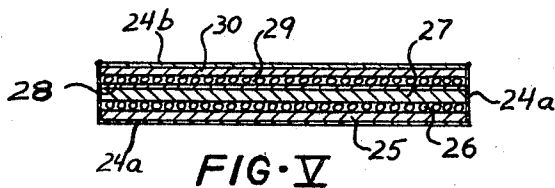
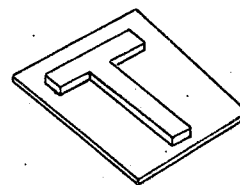
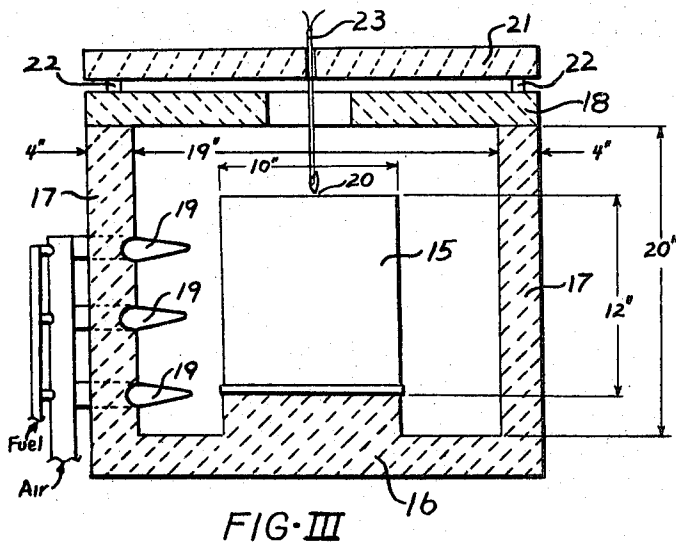
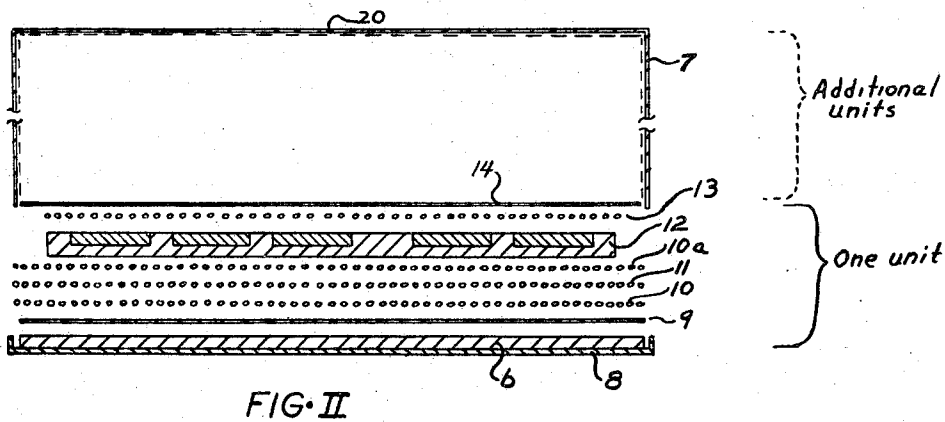
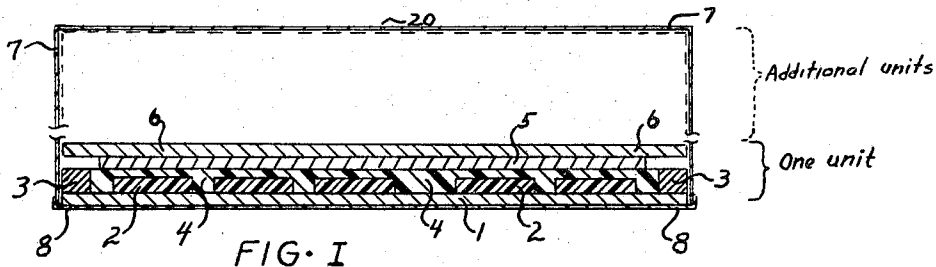


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MOLDED METAL PARTS, AND VAPOR PHASE SINTERING PROCESS, MOLDS
AND COMPOSITIONS FOR PREPARING SAME
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MOLDED METAL PARTS, AND VAPOR PHASE SINTERING PROCESS, MOLDS AND COMPOSITIONS FOR PREPARING SAME

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ABSTRACT OF THE DISCLOSURE

The disclosed process uses metal vapor of a selected group of metals to simultaneously sinter and alloy a mass of loose metal powder shaped and heated in a porous, non-metallic, non-oxidizing mold, thereby to form in one step a molded and alloyed article having the desired final shape. No vapor-forming metal is in contact with said loose metal powder, so that only the metal vapor acts on said powder. The vapor-forming metal is selected from the group consisting of magnesium, zinc, cadmium, arsenic, rubidium, cesium, potassium, sodium, and mixtures thereof. The loose metal powder is selected from the group consisting of iron, cobalt, nickel, manganese, titanium, zirconium, columbium, vanadium, copper, silver, gold, alloys in which one of the foregoing elements constitutes the base, composite powders, and mixtures of the foregoing.

This invention relates to (1) molded metal products, parts or pieces prepared from metal powder(s) with the aid of metal vapor such as zinc or magnesium vapor, (2) the process for preparing said products, (3) the molds used in said process as well as the process for preparing said molds, (4) and certain metal compositions used in and/or resulting from said molding process.

In brief description, the molded products and parts of the invention are prepared by filling a mold cavity with metal powder(s) without applying more than slight pressure, placing the so-filled mold in a retort containing a measured amount of vaporizable metal (e.g. zinc, magnesium, etc.), substantially closing the retort (by preference a small vent opening is provided), heating the substantially closed retort above the vaporization temperature of the vaporizable metal, thereby to permeate the atmosphere of the retort with said metal vapor, cooling the retort and contents sufficiently to prevent oxidation of the metal contained in the retort, and finally recovering the resulting molded metal part(s) from the retort. For this purpose, the molds used in providing and defining the mold cavities for the sought parts are prepared from carbon and are purposely made in such a way as to be quite porous, whereby the metal vapor gains easy access to the metal powder(s) contained in the mold cavities. Also the molds are baffled with vapor-impermeable baffles which serve to properly guide and distribute the metal vapor evenly in reference to the mold cavities. The molded parts prepared in accordance with the invention can be prepared by starting with any elemental metal(s) and/or alloy(s) (and with or without composite powders) melting above the temperature at which the metal vapor is generated and sustained. However, I prefer the metals grouped in the Periodic Table and known as the heavy ductile metals, and which commonly include, iron, cobalt, nickel, copper, silver and gold. I also prefer for some purposes mixtures of copper or iron with nickel. I especially prefer to start with nickel powder where the resulting molded parts are intended for jewelry usage because of the excellent color, polish, and corrosion and tarnish resistance exhibited by such molded parts when the finished alloy is binary and contains 32-35% zinc, balance nickel, or when the finished alloy is ternary and contains about 11.2-11.5% zinc, balance equal weights of nickel and iron.

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Accordingly, the objects of this invention are:

(1) To provide novel molded metal articles by starting with selected metal and/or composite powders;

(2) To provide a novel process for preparing said molded metal articles;

(3) To provide novel porous molds adapted for use in the vapor-sintering process of the invention; and

(4) To provide certain novel metal compositions which are particularly adapted to the purposes of the invention.

The foregoing and other related objects of the invention will be understood more fully from the following description of the invention, taken in conjunction with the attached drawings in which

FIG. I is a vertical sectional view of a typical assembly used in forming a mold of the kind employed in practicing the invention;

FIG. II is an exploded vertical sectional view of a typical assembly of molds and mold parts in a retort of a type adapted for the commercial practice of the invention, certain vertical dimensions being exaggerated for clarity;

FIG. III is a vertical sectional view of a typical heating furnace and retort assembly suitable for the practice of the sintering process of the invention;

FIG. IV is an isometric view of a typical jewelry item molded in accordance with the invention, the view specifically illustrating an ornamental plate carrying the initial T; and

FIG. V is a vertical sectional view of a typical pack assembly referred to in Example 9, the vertical dimensions of the drawing being exaggerated for clarity.

The invention will now be explained in connection with FIGS. I, II and III of the drawings, it being understood that such explanation illustrates only one particular and preferred embodiment of the principles of the invention, with nickel being used to represent any appropriate starting metal powder and zinc being used to represent any appropriate vaporizable metal. Referring now to FIG. I, which illustrates a preferred manner of preparing a mold, a flat base plate 1 of porous carbon (prepared in the general manner about to be described in connection with the mold itself) is placed on any suitable flat supporting surface and one or more patterns 2, 2 are rested on its upper surface in any desired arrangement and disposition. A metal rim member 3, typically of iron and of a size, conformation and thickness adequate to define a cavity within which the desired mold can be formed is placed on said base plate 1 so as to surround the patterns 2, 2 and so as to leave room for forming a mold surrounding each and all of said patterns. The cavity so defined by said base plate 1, said rim member 3 and said patterns 2, 2 is then filled with a plastic mixture 4 composed of powdered carbon (preferably powdered graphite) and hardenable but initially normally-liquid organic resin binder. The physical and chemical attributes of said binder will be described in more detail hereinafter, but for the present purposes the binder can be identified (solely for purposes of illustration) as an acid-activated furfuryl alcohol resin. Said mixture of powdered carbon and activated liquid binder (illustratively composed of about 3 parts by weight of powdered carbon and 1 part of binder) is rammed into the cavity in any suitable manner (i.e., by tamping it in by hand or by ramming it into place with a mechanical hammer or conventional ramming press). After the cavity has been filled with said mixture, the top surface is struck off with a blade so as to be smooth and at the same time level with the top surface of rim member 3. A flat porous carbon plate 5 having lateral dimensions smaller than those of rim member 3 is placed on said smooth upper surface of the rammed mixture in such position as to be within but out of contact with rim member 3. Another porous carbon plate 6, substantially a duplicate of plate 1, is then placed on top of plate 5 with its edge in vertical

alignment with the edge of plate 1. If additional molds are to be made, then plate 6 can be used as the base plate for the next assembly, and what has been described above can be repeated until any desired number of molds has been prepared, thus yielding a columnar stack of unit assemblies having a predetermined peripheral conformation. If only one mold is to be prepared, then plate 6 simply serves as a top or cover plate for the unit.

Plates 5 and 6 are used to maintain the mixture 4 (and the resultant mold which it forms) in a flat condition during the next step of firing the mold unit(s) to carbonize the binder. It will be understood that where two or more mold units have been stacked in the manner described, then plates 5 and 6 function in like manner in all units.

The next step in preparing the molds is to heat them to an elevated temperature at which all of the resinous binder is carbonized. It will be understood that some time after the powdered carbon/binder mixture has been rammed to form a mold, the normally-liquid binder, due to the presence of suitable activator (hardener, catalyst, converter) becomes converted to a solid condition. Hence the rammed mixture becomes hard and stiff, and it can then be separated from the patterns, if such is desired. However, for commercial practice of the invention, I prefer not to so separate the molds from the patterns and instead prefer to use patterns which have been made from a material which can be dissipated from the mold units during the carbonizing firing. Thus patterns made of paraffin, waxes, synthetic resins or other thermally-decomposable and evanescent material can be so used. Considering now that patterns 2, 2 are made of such a material, the single mold unit of FIG. 1, or a stack of mold units corresponding thereto, is next disposed on the cover of a moderately tight-fitting can. The can itself, having a small vent opening in its bottom, is slipped down over the mold unit or stack of units and joined with its cover, thereby enclosing the mold unit or units. As will be understood from the subsequent description of FIG. III, the can and cover used for this purpose can be one of the retorts used in the practice of that part of the invention. The filled can is next placed in any suitable heating furnace wherein it is heated to carbonizing temperature (e.g. about 1200° F. where the binder is said activated furfuryl alcohol resin). Dense black smoke exits from the vent opening in the can during the carbonization period and heating should be continued until the issuance of said smoke ceases. The can, still closed, can then be removed from the furnace and allowed to cool to room or other convenient handling temperature, at which time the can is separated from its cover and lifted away to expose the fired mold unit or units. Each unit is then carefully disassembled, primarily for the purpose of removing the rim member 3 but the disassembly also provides an opportunity for inspection of the carbonized mold and in the commercial practice of my molding process it is conveniently combined with (a) the step of filling the mold cavities with metal powder and (b) the step of reassembling the filled molds for subsequent treatment with metal vapor (i.e., retorting or vapor sintering).

Referring now to FIG. II, which illustrates a preferred way of preparing an assembly for retorting, there is shown a thin-walled metal retort 7 and tight-fitting cover 8. The assembly of molds and baffles which is to be enclosed within the retort is built up by starting with the inverted cover 8. A porous carbon plate 6 is first laid on the cover. Said plate can be one of those removed during the disassembly of carbonized mold units described above in connection with FIG. I. Thus as the carbonized mold units are being disassembled, one of the plates 6, 6 can be used to start the assembly which is to be built up for retorting. The plate 5 of the carbonized mold assembly is not used and is laid aside. Then the carbonized mold itself is removed and is ready for filling with metal powder. For this purpose it is simply rested on a supporting surface and metal powder (e.g. fine nickel powder, minus

325 mesh) is poured into each cavity and levelled by drawing a straight edge across the surface of the mold. If this operation fails to remove all excess metal powder, the slight amount which remains can be ignored. The filled porous mold is then ready for insertion into the assembly of parts for the retort. However, before it is added to said assembly, a thin, flat, ferrous metal baffle plate 9 is laid on plate 6 and its surface is covered with a thin layer of graphite powder 10 (e.g. minus 35 mesh). Then a layer 11 of zinc powder (e.g. 20 mesh powder) representing a proper weight of zinc in proportion to the weight of nickel powder in the mold cavities (a minimum ratio of 1:20 should be observed and preferably the ratio is between 1:20 and 1:1) is sprinkled on the layer 10 of graphite powder. The zinc layer 11 is in turn covered with a thin layer 10a of graphite powder. These layers (9, 10, 10a and 11) form a porous, slightly compressible bed adapted (a) to support the mold which is next to be added to the assembly, (b) to distribute the supply of zinc fairly uniformly across the bottom face of the mold, and (c) to provide a carbon/zinc blend that will avert oxidation of the zinc and reduce any zinc oxide present while the finished retort assembly is being heated up to the vaporizing temperature of the zinc.

The filled mold 12, described above, is now placed on top of graphite layer 10a. Then a thin layer 13 of powdered graphite (e.g. minus 35 mesh) is sprinkled or sifted over the entire upper surface of said filled mold. Next, another thin flat ferrous metal baffle plate 14 is laid on said layer 13. This completes one unit as built up for retorting. If a plurality of filled molds is to be retorted together then said unit can be repeated the desired number of times thereby to build up a stack of the desired size. The retort 7 is then placed over the mold unit or units and joined at its lower edge with cover 8. It will be understood that the retort 7 and cover 8 are dimensioned so as to be snug-fitting and substantially completely filled by the unit or units being enclosed. That is, the aim here is to have very little air remaining within the retort, most of it being displaced by the said unit or units. Thus the height of the retort will vary with the number of mold units built up over cover 8 unless it is preferred to use a retort of uniform size and to substitute a column of graphite plates to fill that part of the retort not occupied by molds. Also it will be appreciated that by making the molds initially with dimensions yielding a snug fit in retort 7, no difficulty arises in this connection when the mold units are being built up for retorting. Another reason for having a snug fit between the retort and all parts of the mold unit(s) is that such a fit promotes uniform and rapid heating of the unit(s) when the retort is fired by external heating.

Referring now to FIG. III, a filled retort prepared as last described above is represented by reference character 15 and is shown in firing position on the hearth 16 of a furnace chamber defined by walls 17, 17 and top 18. While optional, I prefer also to place a roof 21 over top 18 but spaced therefrom by spacers 22, 22, thereby to control the furnace draft. Heat can be generated in any desired way around and about retort 15, but I prefer to use fuel gas/air burners 19, 19 pointed so as to apply their flames tangentially to the inner walls of the furnace and so heat the retort 15 by radiation. This method prevents direct impingement of the flame on the retort and prolongs the life of the latter. Such burners not only give rapid heating but can also be adjusted so as to give flame which is non-oxidizing or reducing in character, as desired. By so adjusting the burners, the useful life of the retorts can be prolonged. If oxidizing flame, or electric heat (e.g. resistance or induction) generated in the usual oxidizing atmosphere is employed, the thin low cost expendable type metal retorts can easily be burned through before the metal vapor therewithin has had full opportunity to combine with the metal powder in the mold cavities. By maintaining reducing reducing conditions around the retort,

such burning through is eliminated and the thin-walled retorts can in fact be used a number of times before being discarded. Those skilled in the art will recognize that a protectively-reducing atmosphere around the retort can be established and maintained in various ways other than by incomplete burning of a combustible fuel/air mixture. However, I prefer the latter because of its rapid heating rate and ease of manipulation and adjustment. Nevertheless, my objectives can be achieved equally well with other kinds or types of furnaces, as will be obvious to those skilled in the art.

During the retorting, the retort and its contents are brought up to the vaporization temperature of the vaporizable metal being used, e.g. zinc, and preferably are brought to a slightly higher temperature (1550°–1750° F. for zinc as the vaporizable metal used to vapor sinter nickel, iron, copper or equal mixtures of nickel with copper or iron). During retorting, some small amount of metal vapor exits through the vent hole 20 and produces a readily identifiable flame. I purposely make the vent hole quite small (e.g. .060" in diameter) so as to minimize said loss of vapor, but the hole is not eliminated because the flame of vapor serves the very useful purpose of indicating that satisfactory conditions then prevail within the retort. Also the ebbing of the flame can be used to indicate that the pre-weighed zinc supply is exhausted and that the necessary amount of vapor has been supplied to the metal powder in the molds, thereby assuring uniformly reproducible results from one retorting to the next. Thermocouple 23 is positioned in the flame.

As will be understood from the description of the way in which the units of each mold assembly are prepared prior to retorting, the supply of vaporizable metal needed to react with each cavity-full of metal powder is located out of physical contact with the loose metal powder but only a short distance away from the latter. Hence little time is needed after the vaporizable metal has reached its vaporization temperature and after the selected peak furnace temperature has been reached. In other words, no "soaking time" is needed after the vapor flame begins to diminish providing the retort is then at peak operating temperature. If the temperature of the retort is below peak when vaporization of measured zinc is complete, heating is continued and the temperature raised continuously until the desired operating maximum is attained. Cooling of the retort is begun immediately when both vaporization of the zinc is complete and the molds are at the desired operating temperature.

Since the mold assemblies (units) consist almost entirely of carbon and/or graphite, they have excellent thermal conductivity. My experience has established that the assemblies heat quite uniformly throughout. Suffice it to say that I have yet to observe any evidence of under-heating at the centers of the molds due to thermal gradients, once the retort has been heated sufficiently to produce the tell-tale vapor flame at the vent hole. As for time-at-temperature needed to effect penetration of metal vapor to the center of the masses of metal powder in the mold cavities themselves, I have found that the vapor will permeate each cavity-full completely in thicknesses up to 1/4" by the time vaporization of the set amount of zinc is complete. This, of course, occurs automatically when the temperature of the molds reaches 1663° F., the boiling point of zinc at 760 mm. Hg pressure. The action of sintering in the powder mass as the result of the alloying of the two phases (powder and vapor) is intensified when the interaction therebetween produces constituents which are liquid at or below the boiling point of zinc. For instance, in the case of copper powder sintered with zinc vapor, solid copper will dissolve more than 30% zinc at temperatures well below that necessary to boil zinc at atmospheric pressure. Therefore, temperatures leading up to 1663° F. will cause limited liquefaction of each copper particle, as it transforms to brass, and consolidation is thereby effected more thoroughly.

I have observed that an improper balance of zinc vapor and maximum operating temperature will result in complete melting of the resulting brass and a consequent loss of shape and dimension of the part occurs. When proper amounts of vapor are supplied by the simple expedients of exhausting a specific amount of zinc at, or in the time taken to reach, a specific peak temperature, sintered brass parts of uniform quality are produced. Depth of penetration of the zinc vapor is easily measured in the cross section of a molded part made from copper powder since the color of brass is easily distinguishable from that of copper. With other starting metal powders, color may be no criterion, and penetration can best be determined by chemical analysis of samples taken at various depths within the finished part. For the reasons given, I prefer to practice the invention by bringing the retort to a temperature of 1675° F. in no less than three hours, using a furnace dimensioned as shown in FIG. III and starting with the furnace chamber at room temperature. This period of heating allows uniform and thorough soaking of the molds and metal powders, and eliminates the need for any holding period at 1675° F. Longer heating times can, of course, be used for special purposes or for thick masses of metal powder. However, for nickel base jewelry items, where the molded articles seldom have thicknesses over about 1/4", a three hour heating cycle at 1750° F. has been found to be adequate for a retort containing 15 pounds of nickel powder and 15 pounds of mold weight when starting with a cold furnace chamber. This gives finished articles that are still porous yet have been thoroughly integrated by the metal vapor into structures which are strong, malleable and sonorous. More description of the finished articles of the invention is given hereinafter.

After the desired heating cycle and temperature have been attained, the retort is allowed to cool and measures should be taken during such cooling to prevent oxidation of and early failure of the retort with a consequent oxidation of the metal articles within the retort. To this end the burners 19, 19 can be turned to their lowest levels giving stable flames which are smoky. Thus little heat is generated and a reducing atmosphere is provided. Further to this end the opening in roof 18 of the furnace can be reduced in size (as by inserting a plug) so as to be just large enough to vent the products of combustion of the burners. Another way to effect protective cooling is to plug said furnace opening so as to leave a pin hole opening, and turn off the air supply to the burners. The burners can then be adjusted to maintain a flame outside the furnace just above said pin hole opening in the plug. This fills the furnace with combustible fuel and prevents influx of air.

After the retort has cooled below about 800° F. further protection against oxidation is no longer needed. Hence the retort can be removed from the furnace and allowed to cool in the ambient atmosphere until cold enough to handle. It can then be opened and its contents removed. All the porous carbon plates can be saved for reuse. The molds themselves, however, are expendable since in most instances where the finished articles are of intricate design and articles are held firmly within the mold cavities and the molds must be broken to release them. Some attachment of the articles to the cavities is strictly a mechanical one and is due to the initial porosity of the molds. Little pin points of metal penetrate the pores and serve to anchor the articles to the carbon. The carbon represented by the broken molds can be saved and eventually reground for further use. The attachment of the articles to the carbon occurs mainly when the graphite powder used in preparing the molds is 35 mesh. Molds made of screened graphite powder passing a 65 mesh screen do not adhere to flat surfaces of molded parts but do adhere where in contact with fine details in design. This part of the mold can be easily removed from the metal article by wire brushing. Sometimes the molded articles have thin webs of metal attached to them (result-

ing from incomplete removal of excess metal powder from the mold surfaces after the cavities were filled in the first instance). Such metal "flashing" can be broken off easily. The molded articles so recovered in a clean but essentially "as-molded" condition exhibit a microroughness resulting from the initial porosity of the molds. This microroughness is easily removed by sanding, filing, grinding, etc., after which the articles can be smoothed and polished. FIG. IV illustrates the finished articles removed from the molds of FIGS. I and II; as far as dimensions are concerned the finished "as-molded" articles are true replicas of the patterns except that they exhibit a slight shrinkage in all dimensions. This is due to the shrinkage of the molds themselves during the carbonization firing.

The process for making my molded articles having now been described in connection with a particular embodiment, the following generalizations concerning the process can be made:

(1) Raoult's law applying to dilute solutions states that the vapor pressure of a solution is lower than that of the pure solvent by an amount that is proportional to the concentration of the solute. The term solvent generally refers to a liquid but more broadly it can mean the component of a gaseous, liquid or solid mixture that is present in excess of all other components in the system. As an example, the vapor pressure of an "ordinary" solution, in which water is the solvent, is lowered 170 mm. Hg for each gram of solute in 1000 g. of water and up to two or three times this amount for "non-ordinary" solutions. For solvents other than water a characteristic value for each is observed. This decrease in vapor pressure can be expressed another way by saying that there is an increase in the temperature at which the vapor pressure of the solution represents that of the pure solvent. Corresponding to this elevation in temperature, there is an increase in the temperature at which the vapor pressure of the solution will exceed an external pressure of one atmosphere or 760 mm. Hg. This constitutes a rise in the normal boiling point of the solution.

When two or more miscible metals form an alloy as a solid or molten solution, Raoult's law may be applied and the partial pressures p_A and p_B of the metals and in the binary system are approximately equal to:

$$p_A = P_A N_A$$

and

$$p_B = P_B N_B$$

where:

P_A = vapor pressure of pure metal A

P_B = vapor pressure of pure metal B

N_A = mol fraction of metal A in the alloy

N_B = mol fraction of metal B in the alloy

When metals show a tendency toward immiscibility, the partial pressures show a positive deviation from Raoult's law by increasing. Hargreaves ("The Vapor Pressure of Zinc in Brasses," Journal Institute of Metals, 64, 115, 1939) has shown that additions of aluminum effectively increase the vapor pressure of a brass of a given zinc content by a marked amount. Zinc and copper when combined in a simple binary alloy undergo a mutual decrease in activity and their vapor pressures show a very negative deviation from the law as they become much less as a brass. The extent of the deviation increases as the molal ratio N_A/N_B between the metals increases and indeed it has been reported by Hargreaves that the vapor pressure of solid brass is much lower than the vapor pressure of pure zinc, the amount being related to the copper content. These fundamental findings to be described again in the following passages were seen to be directly applicable to the metallurgical conditions prevailing in the course of the process of the present invention.

The low boiling point of such an abundant and useful metal as zinc has prompted the establishment of its vapor pressure over a wide temperature range. With a vapor

pressure varying from one mm. Hg at 910° F. to 760 mm. Hg at 1663° F., zinc has very high vaporization rates and this unique property has led to the development of a number of processes utilizing the feature.

The vaporization of zinc has long been of interest, particularly in the metallurgy of brass ever since Roman brass was made by heating copper with charcoal and a zinc carbonate ore to red heat in a closed crucible. Metallic zinc reduced from the ore by the charcoal vaporized and diffused into the solid copper. When the melting point of the resultant brass was depressed sufficiently, the alloy liquified and flowed into the crucible bottom. Recently Hargreaves reported in his study of the changes occurring at the surface of solid brass during annealing that the vapor pressure of zinc in 60-40 brass (60% Cu) was one mm. Hg at 1085° F. By comparing this value with one given previously for pure zinc it can be seen that the 60-40 alloy can be heated 175° F. higher than pure zinc before vaporization from the brass reaches the order shown by zinc alone. The vapor pressure of an alloy of 70% Cu and 30% Zn was found by Hargreaves to be one mm. Hg at 1150° F., serving to further illustrate the effect of copper, which is practically non-volatile compared with zinc, in depressing the vapor pressure of zinc in the alloy.

From these data it can be reasoned that if zinc is heated in close proximity to copper powder and the formation of oxides of the metals avoided, at approximately 900° F. and above it is to be expected that alloying will take place between the vapors of zinc and the particles of copper. Then, since the vapor pressure of zinc in the alloy initiated by this reaction is depressed by the presence of so large an amount of copper in relation to the zinc vapors formed, a reversible vaporization of zinc is prevented and the alloying action continues unabated as the temperature of the process is increased steadily to the boiling point of the zinc where the last of the liquid phase evaporates and the supply is exhausted. At this point, if the supply of zinc was properly gaged to result in the formation of a brass analysis that will not be subject to gross melting at the boiling point of zinc and slightly above (1675° F.), a reproducible sintered brass article of uniform shape is produced.

To further illustrate the fact that little zinc loss from the brass is possible by a reversible reaction, we can compare the vapor pressure of 760 mm. Hg of pure zinc at its boiling point with data compiled by Hargreaves showing the actual vapor pressure of zinc in a brass containing 90% copper to be 12 mm. Hg and in an 84% copper brass to be 25 mm. Hg at the same boiling point temperature of 1663° F.

The data of Hargreaves have been presented to show that certain basic assumptions can be made concerning the process of sintering copper powder by the use of vaporized zinc. It can be further reasoned that as alloying continues during the range of heating needed to liquefy zinc at 787° F. and to boil it at 1663° F., each copper particle becomes a brass particle of increasing size, and by diffusion, of increasing uniformity. As size increases, the contact area between particles enlarges adding to and strengthening the consolidating effect. With proper control of zinc and by limiting the temperature of the process to that needed to complete vaporization of the zinc, the formation of a liquid phase consistent with copper-zinc equilibrium conditions can be utilized to give a limited amount of liquid phase sintering to further densify sintered copper articles without the loss of shape or dimensions.

Adding to the evidence already furnished to support the theory that zinc utilization is reasonably efficient, I have the results of a zinc vapor-sintering test made on a single 1/4" thick mold carrying 5 1/2 oz. of copper powder in the form of fifty 1/8" parts. Two oz. of zinc were charged with the mold and a peak temperature of 1550° F. was applied.

The initial weight of copper powder, transformed to yellow brass articles by the sintering, gained 1.75 oz. This corresponds to a 24% zinc addition to the alloy. A peak temperature of 1550° F. has been used for virtually all zinc vapor sintering of a copper powder. Vaporization of zinc is complete at this temperature and monitoring of the cycle is done exactly as it is when higher temperatures of 1675° F. and above are used to produce redder brasses by adding less zinc to the initial charge. A very important consideration, as will be seen, is that of allowing enough time for vaporization to proceed to completion regardless of the temperature used.

The use of zinc vapor to sinter nickel requires even less attention to details than necessary to vapor-sinter copper powder. Temperatures used are higher than for brass because 1900° F. represents the solidus for a 50% zinc-50% nickel alloy, and if substantial liquid phase sintering is desired, this temperature needs to be reached unless an alloy comparatively high in zinc is desired. For the latter, an excessive amount of zinc can be charged and the resulting alloy produced at lower temperatures compatible with the Ni/Zn equilibrium diagram which shows the solidus continuously depressed by zinc addition. In my work with nickel I have found a balance of zinc and temperature that produces articles of pleasing color showing neither the pinkish cast of nearly pure nickel nor the dull gray of high zinc alloys. The temperature advised for nickel is 1750° F.

In the case of nickel, I find it easy to accept the theory of vapor phase sintering that I set forth above for the alloying and consolidation of copper. It is conceivable that any nickel particle is capable of alloying with enough zinc furnished in the vapor state to produce a resultant binary alloy of a moderately low temperature solidus which would begin to liquefy first on its periphery and later if at all at its center as diffusion progresses. Certainly, at some stage of the heating, the continued rise in temperature and increase in zinc content of the alloy will produce some subtle and invisible melting that is not identifiable in the final structure. The extent of bonding and consolidation of the nickel particles seems to warrant this sort of conclusion.

Hargreaves, in other work, measured the vapor pressure of an alloy of nickel, copper and zinc and reported a substantially lower vapor pressure than in the simple binary brass alloys. He states: "one nickel atom has the same effect on the depression of the vapor pressure of zinc as have approximately 1.3 atoms of copper." Thus the loss of zinc from an alloy of nickel and zinc containing a high ratio of nickel would be negligible even at temperatures in excess of 1900° F., assuming it would be necessary to go higher.

(2) As noted, any metal and/or composite powders melting above the temperature used to vaporize the vaporizable metal and capable of alloying with it can be used as starting powders. The antecedent process used to prepare said powders is not critical. The starting powders can be of any desired particle size and particle size distribution, including formulations which have been graded carefully to give optimum packing. For jewelry, bearings, filters, etc., powder of 20 mesh and finer would normally be used. For specialty items, however, coarser powders could be appropriate. For jewelry in particular, I prefer to use fine powders, e.g. minus 200 mesh and preferably 325 mesh and finer powders. Such fine powders produce finished articles having microporosity which is not visible to the unaided eye. As noted previously, mixtures of desired metal powders can be used. For example, while iron powders produce molded parts which are serviceable, the parts still oxidize in moist atmospheres. By mixing iron and nickel powders together, e.g. equal amounts by weight, such rusting even in marine atmospheres can be avoided. I have tested jewelry items, made by vapor-sintering nickel powder with zinc vapor, by exposing same to marine atmospheres for long periods of time and have found no

evidence of corrosion or tarnish of the silver-like finish except on mirror-polished surfaces, which show slight dulling. A finely ground or brush finish shows no change in luster or color. Pre-alloyed powders can be used in practicing the invention. However, I have found that in some instances they react somewhat less favorably with the integrating metal vapor than do corresponding mixed elemental powders.

(3) While I prefer to use zinc as the vaporizable metal when practicing the process described above, magnesium vapor and mixtures of magnesium and zinc vapors can be used successfully in retorts which are at atmospheric pressure, as can other metals such as cadmium, mercury, arsenic, rubidium, cesium, potassium and/or sodium. While I presently prefer atmospheric retorting because of its relative simplicity, it should be understood that the invention can be practiced by using closed retorts which (a) have been evacuated to any desired sub-atmospheric pressure, or (b) have been pressurized with inert gas such as nitrogen, argon, helium, etc., to any desired super-atmospheric pressure. Thus, operating temperatures and pressures can be correlated to the conditions needed to operate with the selected vaporizable metal(s) and/or starting powders.

(4) The porous molds, plates, etc., described above can be made of any desired form of carbon, e.g. coke, charcoal, graphite, coal, etc. However, I presently prefer graphite because it is commercially available in grades having known purity, and because it does not deteriorate in my process and hence can be reused with a minimum of risk and uncertainty as to its operating behavior.

(5) The normally-liquid organic resinous binder(s) used in preparing my porous molds and mold parts can be of widely divergent chemical nature, as can be the agents which convert the normally-liquid materials to a solid state. The term "organic" as applied to these components of my process should be understood, of course, to exclude the organometallic compositions, since such materials leave metal-containing residues when carbonized. Thus for illustration only, I mention the following types or classes of organic resins: phenol/aldehyde resins, alkylated phenol/aldehyde resins, amine/aldehyde resins, alkylated amine/aldehyde resins, alkyd resins, oleoresinous materials, maleic-type unsaturated polyester resins, unsaturated-alcohol-type unsaturated polyester resins, epoxy and other oxirane oxygen types of resins, terpene resins, vinyl resins, polyurethane resins, styrenated alkyds, low-to-moderate molecular weight polyolefins, etc., including mixtures of the foregoing with each other and/or with natural resins, gums and waxes. The converting agents, are, of course, nonuniversal and function selectively with particular resins only. They include such materials as oxygen of the air, mineral acids, organic acids, alcohols, aldehydes, ketones, peroxides, etc. It will be understood, of course, that the resinous binder(s) which I employ constitute a minor and insignificant feature of the invention since they are merely used to carry carbon in a form which can be liberated in-situ during carbonization, thereby to generate carbon as the real and ultimate binder for my starting graphite powders. Thus the aim is simply to so manipulate the starting powder that a finished mold can be secured therefrom which is both porous and composed essentially of nothing but carbon. Any organic, carbonizable binder which serves these ends is therefore appropriate, and is herein contemplated.

(6) The molds and their contained metal powders, enclosed as described within an impermeable retort containing a supply of vaporizable metal, can be heated by any suitable external heating means, e.g. electric, mixtures of oxidizable fuels plus oxidizer(s), solar heat, etc. As noted, however, I prefer fuel gas mixtures since such heating means can provide rapid heating, constitute a source of heat not affected by metal vapor, and can furnish a controllable atmosphere which at choice can be non-oxidizing or reducing.

(7) Cooling of the hot retort and its contents after generation therewithin of the permeating metal vapor can be effected in any suitable manner, e.g. by slow, controlled rate of cooling, quenching in appropriate liquid(s), cooling by jets of gas or liquid, and/or combinations thereof. It will be understood that my carbon molds and mold parts exhibit good thermal shock resistance and hence can be cooled rapidly without destruction. However, where quench cooling is employed the retorts should of course be constructed of metal or alloy adapted to withstand a number of rapid cooling cycles without deterioration, unless it is desired to use retorts which are expendable and are discarded after each cycle of use, e.g. very thin (0.010" thick) low carbon steel cans, clay, or like retorts. Retorts made of essentially non-pervious graphite can be used to confine the metal vapor, with or without an outer protective container or coating designed to keep the graphite from burning away too rapidly.

(8) What has been said last above applies equally well to the cooling of the cans containing the molds and mold parts which need to be subjected to the carbonization firing.

(9) While one manner of filling mold cavities with metal powder has been described above, other ways of filling can of course be practiced. It should be understood that according to my principles the metal powder in the mold cavities is not in a compacted condition (i.e. is in no sense analogous to a briquette) and instead is in a loose, non-integrated form. Nevertheless, it should be understood that variations of the principles are possible and sometimes appropriate. For example, one can partially fill a mold cavity with loose powder, then insert a briquetted core member of desired shape and finally fill all remaining space of the cavity with loose powder. Alternatively, one can partially fill a cavity with one kind of powder and then fill the remaining space of the cavity with a different kind of powder, thereby to secure a laminated structure. More than two different kinds of powder can of course be used similarly, e.g. to secure three or more laminations composed of elemental powders, or to secure a plurality of layers some of which are composed of elemental powders and others of which, if desired, can be composed of mixed, pre-alloyed and/or composite powder(s). Again, solid metal inserts (which are not melted in the process) can be combined with loose powder for producing reinforced and/or partially fabricated units.

THE MOLDED METAL PARTS

As noted above, my molded parts, although somewhat porous, are firmly integrated metallic structures. A molded strip, for example 1" x 8" x 1/16", is flexible, resilient and sonorous when struck rather than giving the dull non-sonorous thud characteristic of usual sintered metal parts. My parts can be coined, rolled, forged cold to some extent, and otherwise shaped and densified by mechanical working. Metallographically they exhibit the characteristics of true alloys, most easily identifiable when the starting metal powders are finer than about 325 mesh. With coarse powders, the conversion of the starting particles to alloy depends on the amount of time permitted for diffusion of the vaporized metal into said particles as well as on the amount of vaporized metal made available to the particles. Thus with coarse starting powders or a small charge of e.g. zinc, cores of unmodified starting metal can be found by examination of a polished cross section of the vapor-sintered part while the outer portions show the expected alloy structure of equi-axed grains which seemingly are of homogeneous composition. When starting with minus 325 mesh copper powder, a treatment with e.g. zinc vapor at 1550° F. converts all the starting particles to alloy. A polished cross section of the sintered piece exhibits the appearance and color which is characteristic of brass. By starting with fine

nickel powder, a treatment with zinc vapor at 1750° F. converts the particles to alloy. However, in this instance the colors of nickel and zinc are so similar that unmodified starting particles of nickel are difficult to identify by color alone. When a polished section is observed in gross its bright metallic luster is very closely similar to that of silver and hence is noticeably different from that of nickel or zinc. The alloy also exhibits good resistance to corrosion and tarnish, as already pointed out above. The color remains very attractive (a) after long exposure in contact with the skin, and (b) after long exposure in contact with most foods, beverages, common medicinal ointments, skin creams, lotions, etc., and hence the alloy is well adapted for use in jewelry items.

It should be understood that my molded parts need not be polished to be attractive in appearance, particularly for jewelry and like usage, since very attractive pieces can be prepared by simply sanding certain areas, thereby achieving contrasting appearances. For example, a name plate or an initialled belt buckle can be molded in the manner described above and "finished" by sanding only the top surface of each letter. The so-sanded surfaces exhibit a bright metallic appearance while the remainder of the item provides a dark, lusterless background. It will be understood that said dark background appearance results from the microroughness of the "as-molded" surfaces, and as much or as little of this as is desired can be retained for its decorative appeal. In other words, for some purposes my "as-molded" pieces can be used as such, or can be given only little "finishing." Thus "finishing" operations can be held to a minimum, if desired.

For non-jewelry usage my molded parts can be given accurate "as-molded" dimensions and hence can be made for a variety of end uses, e.g. machine parts, decorative hardware items, parts for electrical equipment, objects of art, etc.

PARTICULAR ALLOYS AND METAL COMPOSITIONS

As pointed out hereinabove, the starting weight ratio of volatile metal(s) to starting powder should be at least 1:20. At the other extreme, ratios of 100 to 1 and higher are possible, but of course these high ratios give finished articles which are composed mostly of the vaporized metal(s). I prefer to operate with ratios between 1:20 and 1:1 and as noted especially prefer the even narrower ratios between 1:4 and 1:2, inclusive.

For jewelry and allied items made from nickel and zinc, I particularly favor the production of (a) finished parts composed essentially of the binary nickel/zinc alloys containing about 20-35% zinc, balance essentially all nickels, or (b) finished parts composed essentially of the ternary nickel/iron/zinc alloys containing about 5-15% zinc, balance essentially all iron and nickel in about equal parts of each by weight. I especially prefer such ternary alloys containing about 11.2-11.5% zinc. However, another ternary alloy which I presently like for some jewelry items is that composed of copper/nickel/zinc.

COMPOSITE POWDERS

A development arising out of the wet precipitation methods for producing metal powders is the manufacturing of so-called "composite powders." These powders consist of a core material coated with e.g. nickel. It is possible to envelope the core material completely with nickel, provided a coating at least 1-2 microns thick is deposited. Composite powders presently are predominantly finer than 325 mesh. Some core materials which have been coated with e.g. nickel include iron, copper, chromium, graphite, tungsten, tungsten carbide, phosphorous and aluminum. The first obvious advantage of such powders is that materials which are readily oxidized can now be made a part of my sintered articles, e.g. materials such as aluminum, phosphorous, tungsten, and chromium. As exemplified hereinafter, the carbides such as tungsten

carbide can also be included as starting metal powders in the practice of the present invention.

Another advantage obtained by using composite powders results when elements that are strong carbide formers are selected for vapor phase sintering with e.g. zinc. In the case of elements such as titanium, columbium, tantalum and others, some reaction between these elements and the carbon/graphite molds is to be expected. If such formation of carbides is determined to be detrimental to the articles formed by vapor-sintering, then suitably coated composite powders can be used to replace them since the coating on the composite powders, even when modified with e.g. zinc, acts as a barrier layer between the core material and the carbon or graphite.

Nickel, cobalt and copper are the principal metal coatings presently being made available on a variety of core materials. In addition to those named above, other core materials being offered are: alumina, chromia, zirconia, silica, vanadia, titania, SiC, TiC, Cr₃C₂, TiB₂, VB₂, CrB₂, MoSi₂, Si₃N₄ and TiH₂.

It will be understood that the production of composite powders of the kinds described above forms no part of the present invention and that the foregoing discussion merely relates to the scope of the term "composite powders" as used in this specification.

Reverting now to the main heading above of "Particular Alloys and Metal Compositions," it will be understood that when composite powders are used in whole or in part as starting powders, the practice of the present invention can yield finished articles having a broad scope as far as ultimate chemical composition is concerned. Thus the metal powders which can be used alone or with composite powders as starting powders include the ductile heavy metals named above, columbium, tantalum, vanadium, manganese, titanium, zirconium, and alloys and/or mixtures in which one of the foregoing metals forms the base; i.e. constitutes the larger or largest amount by weight in the total. All such starting metal powders are amenable to vapor-sintering, particularly with zinc.

It should now be clear that when practicing the vapor-sintering process to produce particular finished compositions, the retorting may in some cases need to be carried out at superatmospheric pressure and in others at subatmospheric pressure. Considering zinc as a typical vaporizable metal, for alloy systems wherein the melting point of an element, alloy or component of a composite powder to be alloyed with zinc is considerably above 1663° F., the use of pressure in excess of atmospheric can be considered. By the use of a pressurized system, the vaporization of zinc is impeded until the temperature of the system is sufficiently high to insure the formation of alloy phases between zinc and the element that will aid integration. When a component of the system has a melting point below a selected vapor-sintering temperature, and melting is to be avoided, then the retort can be operated at an appropriate subatmospheric pressure, whereby to secure an adequate vapor pressure of zinc at a temperature low enough to avoid said melting. If melting of a component of a batch of starting material is not detrimental, then of course the parameters of pressure, temperature and time can be adjusted as desired.

The following examples illustrate the principles of my invention and include the best modes presently known to me for practicing the invention in accordance with those principles.

Example 1

Articles of jewelry are prepared from nickel powder (82% minus 325 mesh) and zinc vapor, using starting proportions of 8 oz. nickel powder to 2.5 oz. zinc powder (20 mesh). The molds for the articles were prepared in the way described above in connection with FIG. I, using patterns made by pouring molten polyethylene glycol and by using a molding mixture composed of 3 parts by weight of graphite powder (minus 35 mesh), 1 part by weight of commercial furfuryl alcohol resin, and 1.5-2%

by wt. (based on resin) of commercial acid converter. The converter (a solid powdery material) was mixed thoroughly with the graphite powder, after which the liquid resin was added and thoroughly mixed with the dry powders until a uniform plastic mass was secured. This plastic mass was then tamped around the patterns, levelled off and otherwise treated as described above. The so-formed molds were fired at 1200° F. for carbonization and elimination of the patterns. The resulting molds are filled with the nickel powder and stacked with baffle plates, etc. in the manner explained in connection with FIG. II, the zinc powder being here introduced in the proportions noted above. The resulting assembly is then enclosed in an expendable steel can and heated to 1750° F. in the furnace of FIG. III in a period of three hours of continuous temperature rise, and cooled immediately while still in the furnace. The molded metal articles are recovered, wire-brushed, sanded lightly and polished. The polished surfaces are silver-like in appearance and the articles are wholly of merchantable quality. Chemical analyses taken at random of entire cross sections of 1/8" thick parts established the articles to have a composition of 32-35% zinc, balance nickel.

Example 2

Example 1 is repeated except that patterns are made of acrylic plastic, minus 325 mesh copper powder is substituted for the nickel powder, and the heating cycle is terminated when a temperature of 1550° F. is reached. The finished articles, when polished, exhibit the color of yellow brass, and can be soft-soldered to brass wire, jewelry findings of brass, steel wire, etc. Chemical analysis of an entire cross section of an 1/8" thick part shows the article to have a composition of 33% zinc, balance copper.

Example 3

An ornamental nameplate measuring about 2" x 6" x 1/4" is made substantially in the manner of Example 1 except for the following variations:

- (a) A nameplate pattern is used,
- (b) In building up the mold assembly for retorting, the total zinc powder of Example 1 is divided into two equal portions, one portion being distributed between the lower baffle plate and the filled mold, while the other portion is distributed between the filled mold and the upper baffle plate.

The finished nameplate, when analyzed chemically, is found to have the same percentages of zinc and nickel as in Example 1.

Example 4

A molded amalgam part is prepared in the manner described in Example 1 by using silver powder as the starting powder and by using mercury as the vaporizable metal. In the vapor-sintering treatment, a maximum temperature of 1200° F. is employed, with a starting weight ratio of 3:1 between the silver powder and the mercury. The mercury is sprinkled on the graphite powder in the same general way as the zinc powder is distributed in Example 1. The resulting molded article is a silvery white alloy containing 20-30% mercury.

Example 5

Plates adapted for use as anti-fouling ship-bottom attachments are made from copper powder as the starting powder and from arsenic as the vaporizable metal. The process is carried out essentially in the manner described in Example 1, the weight ratio of arsenic to copper being 1:4, and the maximum furnace temperature during the vapor-sintering treatment being 1200° F.

If desired, similar plates which are laminated with copper can be prepared by inserting a flat sheet of copper, e.g. copper foil, on the bottom of each mold cavity before pouring in the copper powder. In such case, the vapor-sintering treatment bonds the copper/arsenic layer to the

foil, and the said layer can be made very thin, e.g. 0.050" or less.

Example 6

An abrasive block measuring about 1" x 3" x 1/8" is prepared by starting with nickel-coated silicon carbide (composite) powder and vapor-sintering it with zinc vapor. A weight ratio of zinc:composite powder of 1:3 gives a finished block having a suitable wear rate when used on soft metals such as electrical contact points.

For preparing tougher abrasive articles adapted for use on iron, stone, etc., the starting powders can consist of a mixture, e.g., iron powder mixed with the composite powder, in proportions commensurate with the wear rate desired under the intended conditions of use.

Example 7

Molded copper/zinc articles containing about 5% zinc by weight are made in the manner described in Example 1 by starting with formulations of copper powder which have been carefully graded in respect to particle size distribution so as to give optimum packing when poured in the mold cavity; the formulations are as follow:

For irregular particles:	Percent
—150 +200 mesh -----	20
—400 +200 mesh -----	80
For spherical particles:	Percent
—100 +150 mesh -----	60
—325 +150 mesh -----	40

The finished articles are found to be well integrated, albeit still porous, by the small amount of zinc which permeates the starting powders during the vapor-sintering treatment.

Example 8

Jewelry items are prepared in the manner described in Example 1 except that the starting nickel powder thereof is replaced in toto with an equal weight of "nickel silver" powder (i.e. a 65% Cu/18% Ni/17% Zn alloy).

Example 9

In this example, the principles of the present invention are applied to prepare a vapor-sintered Ni/Zn coating on a sheet of columbium, thereby to secure a coated sheet better able to withstand the intense heat of re-entry experienced on, e.g., leading edges of airfoils on space craft. Reference should be made to FIG. V of the drawings where it is shown that the retort in this instance is a welded steel envelope made from a pan 24a and a lid 24b. The envelope tightly encloses an assembly consisting of (a) a base graphite plate 25 carrying a weighed layer 26 of 35 mesh zinc powder, (b) a porous graphite spacing plate 27, its upper surface having been given a wash coat of bentonite (to prevent formation of columbium carbide by contact between the graphite and the columbium sheet), (c) the columbium sheet 28 which is to be coated, (d) a layer 29 of fine nickel powder (minus 200 mesh or finer), and (e) a top porous graphite plate 30. Preferably such an assembly is made up by starting with an open drawn steel pan 24a of e.g. rectangular configuration so dimensioned as to be a close fit around the above assembly. After the assembly has been stacked within the pan, the flat steel lid 24b is put into place and welded at its edges to the pan. An evacuation port (not shown) can be included in either the pan or the lid to permit withdrawal of residual air within the envelope. Such withdrawal is not usually necessary and when practiced no strict degassing treatment is needed. After the internal pressure has been suitably lowered, the evacuation port can be welded shut in the conventional manner.

For the intended purposes of the Ni/Zn coating, the starting ratio of nickel to zinc can vary on a weight basis from about 1:1 to about 1:20, the ratio being chosen in accordance with the expected service conditions to be encountered. It will be understood that while zinc-coated

columbium has been found to be more resistant than bare columbium, the inclusion of high melting metal (here the nickel powder) in the coating serves to depress the vapor pressure of zinc and hence prolongs its service life, thereby giving the columbium protection for a longer period of time. Moreover, the nickel component in the present coating raises the melting point, all to the same end.

The enveloped assembly is heated, as will be understood, to vaporize the zinc of layer 26, thereby to vapor-sinter the nickel of layer 29 to itself and to the contacting surface of the columbium sheet 28. The maximum temperatures to be attained in such heating vary with the Ni/Zn ratios being used. For the ratio of 1:20, a temperature of about 1700° F. is used, while for the 1:1 ratio the maximum temperature is about 1900° F. A straight line relationship can be used for intermediate ratios.

It should be understood that other metals besides columbium can be coated with vapor-sintered Ni/Zn coatings for similar protective effects, such as columbium-base alloys, vanadium-base alloys, and other high-melting metals and alloys which form intermetallic compounds with zinc and/or nickel. The nickel in such coatings can be replaced in whole or in part with cobalt.

It will be noted in FIG. V that the nickel layer 29 rests on the upper surface of the columbium sheet 28. This is to insure firm contact between the two. If it is desired to coat both surfaces of the columbium sheet in one operation, the needed contact between nickel powder and the under surface can be secured by painting the under surface (or both, if desired) with a suspension of nickel powder in a nitrocellulose/ethyl acetate binder solution, and drying the applied coatings before making up the assembly in the enclosing envelope.

In final review of the invention, it should be noted that while I have described the preparation of various articles by my vapor-sintering process, various after-treatments can be applied to said articles, if desired. For example, an article molded by the process described in Example 1 can be re-run in a second vapor-sintering treatment with a small added amount of, e.g., zinc, thereby to increase the amount of zinc at and close to the surface of the article. Such a treatment can be carried out so as to effectively seal the surface, thereby making the so-finished article amenable to electroplating. For a like purpose articles produced by the process of, e.g., Example 1 can be dipped into molten zinc, whereby to seal the surface. Again, one can subject an article prepared by, e.g., Example 1 to localized heat sufficient to cause slight melting of the whole surface of the article or of only discrete selected portions thereof. High frequency inductive heating, with or without selective cooling probes, can be used effectively for this purpose. On jewelry items in particular, such melting at the surface (in whole or in part) can be useful in modifying sharp edges and points of detailed design into softly rounded edges and points, thereby to secure a decorative effect which is difficult to secure from the mold itself. To the same end, however, a somewhat similar effect can be secured in the vapor-sintering treatment (as opposed to a special after-treatment) by intentionally raising the temperature (after the normal treatment would otherwise be terminated) so as to cause superficial melting of the vapor-sintered article. However, this requires very close control of furnace temperature and is more easily carried out accurately with a retort holding only a few molds than with a retort holding a tall stack of molds. It will be understood that this feature is mainly one of using a furnace which has been designed carefully so as to give uniform heat throughout the entire zone in which the retort is located.

Still another after-treatment (or an in-retort treatment) giving pleasing effects for some purposes is that of subjecting the as-vapor-sintered article to an intentional thermal gradient sufficient to cause melting in a selected region or portion, e.g., at one end. In this way sharp molded

features are retained at the unmelted end while slumping, contraction and loss of detail is continuously graduated as the melted end is approached.

Having now described my invention, what I claim is:

1. The process which comprises the steps of (I) heating an almost gas-tight retort confining under non-oxidizing conditions an assembly comprising (a) a mass of loose uncompact metal powder poured into and given a desired shape by the supporting surfaces of a top-filling cavity carried in a porous mold member composed essentially of non-metallic refractory material which is non-oxidizing to said metal powder, and (b) a predetermined mass of vaporizable metal disposed outside of said cavity and out of physical contact with said loose metal powder in said cavity, to an elevated temperature (1) generating non-oxidized metallic vapor of said vaporizable metal within said retort but (2) below the melting point of said metal powder, (II) continuing said heating under said non-oxidizing conditions until metal vapor has acted on said mass of loose metal powder to vapor-sinter the latter into a unitary, self-sustaining metallic body having the shape imposed on said metal powder by said cavity, and (III) cooling said assembly under conditions preventing oxidation of said unitary metallic body, thereby to recover said body; said vaporizable metal being selected from the group consisting of magnesium, zinc, cadmium, arsenic, rubidium, cesium, potassium, sodium and mixtures thereof, and said loose metal powder being selected from the group consisting of iron, cobalt, nickel, manganese, titanium, zirconium, columbium, vanadium, copper, silver, gold alloys in which one of the foregoing elements constitutes the base, composite powders, and mixtures of the foregoing.

2. The process as claimed in claim 1 wherein the starting weight ratio of vaporizable metal to total metal powder in said loose mass is at least 1:20.

3. The process as claimed in claim 2 wherein said porous mold member is composed essentially of carbon, wherein said retort has a small vent opening, and wherein said heating is accomplished by applying heat externally of said retort.

4. The process as claimed in claim 3 wherein said loose metal powder consists essentially of particles finer than about 325 mesh.

5. The process as claimed in claim 4 wherein said assembly occupies substantially all of the interior volume of said retort.

6. The process as claimed in claim 5 wherein said porous mold member is platelike with substantially flat, parallel faces and is stacked in said retort with other parts identified below and in the following sequence starting from the bottom:

(a) a thin, substantially flat ferrous metal baffle plate carrying on its upper face a mixture consisting essentially of graphite powder and said predetermined supply of vaporizable metal in particulate form, and (b) said porous mold member carrying loose metal powder in a cavity thereof,

and wherein said retort is made of thin ferrous metal and the vent opening is in the wall thereof which is above the stack of parts identified above.

7. The process as claimed in claim 6 wherein each cavity in said mold member has a vertical dimension of up to about one-fourth inch.

8. The process as claimed in claim 7 wherein the starting weight ratio of vaporizable metal to total metal powder in said loose mass is between about 1:20 and 1:1, inclusive.

9. The process as claimed in claim 8 wherein said vaporizable metal is zinc.

10. The process as claimed in claim 9 wherein said loose metal powder consists essentially of nickel.

11. The process as claimed in claim 9 wherein said loose metal powder consists essentially of copper.

12. The process as claimed in claim 9 wherein said loose metal powder consists essentially of a mixture of about equal weights of nickel and copper powders.

13. The process as claimed in claim 9 wherein said loose metal powder consists essentially of a mixture of about equal weights of nickel and iron powders.

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