at its melting point (960° C.) to coat and/or impregnate a refractory metal compact which has a thin film of nickel disposed therein. In certain circumstances, however, it is desirable to employ a temperature sufficiently above the melting point of the coating metal and a reducing atmosphere such that the oxide film on the coating metal can be reduced during the coating and/or impregnation, so as to facilitate the coating and/or impregnation. For example, impregnating with gallium, indium, tin and alloys thereof is usually carried out at above 400° C. so that the oxides thereof are reduced in a reducing atmosphere.

Any convenient technique can be employed to effect the required contacting and bonding between the thin adherent metal film and the coating metal. One typical technique is schematically illustrated in FIG. 5 and has been previously described. It comprises placing the pretreated compact on a block of the coating metal in a furnace containing a reducing atmosphere, and thereupon melting the block, causing the metal to permeate and fully impregnate the compact. Other techniques include reversing the positioning of the compact and block, or spraying the molten coating metal on the compact, floating or immersing the compact in a pool of molten coating metal, etc.

The present process provides substantial advantages over conventional methods of coating and impregnating compacts. Not only does the present process assure complete bonding of the compact and complete impregnation of the compact in a shorter period of time than formerly, but it also decreases the temperatures normally required to carry out the coating and/or impregnation. Thus, for example, instead of having to increase the temperature of a tungsten compact to above 800° C. in order to remove sufficient tungsten oxide to permit any substantial impregnation of the compact, impregnation of a tungsten compact containing a thin film of nickel with a coating metal comprising tin can be carried out at about 400° C. Moreover, such impregnation is complete and rapid, whereas in most instances in which the tungsten compact is of large size, the use of the 800° C. + temperature, without the thin adherent film, will not assure complete impregnation with tin, even over a much longer period of time. Accordingly, the persent process assures more uniform and rapid results in a less expensive manner for the production of high quality composite compact products. Further advantages of the invention are as set forth in the foregoing.

All modifications, changes, alterations and substitutions in the present process and product as are within the scope of the appended claims form a part of the present invention.

What is claimed is:

1. An improved process for coating a difficultly wettable porous metal compact comprising a refractory metal selected from the group consisting of tungsten, molybdenum, zirconium, columbium or alloys thereof with a coating of a metal having a lower melting point than the metal of said compact and selected from the group consisting of gallium, indium, silver, tin and alloys thereof which comprises:

(a) impregnating said porous metal compact with an aqueous solution of a heat decomposable salt of a metal selected from the group consisting of nickel, copper, cobalt, and iron;

(b) drying and melting said salt to form a continuous coating on essentially all internal and external surfaces of said compact;

(c) heat decomposing said salt to the oxide and thereafter reducing said oxide to the metal; and

(d) coating the impregnated metal compact with said lower melting point metal at a temperature above the melting point of said lower melting point metal but below the temperature which would result in alloying of said compact metal.

2. The process of claim 1 wherein said refractory metal is tungsten or zirconium, wherein said salt comprises nickel nitrate or copper nitrate in about 5–30 weight percent concentration in said aqueous solution, wherein said nitrate after drying in situ is melted at about 60–120° C. and flowed over the internal and external surfaces of said refractory metal to assure the production of an essentially continuous adherent film, wherein the heat decomposition is effected in air at about 140–200° C., wherein the resulting oxide is reduced in hydrogen at least about 270° C., wherein said lower melting point coating metal is selected from the group consisting of gallium, indium and tin and said metal compact is substantially completely impregnated with said coating metal in a reducing atmosphere at above about 400° C.

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