MANUFACTURE OF ARTICLES FROM POWDERED METALS

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Filed Feb. 9, 1968, Ser. No. 704,400

Int. Cl. B221 7/00

U.S. Cl. 75—208

10 Claims

ABSTRACT OF THE DISCLOSURE

Manufacture of articles from powdered metals, particularly powdered precious metals, characterized in that the powdered metal is first mixed with a binder to form a putty or paste, the paste thereafter being formed or sculptured by hand into the desired shape, and the shape then heated whereby the binder is driven off and the powdered metal sintered into a compact mass.

BACKGROUND OF THE INVENTION

Although not limited thereto, the present invention is particularly adapted for use in the manufacture of articles formed from precious metals such as jewelry and metallic dental prostheses. Metallic dental prostheses such as crowns, inlays, partial plates and the like are conventionally prepared by one or more variations of the "lost wax" process. In this process, a wax pattern is first made of the article; the wax pattern is provided with sprues, vents and a pouring cup and invested in a suitable refractory mold; the wax is eliminated from the mold by heating at a relatively low temperature; the mold is fired; and molten metal is then cast into the heated mold.

While such casting techniques have been known and employed for many years, the individual steps of the overall technique are tedious and excess metal has to be cast for the formation of sprues, risers, vents, buttons and the like. Furthermore, the system of casting, whether from an electric or flame heated furnace, tends toward the loss of higher vapor pressure alloying elements, and results in variations in casting quality and porosity due to gases evolved during casting.

In the case of a dental bridge, it is often necessary to cast a coping for each individual tooth and thereafter solder these individual copings together. This is a tedious and time-consuming process and requires a high degree of skill. For that matter, it is probably the most difficult part of the fabrication of a dental bridge from cast metallic components.

SUMMARY OF THE INVENTION

As an overall object, the present invention provides a method and material for forming sintered metal articles from powdered metals without the necessity for pressing the powdered metal into a mold prior to sintering as is conventional.

More specifically, an object of the invention is to provide a sintering process for the formation of metallic articles wherein the powdered metal is first mixed with a binder to form a putty or paste, the paste thereafter formed into the desired shape, and the shape then heated whereby the binder is driven off and the powdered metal sintered into a compact mass.

In accordance with the invention, a putty-like mass is provided comprising very finely divided metallic particles mixed with a binder which, while permitting a degree of fluidity, also is capable of providing strength of construction up to the point at which sintering and bonding of the particles takes place. This metal putty may be formed into a solid mass, or hollow articles may be formed by implaning the putty on a refractory die, suitably treated to provide separation of the final metal construction. The putty is carved or sculptured with an appropriate instrument to the required contours and is first gently dried and then placed in a furnace at low temperature. During this step of the process, the binder is driven off. The temperature of the furnace is then raised to the point of sintering and bonding of the metallic particles. After a brief sojourn at this temperature, the system is cooled and a metal structure is provided capable of being burnished, polished or otherwise mechanically finished and, in the case of dental prostheses, capable of being surrounded by porcelain, plastic or the like.

In any dental prosthesis, it is necessary to have as good a fit as possible to the underlying tooth and gum structure. In the sintering process, the shape formed by carving or sculpturing will tend to shrink to some degree since, among other reasons, the binder is expelled from the putty from which the sintered product is formed. Therefore, in accordance with another aspect of the invention, the shape is first formed on a refractory die which is an exact replica of a prepared tooth, then sintered, and thereafter removed from the furnace and cooled. The shape is then removed from the refractory die and a shoulder or collar of the paste is formed around the base of the die. The previously-sintered shape is again placed over the die and forced downwardly such that its lower periphery is pressed into the soft putty collar. Thereafter, the article is again sintered; and very little shrinkage takes place, insuring a good fit to the underlying tooth structure.

The above and other objects and features of the invention will become apparent from the following detailed description taken in connection with the accompanying drawings which form a part of this specification, and in which:

FIGURE 1 is an isometric view of a die upon which a gold coping for dental prosthesis is built up, together with a plate on which the metallic putty of the invention is disposed and a spatula which is used to build up the putty on the die;

FIG. 2 shows the manner in which the putty is built up on the die;

FIG. 3 shows the completed article built up from the putty of the invention prior to firing;

FIG. 4 shows the completed, sintered coping as it is removed from the die; and

FIG. 5 shows the manner in which a shoulder is added to the previously-formed coping to accommodate for possible shrinkage occurring during sintering.

FORMATION OF THE METAL POWDER PUTTY

In the practice of the invention, a metallic putty is initially formed comprising metal particles mixed with a suitable binder. The physical requirements for a usable system are that the metal particles should be in spherical powder form with individual particles no larger than about 25 microns in diameter and preferably in the range of about 2 to 15 microns. This size is necessary to insulate adequate particle interaction (i.e., fusing during sintering) at temperatures significantly below the intrinsic melting point of the metal and provide maximum density. The particles should be spherical in shape so as to provide for (a) easy application of the putty to a die (i.e., spheres will roll on each other rather than pack into an immobile mass), and (b) minimal surface area per particle so as to minimize firing shrinkage.

These metal spheres are suspended in a binder or medium permitting maximum metal concentration together with ease of cohesion, this cohesion persisting to
temperatures at which sintering or alloying occurs of the metal spheres. Clearly, the smaller the particles, the lower will be the temperature of cohesion through sintering. However, the sintering process can be brought about by means of a low temperature binder of sufficient strength to permit shape retention up to the point of particle cohesion by sintering, but thereafter all medium and binder must be volatile and eliminated by heating.

The binder must be an adhesive suspended within a solvent. Binders which have been found to be suitable include, without limitation, ammonium caseinate, ammonium stearate, pectin, heximine, ethyl cellulose, anilacryne, triacetetyl starch, dextrin, casein and tetra-phenyl ethylene. Other binders may also be used, the important consideration being that the binder must retain its binding properties up to about 400°F. while at the same time must be volatile such that it can be eliminated by heating. The solvents with which the binder is mixed include, again without limitation, propylene glycol, water, ethylene glycol, light paraffin oil, butyl acetate, butyl benzolate, diacetone alcohol, and dibutyl phthalate. Again, the solvent must be compatible with the binder and at the same time must be volatile such that it can be driven off by heating.

**FABRICATION OF THE ARTICLE FROM PUTTY**

The putty thus formed is identified by the reference numeral 10 in FIG. 1 and is conveniently disposed on a disc 12. In the example of the invention given in the drawing, the putty preferably comprises powdered gold spheres or alloys of gold in an appropriate binder, which putty is used to form a coping for a dental crown. Such a coping is then coated on its outer surface with porcelain, the gold supplying strength and accurate fit and the porcelain providing esthetics and function.

In forming a jacket crown, a thickness of the tooth structure is first removed by a dentist and then a wax, rubber or the like impression is made of the tooth so prepared. Poured into this impression is a castable refractory die composition upon which a gold coping can be formed as was mentioned above. This gold coping is ordinarily formed by means of the wax method which requires investing a wax model, the use of sprues and the like. After the coping is thus formed, it is completely or partially coated with porcelain.

In FIG. 1 the die, comprising a model of the tooth which is cut down by the dentist, is identified by the reference numeral 14. A portion of the gold putty 10 is placed upon the end of a spatula 16 and applied around the die 14 as shown in FIG. 2 by means of the spatula 16. In this process, the coping is built up and carved from the putty. After this, the lower portion of the coping being identified by the reference numeral 18A in FIG. 2. This build up of the coping with the gold putty 10 continues until the coping is completed as shown in FIG. 3 where the coping is identified by the reference numeral 18B. It should be pointed out that prior to the application of the putty to the die 14, the die is first painted with a separator which preferably comprises a dispersion of mica or other alumino-silicate in microcellulose solution. This separator enables easy separation of the completed coping from the die 14 after sintering.

**SINTERING OF THE FORMED PUTTY**

After the putty is thus built up into the coping 18B as shown in FIG. 3, the entire assembly is pre-fired at a temperature of about 800° F. to about 1200° F. for about five minutes. In this process, the putty and its solvent are driven off; however the putty, due possibly to partial sintering, retains its shape. Thereafter, the temperature is increased up to about 1860° F. at a rate of about 100° F. per minute. It is necessary to hold the temperature at the sintering point of 1860° F. for only a few minutes. Thereafter, the die 14 and sintered coping may be removed from the furnace. After cooling, the completed, sintered coping 18C shown in FIG. 4 may be pulled from the die 14. During this process, there will be a reduction of shrinkage and in some cases a reduction of the edge of the completed coping 20 to move upwardly away from the die. This is undesirable for the reason that it is of utmost importance that the coping and completed crown fit closely to the gum or other substrate over which it is placed. Accordingly, if such shrinkage occurs, it is possible to form a collar from the putty 10 around the base of the die 14. This is shown in FIG. 5 where the collar formed from putty is identified by the reference numeral 22. After the collar 22 is thus formed, the previously sintered coping 18C may again be placed over the die 14 and forced down into snug abutting relationship with the collar 22. The sintering process is then repeated; and the collar fuses completely to the previously formed coping 18C. Any shrinkage in the collar 22 is of a minor nature only and, consequently, a good fit is assured. If desired or necessary, a portion of the previously formed coping 18C may be removed from its bottom peripheral portion 20 prior to the coping being inserted over the die 14 and into engagement with the putty collar 22.

The thus-formed article is, for the most part, non-porous. However, to insure that voids are eliminated, it is possible to prepare a precious metal putty, for example, by admixture of the metal powders with a resinous solution of a noble metal. For example, gold, platinum, or rhodium powders may be jointly prepared as a putty with a silver resistate containing 30%-40% silver. The silver resistate portion acts as a binder and, on ignition, leaves the silver content to alloy with the other precious metals and seal off all voids.

Alternatively, the precious metal putty prepared as originally described above can be applied to the die, and then fired and then have applied to it again a precious metal resistate solution which will seep into and fill pores by capillary action. The system being again dried and fired, the residual precious metal from the resistate will fill out and seal off any voids.

Again, voids in the structure may be eliminated by the mechanism of liquid-phase sintering, i.e., the metal powder mixture composition is adjusted so that two or more ingredients will interact to yield a relatively low melting point eutectic liquid which will wet the other metal particles and flow, by capillarity, into voids in the sintered structure. Thereafter, on further heating, this eutectic liquid will, by volume diffusion, form, with the mass of metal particles, an alloy of higher melting point.

**Examples**

As an example of the invention, 99.98% pure gold was prepared in spherical form and screened to give particles which were smaller in size than 20 microns in diameter. Fifty grams of this powder were formed into a putty-like mass by blending with 3 cubic centimeters of 12% ammonium caseinate in propylene glycol. A ceramic die such as die 14, coated with a refractory separating medium, was taken and the gold putty, prepared as indicated, was applied to the coated die and shaped to conform to a normal coping configuration. The whole system was dried gently in front of a furnace at about 600° F. and then inserted into the furnace. The temperature of the furnace was raised to 1860° F. at about 75° per minute. After removal from the furnace and cooling, the fired gold shape was seen to conform closely to the die structure and could be easily detached and employed for construction of a porcelain or plastic on gold prosthesis.

As another example, an alloy of gold, platinum, palladium and silver was prepared in spherical powder form, the particles being of a diameter less than 20 microns. Fifty grams of this powder were then formed into a putty by blending with 3 cubic centimeters of ethyl cellulose in dibutyl phthalate. The procedure of constructing a coping
was again followed. That is, a ceramic die, coated with a refractory separating medium, was taken and the putty applied to the coated die and shaped to conform to a normal coping configuration. The die with the putty coping was then sintered for five minutes and then inserted into the furnace where the temperature was raised to 1860° F. at a rate of about 100° F. per minute. The resulting copings had applied thereto porcelain of a matching coefficient of thermal expansion and fired to the gold alloy structure to yield a porcelain on gold prosthesis.

As another example, the die for a gold coping prepared as in the first example above had applied around the base thereof a collar of the previously-formed putty. Thereafter, the previously-sintered coping was reapplied over the die and forced down onto the soft mass forming the collar. Any excess material was scraped off and the preheating and sintering process repeated as above. At this time other geometrical requirements of the coping were added, i.e., lingual collars and connection uprights as is necessary in the case of splinted units, that is to say, multiple units which will be attached together. Upon removal from the furnace and cooling, the putty collar was found to have fused to the bottom of the original coping and fit exactly to the substrate die.

As another example, a mixture was formed of gold, platinum, palladium, and silver powders of less than 20 micron size, and sintered to a reasonably coherent (76%) theoretical density mass at 1860° F. Added to this powder mixture was 2%–5% of silicon or aluminum powder (less than 20 micron size). On heating, as before described, the silicon or aluminum particles initially interacted with the gold particles (which were in the majority) to form a low melting point eutectic (5% Si-95% Au has Tm=400° C.). This fluid eutectic rapidly permeates the sintered body and inducts voids and, as the temperature and time of heating are increased, further reacts with the excess gold or other metal by volume diffusion to give a higher melting point alloy.

Or again, mixtures of titanium and nickel powders can be prepared in ratio close to 4:1. On firing, these first form a eutectic containing 75% Ti and 25% Ni, melting at 950° C. (1740° F.), which fills voids in the structure and then diffuses into the remaining particles to give a higher melting point alloy. In sintering such a system it is, of course, necessary to fire under vacuum to avoid oxidation of the alloy. This is done routinely, this liquid phase sintering approach having been employed to prepare structures from mixtures of the following powders: Ti-Ni (4:1, the 3:1 eutectic melts at 950° C.) Au-Pd-Pt-Ag-Si (80:5:5:5:8, the 5% Si-Au eutectic melts at 400° C.) Fe-Ni-Bi-Sn (40:60:6:4, the Bi-Sn eutectic melts at 150° C.) In-Ni (3:7, the 40% In eutectic melts at 915° C.) Fe-Cr-In-Sn (80:20:3:3, the 52% In-Sn eutectic melts at 120° C.) Ag-Au-Si (45:50:8, the 5% Si eutectic melts at 400° C.) Ag-Au-Al (50:45:8, the 5% Si-Au eutectic melts at 420° C.)

It will be apparent that while the above examples relate to the formation of a coping used in a dental crown, the putty of the invention can also be used to form unitary bridge structures or inlay prostheses for both posterior and anterior teeth. Furthermore, the invention is clearly not limited to dental prostheses as such. For example, it can be used to form any metallic article; however it is particularly adapted for use in forming one-of-a-kind articles such as, for example, jewelry or other items formed from precious metals. There is, however, no intention to limit the invention to precious metals as such since other non-precious metals can be formed into a powder and mixed with a binder to form a putty which can be carved into the desired shape and then sintered. Finally, the invention is not constrained to the use of putties of metal powders as such. These may be replaced by oxides, hydrides, organic materials, and the like which may be reduced to the corresponding metal upon firing.

Although the invention has been shown in connection with certain specific embodiments, it will be readily apparent to those skilled in the art that various changes can be made to suit requirements without departing from the spirit and scope of the invention.

I claim as my invention:

1. In the method for forming a sintered metallic article, the steps of mixing finely divided metallic particles of about 2 to 25 microns in average diameter with a binder to form a putty, the binder being such that it will volatilize and purge itself from the putty at a temperature lower than the desired sintering temperature of said metallic particles, forming said putty into a desired shape, heating said formed shape to initially burn off said binder, and thereafter continuing heating of said formed shape to sinter said metallic particles into a fused, essentially non-porous compact mass.

2. The method of claim 1 wherein said finely divided particles comprise particles of a precious metal.

3. The method of claim 1 wherein said metallic particles are formed from two different metals to form an alloy upon sintering.

4. The method of claim 1 wherein said putty is formed into a desired shape by carving.

5. The method of claim 1 wherein said binder comprises a mixture of at least two components, one of said components being selected from the group consisting of ammonium caseinate, ammonium stearate, pectin, hexamite, ethyl cellulose, anthracene, triacetyl starch, dextrin, carbazole and tetraphenyl ethylene, and the other of said components being selected from the group consisting of propylene glycol, water, eugenol, light paraffin oil, butyl acetate, butyl benzoate, diacetone alcohol and dibutyl phthalate.

6. The method of claim 1 wherein said putty is applied by carving over a ceramic die.

7. The method of claim 1 wherein said putty is carved over a ceramic die to form a dental prosthesis.

8. The method of claim 1 wherein heating of the formed shape takes place in two steps, the first step being at a substantially constant temperature below the sintering temperature of said metallic particles, and the second step comprising gradual heating of said putty in the desired shape after said binder has been burned off up to the desired sintering temperature of the metallic particles.

9. The method of claim 1 including the step of applying to the sintered shape a precious metal resinate solution which will seep into and fill pores in the sintered shape by capillary action.

10. The method of claim 1 wherein said metallic particles are formed from a plurality of different metals, at least two of which interact upon heating to form a eutectic liquid which will wet the other metallic particles and flow, by capillarity, into any voids in the sintered mass.

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