

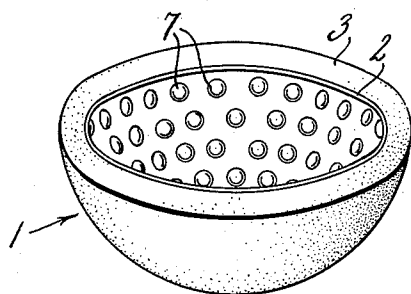
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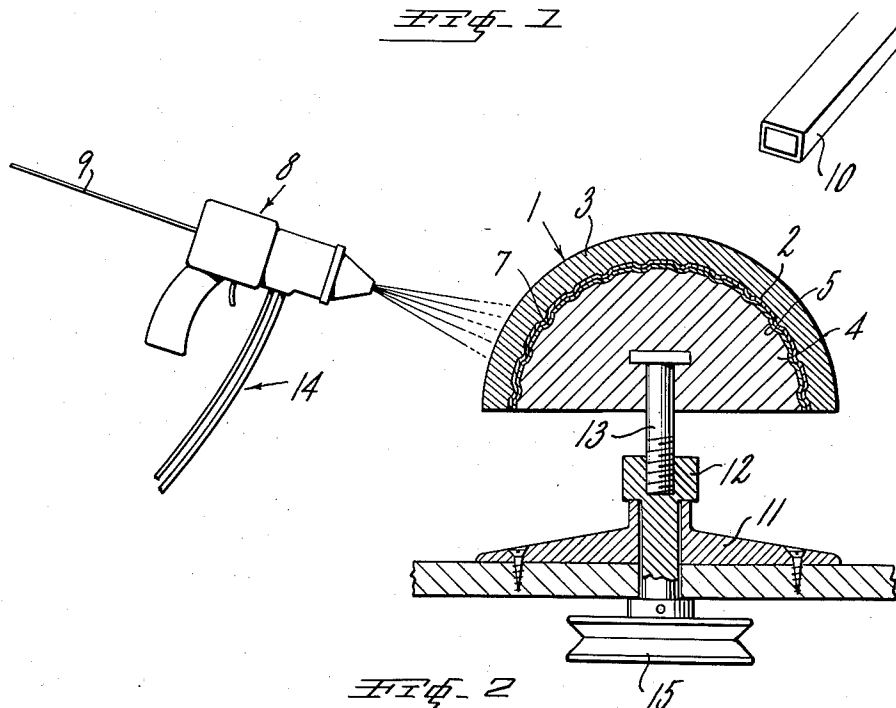
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METHOD OF PRODUCING METAL DEPOSITS

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METHOD OF PRODUCING METAL DEPOSITS

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This invention relates to the production of sprayed metal articles, particularly molds or the like useful in the compression molding of plastics such as synthetic resins, rubber, etc. It also relates to an improved method of metalizing. It further relates to improvements in the flame-spraying of high-melting metals onto smooth surfaces of a model whereby the metal is made to adhere to smooth surfaces without bouncing off and where-in all surface detail of the model is accurately and faithfully reproduced in the adjacent surface of the deposited metal.

Molds which are used under presses, as in compression molding, generally are strong enough to withstand compressive stresses up to at least 5,000 p.s.i., they have a hardness on the order of 30 on the Rockwell C scale, and, if used in molding rubber articles, they are able to withstand temperatures above 650° F. and are inert to rubber. Present methods of making these articles and molds involve cutting or etching a hard metal block and the like. This is expensive, especially if the mold is to be used in making only a small number of articles, as for samples.

Flame-sprayed metal molds and articles made by prior methods, as the one described in Hugger 2,629,907, are much cheaper to make, and it is possible to obtain good surface detail from a model made of cheap material, such as plaster of Paris. In these methods a metal deposit is built up on an adhesive-coated model by spraying the model with molten particles of metal which on cooling solidify. A soft metal of low melting point, e.g., aluminum, is generally used as the sprayed metal, since the known adhesives for collecting the sprayed metal have been incapable of performing satisfactorily at the temperatures, considerably above 1200° F., at which hard metals must be sprayed—usually above 1750° F. As a result, molds when made by prior sprayed-metal methods are brittle, are liable to crack, and may break under stresses above 5,000 p.s.i. This limits their use to non-pressure molding, such as slush molding.

The process generally known as metalizing is widely used in the metal-working industry for the purpose of repairing or re-conditioning worn metal parts, such as shafts and mill rolls which are to be restored to their original dimensions. Metalizing may also be applied to ceramic and other articles. Metalizing is done by flame-spray techniques. The surfaces on which new metal is to be deposited are first roughened, if necessary, then sprayed with the desired metal, usually steel, until the deposit has been built up to the desired thickness. The new surfaces of the built-up parts may then be machined or ground to the required dimensions. In this process there is no particular problem of adhesion of the added metal to the deposition surface. But the lower strength and lack of toughness of the added metal leave much to be desired in prior processes.

It is well known that, in order to strongly bond two metals together, as in brazing, surface oxides and other

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undesirable substances must be removed in order to permit wetting of the base metal by the molten filler metal. This fluxing function may be performed by a separate flux or by a self-fluxing brazing alloy.

My invention lies in part in my discovery that the ductility and toughness of sprayed metal articles and molds can be increased to such a high degree as to allow their use under conditions of high stress, as in compression molding, with accurate reproduction of all surface detail of the model, if the article or mold is composed of layers of selected metals deposited in a certain manner and subsequently heat treated at certain temperatures.

My invention accordingly comprises a method of producing a strong, ductile, flame-sprayed metal coating or object, comprised of spraying simultaneously a plurality of metals having widely different melting points, one of which metals is a self-fluxing brazing alloy, onto the same area of a surface until a deposit of the desired thickness has been built up, and thereafter sintering the object or coating at or above the melting point of the lower-melting, brazing alloy but at a temperature lower than the melting point of any of the higher-melting metals. A mold, or any thick article, produced by my method is not brittle, its shrinkage is negligible, and it does not crack no matter how thick it is. By this method I am able to produce articles in which the sprayed metal parts are characterized by great toughness and very high tensile strength.

In accordance with the practice of my invention, a thin base layer of hard metal is built up on a model by spraying the hard metal onto a silicate-coated model; then a backing layer is spray-deposited over the hard metal by the simultaneous spraying of two or more metals, one of which is a self-fluxing brazing alloy, to the desired thickness. Upon being sintered or heat treated at a temperature above the melting point of the lowest-melting metal, viz., the brazing alloy, but below that of the base layer metal and below that of the high-melting metal in the backing layer, the high-melting metal particles cohere strongly and the low-melting filler metal flows into the interstices of the non-melted particles, whereby, upon cooling, a metallurgical bond of high strength is produced.

Heretofore, it has been difficult to spray onto a smooth model a base layer of relatively hard metal having a spraying temperature of from above 1100° to as high as 1850° F. I have found that this can be done easily and conveniently by spraying such hard metal onto a thin, dried coating of a film-forming silicate such as sodium silicate which has previously been deposited on the model from an aqueous solution thereof.

The term "self-fluxing brazing alloy" is well understood in the industry to signify a brazing alloy which of itself performs the fluxing function of removing surface oxides and other undesirable substances during brazing. Satisfactory performance of the self-fluxing function usually requires the inclusion of a strong deoxidizer such as phosphorus, lithium, boron, cadmium or tin in the brazing alloy.

In the accompanying drawing forming a part of the disclosure:

Fig. 1 is a perspective view of a laminated section of a mold for a golf ball, formed in accordance with my invention; and

Fig. 2 is an elevational view illustrating a sprayed metal mold deposited over a model and showing parts broken away, together with apparatus for producing the article.

In the drawing, an article made according to this invention is shown as a mold section, or half-mold, 1, for producing golf balls, comprising an inner or base

layer 2 of hard metal and an outer or backing layer 3 of several metals. The metals are selected and deposited in the manner to be described herein.

As shown, the apparatus for carrying out the invention comprises a suitably mounted stand 11, rotatably supporting a hub 12 into which is screwed a bolt 13 embedded in the plaster model 4. A layer of adhesive 5, a base layer 2 of metal and a backing layer 3 of two or more metals cover the model 4. A spray gun 8 with fuel lines 14, which is conventional, is utilized to spray the adhesive 5 and molten metal particles onto the model 4. The metals are fed into the gun 8 in wire form 9, as shown, or in powder form. Duct 10 provides a means of supplying hot and cold air to the model during the spraying, as required, from a source not considered a part of this invention.

In an illustrative embodiment of my invention a model 4 is screwed into the hub 12 of stand 11, and a thin layer 5 of an aqueous solution of sodium silicate is sprayed over the model, while it is being rotated by hub 12 and pulley 15 driven by a motor which is not shown, to a sufficient thickness to provide a means for parting the model 4 from the metal shell 1 which is to be deposited over it but not so thick as to obliterate surface detail on the model and prevent its reproduction on the metal base layer 2. An even layer of less than 1 mil thickness is sufficient. Although nylon is an excellent adhesive for adhering metal to a model where moderate spraying temperatures can be used, it can not be used where hard metals with their correspondingly higher melting temperatures are to be sprayed. According to my discovery, a film-forming silicate such as sodium silicate, commercial water glass, will permit adhesion of projected molten metal particles at temperatures as high as 2100° F. A typical solution that may be used is three parts water glass and one part water. For maximum adhesion of the silicate film to the model, the model should be preheated to a temperature above 140° F.

After application of the adhesive 5, it is dehydrated by passing hot air over the model through air duct 10, from a source not shown, and a base layer 2 of a hard metal having a melting point between 1500° F. and 2100° F., such as an alloy of chrome nickel, is sprayed over the coated model 4. This base layer 2 takes the impression 7 from the model. It must do so accurately, but, on the other hand, it must also be hard enough to withstand wear caused by frequent use in molding operations, and if it is on a mold used on rubber stock, it must be inert to the rubber. The selection of metals used to form the base layer 2 is further restricted by their spraying temperatures, since the temperature must be high enough to soften the adhesive 5 covering the model 4 but not so high as to break it down, else the particles will bounce off the model and fail to build up. Where water glass is used as the adhesive, a high-melting metal such as copper can be deposited as a base layer, but, since copper reacts with rubber, it is generally unsuitable for use in contact with rubber stock. "Nicrobraz," an alloy consisting of 15% chromium, 4.50% silicon, 4.00% iron, 3.95% boron and the balance nickel, in powdered form can be sprayed at about 1850° F. on a water-glass-coated model. It produces a hard surface, inert to rubber, with a good reproduction of the model's surface detail, excellent for the compression molding of articles. The thickness of the base layer 2 is not critical, and is determined mostly by the use to which the article or mold will be put. A thickness of 0.005 to .010 inch of "Nicrobraz" on a mold surface is sufficient to ensure sharp impressions in the molding of rubber articles. The technique used to obtain the desired thickness is to work the spray gun back and forth over the article being sprayed, in known manner.

Hot or cold air, as required, is blown over the model 4 by means of air duct 10 during the flame-spraying steps to reduce any temperature differences that may exist be-

tween the model and the molten particles sprayed on it and to prevent cracking and breaking of the model, especially if it is a plaster of Paris model. Heat is also supplied to the silicate-coated model before the metal spraying is started, in order to dehydrate the film of water glass, as drying by mere exposure to the atmosphere is too incomplete to prevent peeling of the silicate film during the metal spraying steps.

In the next step, the base layer 2 is backed with a layer 3 of a plurality of metals, for example, a combination of (a) a Phosphor-bronze having the composition 94.75% copper, 5% tin and 0.25% phosphorus, and (b) a self-fluxing silver brazing alloy containing 80% copper, 15% silver and 5% phosphorus, by simultaneous flame-spraying of both alloys as molten particles. The preferred way of doing this is to feed the metals together through the same flame gun 8 in either powdered or wire form 9. Wires of several metals can be fed into the gun by combining them into one wire, as by making a concentric multi-layered wire in which the core is of one metal, e.g., a self-fluxing silver brazing alloy, and the outer layers are of other metals, as Phosphor-bronze, or by entwining strands of the various metals into one wire of a size which will fit the flame gun. Where the metals are in powdered form, the powders can be intermixed and fed through the flame gun.

The metals comprising the backing layer 3 are selected on the basis of their melting points and ability to metallurgically bond to each other, as in brazing, without the use of flux. By my invention I am able to produce a spray-deposited metallic layer having a tensile strength of 25,000 to 41,000 p.s.i. after it has been heated or sintered at a temperature which is above the melting point of one of the backing layer metals but below that of the others and below that of the base layer metal.

In articles or molds where "Nicrobraz" is used as the base or impression layer, some practical combinations of metals for use in the backing layer 3 include the following pairs:

- 40 Phosphor-bronze, and self-fluxing silver brazing alloy containing phosphorus.
- Copper, and self-fluxing silver brazing alloy containing phosphorus.
- 45 Crome-copper, and self-fluxing silver brazing alloy containing phosphorus.
- Various steels, with self-fluxing silver brazing alloys containing lithium or with self-fluxing copper-nickel brazing alloys containing lithium and boron.
- 50 Beryllium-copper, with a brazing alloy containing lithium.
- Phosphor-bronze, with a self-fluxing copper-phosphorus brazing alloy.

A strong deoxidizer, such as phosphorus, tin, cadmium, lithium or boron, is always included in the backing layer, usually as a part of the self-fluxing brazing alloy, to insure removal of oxides and other undesirable substances formed during sintering (described in a subsequent paragraph) of the deposited metals, thus facilitating formation of a strong metallurgical bond between the sprayed metal particles by promoting wetting of the surfaces of the solid state metals by the liquid state metals. The deoxidizer is a very important feature of my invention.

In order to assure a strong backing layer after sintering, the self-fluxing brazing alloy is selected to fit the characteristics of the other backing layer metals. For example, a silver brazing alloy with 5% phosphorus, 15% silver and 80% copper has been found to be an effective self-fluxing brazing alloy to spray with copper and copper alloys. Self-fluxing brazing alloys containing .5-3% nickel, .5-2% lithium and the balance silver, or .5-20% nickel, .5-2% boron, 15-2% lithium and the balance copper, are examples of alloys which are effective with ferrous materials, nickel, and nickel alloys.

When the desired thickness of backing layer 3 has been deposited, the model 4 is removed, as by breaking or

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cutting it out, leaving a metal shell or mold composed of the base or impression layer 2 and the backing layer 3. The composite shell 1 is then subjected to heat treatment or sintering at a temperature which is above the melting point of one of the backing layer metals, but is below that of the others as well as below that of the metal in the base layer 2. Sintering is generally done in the open atmosphere with the shell packed in charcoal. A reducing atmosphere, such as incompletely burned flue gases, or hydrogen, or a neutral atmosphere such as dry helium may be employed, if desired, but is not essential.

The thickness of the backing layer 3 is a matter determined by the degree of strength required in the mold, which in turn depends on its use. Molds having a thickness of from 0.1 inch to 3.0 inches have been made successfully by my method, with no cracking of the articles.

The mold resulting from the above process consists of a first or base lamellar layer of metal conforming on one side faithfully in surface detail to the prototype model and composed of coalesced lamellar, hard metallic particles, and a backing layer comprised of a matrix of coalesced lamellar particles of a high-melting metal interspersed uniformly throughout the backing layer with another and lower-melting metal metallurgically bonded to said higher-melting metal and filling the voids therein.

A mold or shell 1 made with a "Microbraz" base layer and a backing layer 3 of Phosphor-bronze and self-fluxing silver brazing alloy and sintered at 1350° F. in the open atmosphere was found to have a tensile strength of 41,000 p.s.i., and to have a 15% elongation at break. The same kind of molds that had not been sintered broke under tensile stresses of about 5000 p.s.i. with no elongation. The increased strength and ductility are the result of the metallurgical bond created between the self-fluxing silver brazing alloy particles and the particles of Phosphor-bronze by the sintering operation. The metallurgical bond thus achieved is much stronger than the mechanical bond of normally sprayed metals.

By the method set forth, laminated molds having a hard base layer and tough backing layer suitable for compression molding as well as slush molding of all manner of plastic articles may be made—e.g., for the production of golf-balls, arm rests, electric plugs for female receptacles, hardware, pipe fittings, gears, handles, toys, containers, footwear, and myriad other articles.

For some purposes, such as the production of heavy-duty molds, it is desirable to surround a laminated spray-deposited article, made according to my invention, with a massive body of cast metal, such as cast aluminum. The casting is suitably done in known manner after the spray-deposited metal has been sintered. In this manner a massive article may be built up at much less expense than if the entire article were to be built up by spraying. If desired, further reinforcement and mechanical interlocking may be provided by screws or bolts embedded in or extending into both the sprayed shell and the cast body.

Although I have herein specifically described only some of the variations in the invention, it is understood that the invention is not limited thereby, but is susceptible of change in form or detail within its scope.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. The method of producing strong, ductile metal deposits which comprises simultaneously flame-spraying, a plurality of metals having widely different melting points upon the same area of a surface to which sprayed metal will adhere, the lowest melting point metal being a self-fluxing brazing alloy, and thereafter sintering the metal deposit at a temperature that is above the melting point of the lowest melting metal but below the melting point of the higher-melting metal.

2. The process of claim 1 in which the self-fluxing brazing alloy contains phosphorus as the deoxidizing element, and one of the metals is a copper alloy.

3. The process of claim 1 in which the metals are a

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self-fluxing silver brazing alloy containing phosphorus, and Phosphor-bronze.

4. The process of claim 1 in which the metals are a brazing alloy containing lithium, and beryllium-copper.

5. The method of producing strong, ductile metal deposits which comprises simultaneously flame-spraying a plurality of metals having widely different melting points upon the same area of a rough metal surface, the lowest melting point metal being a self-fluxing brazing alloy, and thereafter sintering the metal deposit at a temperature that is above the melting point of the lowest-melting metal but below the melting point of the higher-melting metal.

6. The method of producing strong, ductile metal deposits which comprises simultaneously flame-spraying a plurality of metals having widely different melting points upon the same area of a silicate-coated surface, the lowest melting point metal being a self-fluxing brazing alloy, and thereafter sintering the metal deposit at a temperature that is above the melting point of the lowest-melting metal but below the melting point of the higher-melting metal.

7. The process which comprises simultaneously flame-spraying a plurality of metals having widely different melting points upon the same area of a surface to which sprayed metal will adhere, the lowest melting point metal containing a deoxidizing element, and subsequently sintering the metal deposit at a temperature at or above the melting point of the lowest-melting metal but below the melting point of the other metals.

8. The process of producing metal articles which comprises the simultaneous flame-spraying of a plurality of metals having widely different melting points upon the same area of a surface having a continuous coating of film-forming silicate, the lowest melting point metal containing a deoxidizing element, and subsequently sintering the resulting metal deposit at a temperature between the melting points of the highest-melting and the lowest-melting metals thereof.

9. In the process of producing metal articles by the simultaneous flame-spraying of a plurality of metals having widely different melting points upon the same area of a surface and subsequently sintering the resulting metal deposit at a temperature between the melting points of the highest-melting and the lowest-melting metals thereof, the improvement which consists in simultaneously flame-spraying a plurality of metals having widely different melting points upon the same area of a surface to which sprayed metal will adhere, the lowest melting point metal containing a deoxidizing element.

10. The method of producing metal molds which comprises coating a model with a continuous film of alkali silicate, flame-spraying a metal base layer onto the coated model, thereafter flame-spraying simultaneously in air onto the same area of the metal base layer, to provide a backing, a plurality of metals having widely different melting points, one of which is a self-fluxing brazing alloy having a melting point below that of the base layer metal and the other of which is an alloy having a melting point above that of the self-fluxing brazing alloy, and sintering the resulting object at a temperature between the melting points of the backing metals and below that of the base layer metal.

11. The method of producing strong, ductile metal deposits which comprises feeding to flame-spray means a wire comprising a plurality of metals having widely different melting points, the lowest-melting point metal being a self-fluxing brazing alloy, simultaneously flame-spraying said metals upon the same area of a surface to which sprayed metal will adhere, and thereafter sintering the metal deposit at a temperature that is above the melting point of the lowest melting metal, but below the melting point of the higher-melting metal.

12. The method of producing strong, ductile metal deposits which comprises feeding to flame-spray means a wire comprising a plurality of metals having widely different melting points, the lowest-melting point metal con-

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taining a deoxidizing element, simultaneously flame-spraying said metals upon the same area of a surface to which sprayed metal will adhere and thereafter sintering the metal deposit at a temperature that is above the melting point of the lowest melting metal, but below the melting point of the higher-melting metal.

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CERTIFICATION OF CORRECTION

Patent No. 2,966,423

December 27, 1960

Daniel Shichman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 2 and 12, and in the heading to the printed specification, lines 3 and 4, name of assignee, for "United States Rubber Corporation", each occurrence, read -- United States Rubber Company --.

Signed and sealed this 16th day of May 1961.

(SEAL)

est:

NEST W. SWIDER

esting Officer

DAVID L. LADD

Commissioner of Patents