# United States Patent [19]

**Breton et al.**

[11] **3,778,586**

[45] **Dec. 11, 1973**


[54] **PROCESS FOR COATING METALS USING RESISTANCE HEATING OF PREFORMED LAYER**


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[22] Filed: **Apr. 2, 1970**

[21] Appl. No.: **25,090**

[52] **U.S. Cl.** .................... **219/76,** 29/472.9, 75/203, 75/211, 75/212, 75/226, 219/117, 219/149

[51] **Int. Cl.** .................... **B23k 9/04**

[58] **Field of Search** .................... 219/73, 76, 117, 219/243; 29/472.9; 75/203, 211, 212, 226; 156/275, 149



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[57] **ABSTRACT**

An improved process for coating a metal substrate with a metallic coating or an abrasive-filled metallic coating metallurgically bonded to the substrate comprising placing on a metal substrate a coating layer having a desired thickness said layer comprising a mixture of a powdered metal or alloy and a binder or a mixture of a powdered metal or alloy, powdered abrasive and a binder; contacting the metal substrate with an electrode connected to a source of high amperage electrical power; contacting, under moderate pressure, the coating layer with a second electrode also connected to said high amperage electrical source and for a short period of timg passing sufficient high amperage electrical current through the substrate and coating layer to decompose the binder and fuse the powdered metal or alloy. The process is useful for producing metallic articles having a corrosion or a wear-resistant coating.

**16 Claims, 4 Drawing Figures**

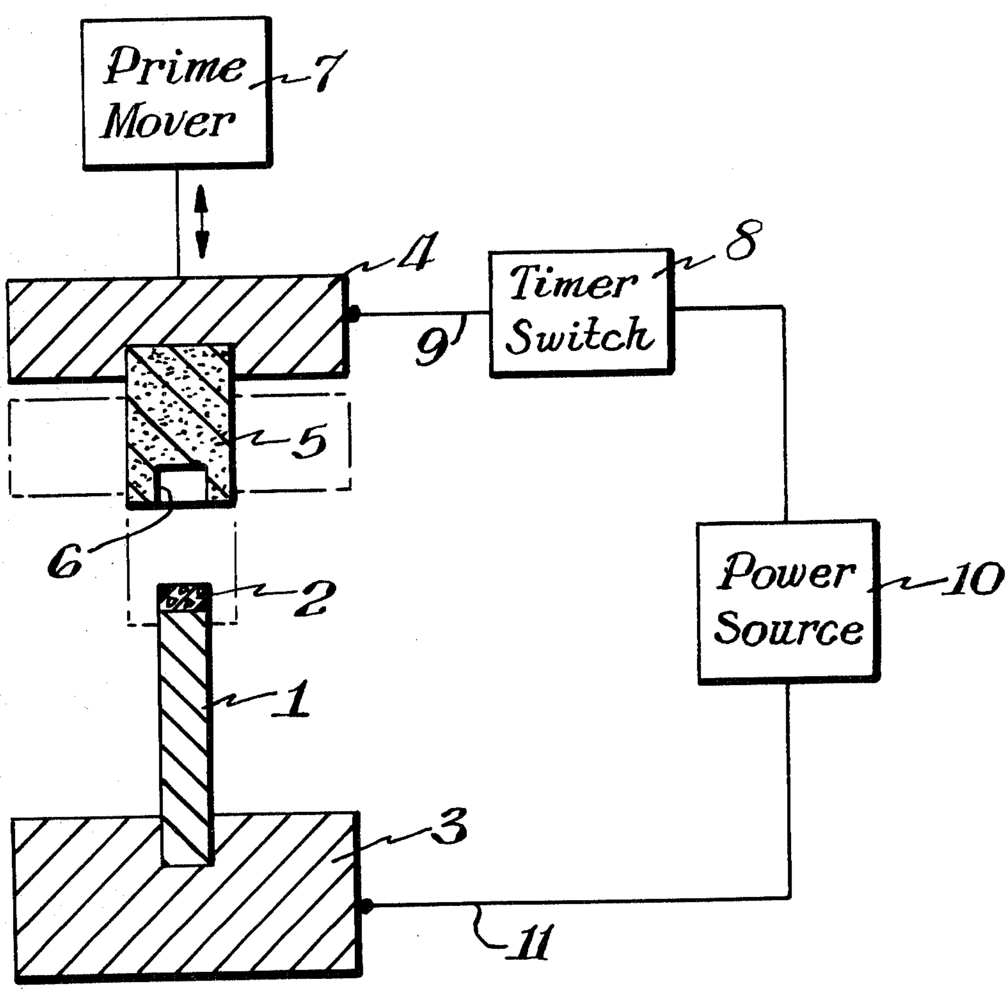



Fig.1.

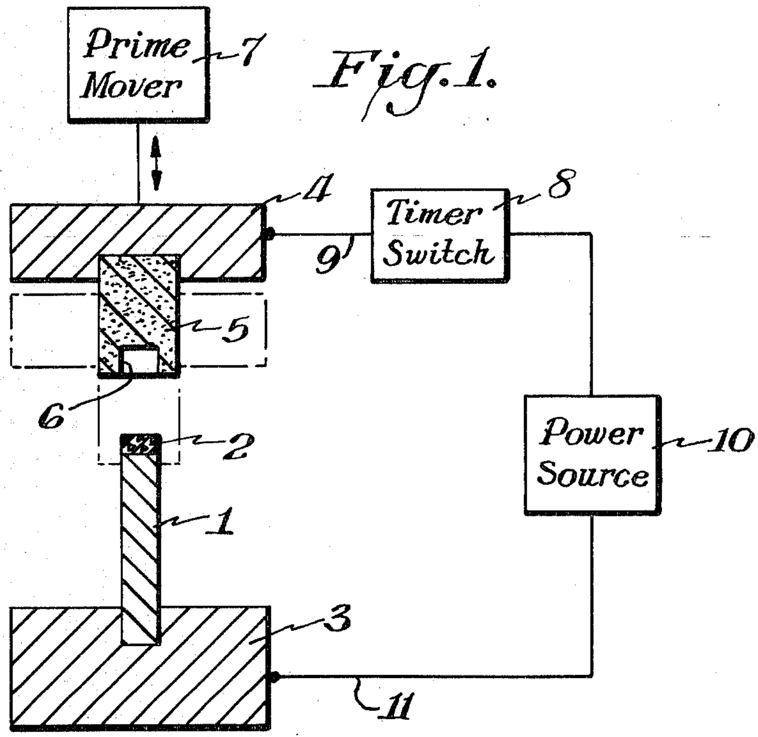



Fig.2.

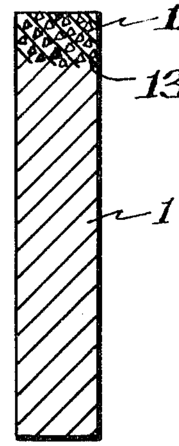



Fig.3.

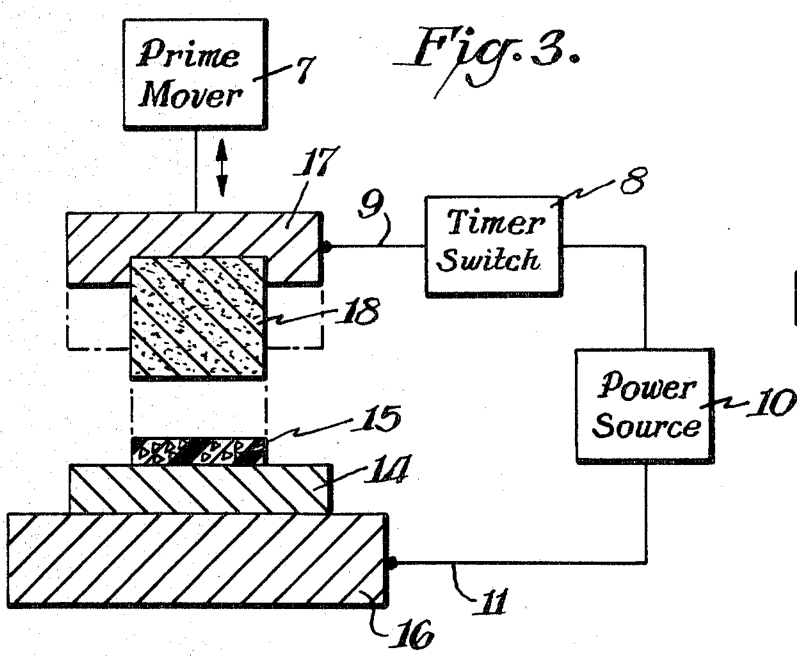
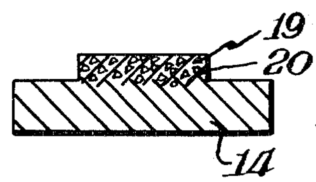



Fig.4.

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# PROCESS FOR COATING METALS USING RESISTANCE HEATING OF PREFORMED LAYER

## BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a novel process for producing a metallic coating on a metallic article of manufacture.

2. Description of the Prior Art

The properties of metallic articles, especially the property of wear or corrosion resistance, may be greatly improved by coating the article with a wear-, or corrosion-resistant metal coating. Prior methods of coating a metallic article with a wear- or corrosion-resistant coating consisted of coating a substrate with a powdered metal or alloy using an organic binder to hold the particles together, followed by heating the substrate in a furnace, with a torch or by induction methods to melt the powdered metal and decompose the binder. These methods are undesirable because they can lead to a loss of mechanical properties due to heat treatment of the substrate and these methods are not amenable to selectively and uniformly coat intricately shaped substrates. We have found that metallic coatings on a metallic substrate can be conveniently and rapidly produced using a high amperage electrical current to heat only the area covered by the powdered metal and without substantially losing any heat treatment of the substrate. By this method, the substrate to be coated is brought into contact with a copper block which together is one of a pair of electrodes. A layer of powdered coating metal or alloy in a binder or a mixture of powdered metal and powdered abrasive in a binder is placed on the area of the metal being coated. The surface of a graphite electrode having a configuration of the area to be coated is brought into contact with the coating layer and the coating layer is subjected by the electrode to a moderate pressure. High amperage-low voltage electrical current from a source of such current is passed through the electrode, through the coating layer, through the metal being coated and through the copper electrode back to the current source. The heat generated decomposes the binder and melts the coating metal. Upon cooling, a hard coating on the substrate is formed. This method produces a metallurgically bonded coating on the substrate in the very short period of time of about 0.1 to 20 seconds. The area to be coated can be controlled precisely by modifying the shape of the graphite electrode brought into contact with the coating layer. The process can be repeated to coat the entire substrate. Only a small area under the graphite electrode is intensely heated.

## SUMMARY OF THE INVENTION

This invention is directed to a process for coating a metallic substrate with a metallic coating, said coating being bonded to the metallic substrate with a metallurgical bond which comprises attaching a layer of a powdered coating material selected from the class consisting of a metal, an alloy, mixtures thereof, and a mixture of the coating material and an abrasive in a binder upon said metallic substrate, said coating material having a solidus temperature lower than that of said metallic substrate; contacting said substrate with a first electrode and said layer with a second electrode said electrodes being connected to a source of electrical current; passing an electrical current through said electrodes, the substrate and coating layer to raise the temperature of said coating layer to at least the solidus temperature of said powdered metal or alloy and cooling to a temperature below said solidus temperature.



This invention is directed to a process for preparing metal, alloy, abrasive-filled metal and abrasive-filled alloy articles of manufacture comprising attaching a layer of a powdered metallic material selected from the class consisting of a metal, an alloy, a mixture thereof and a mixture of the metallic material and an abrasive in a binder upon a non-adherent electrically conducting substrate; contacting said substrate with a first electrode and said layer with a second electrode said electrodes being connected to a source of electrical current; passing an electrical current through said electrodes, the substrate and layer to raise the temperature of said layer to at least the solidus temperature of said powdered metal or alloy; and cooling to a temperature below said solidus temperature.

The process of this invention is useful for coating a metallic article such as a turbine blade, gears, tools and the like with an improved wear- or corrosion-resistant coating. The process of this invention using a non-adhering second electrode is useful for producing articles of manufacture useful as inserts at points of wear of gears, blades, tools, saws and the like.

## BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings which form part of the instant specifications:

FIG. 1 is a schematic diagram of the process;

FIG. 2 is a cross-sectioned view showing an abrasive-filled coated metallic substrate;

FIG. 3 is another schematic diagram of the process;

FIG. 4 is a cross-sectioned view showing an abrasive-filled metal coated metallic substrate.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The substrate to be coated in this invention can be any metallic article composed of metals or alloys such as the various steels, nickel, cobalt, alloys such as nickel alloys, cobalt alloys, copper alloys and the like. The substrate should have melting point or solidus temperature higher than the coating metal or alloy.

The coating metal can be any metal which has a lower melting point, plastic or solidus temperature than the substrate. Preferably, the coating metal is an alloy such as the various low-melting iron based, nickel based, copper based and cobalt based alloys and the like. These alloys are well known in the art. Examples of alloys useful in this invention are further described in the publication entitled "Brazing Manual", The American Welding Society, Inc. 345 East 47th Street, New York, N.Y., 1963. These metals can serve as a matrix for hard facing of a metal substrate. The invention includes the process for coating substrates with a metal or alloy, separately or these materials mixed with an abrasive such as the carbides, for example, a metal carbide including tungsten carbide, tantalum carbide, chromium carbide, titanium carbide, silicon carbide, boron carbide, and the like, the borides such as metal borides, the silicides such as metal silicides, diamond and the like and mixtures of these. When a mixture of coating metal and abrasive is used in the invention the coating metal or alloy serves as a matrix into which the abrasive is dispersed. Preferably, the amount of abrasive used is 0.5–70 percent, by volume, and most preferred 40 to 60percent, by volume, is used.

The coating metal can be a brazing alloy such as those containing, by weight, 0–12 percent silicon, 0–5 percent boron, 0–24 percent chromium, 0–10 percent iron, 0–2 percent carbon, 0–15 percent phosphorus and the remainder is nickel or cobalt. Other alloys such as copper and silver based alloys can be used.

The methods by which the assembly of the coating layer and substrate is produced can vary. The coating metal in powdered form can be mixed with a binder such as shellac, organic polymers such as methyl methacrylate or a flux and this mixture then is doctored upon the substrate in a uniform layer. A variation of this embodiment is to form a coating layer on the substrate by alternately coating the substrate with binder, then sprinkling powdered coating metal or mixture of powdered coating metal and powdered abrasive on the binder or a different binder and repeating the process until the desired thickness is obtained. The binder used in the invention or its thermal decomposition products should not have an adverse effect on the substrate or the coating composition.

The coating layer can be attached to the substrate being coated by means of an adhesive such as shellac, rubber cement, polymethacrylate, polyacrylate and the like. The composition of the binder and adhesive can be the same or different. Similar to the binder, the adhesive or its decomposition products should not have an adverse effect on the substrate or the coating composition. A method of forming the assembly of the coating layer on the substrate is to form a self-supporting sheet of the powdered coating metal mixed with a binder, a mixture of coating metal and abrasive with a binder or laminates thereof and then to cement the sheet on the metal substrate using as an adhesive shellac, rubber cement, various polymer solutions such as benzene solutions of acrylate or methacrylate, other polymers and the like. In this embodiment polytetrafluoroethylene conveniently serves as the binder. For example, a mixture of the coating composition described above and about 1–25 percent, by volume, and most preferred 2–15 percent, by volume, of polytetrafluoroethylene is cross-rolled and a sheet of the desired thickness is formed as described in U.S. Pat. No. 3,281,511. A small quantity of a lubricant such as Stoddard solvent can be added to the mixture to facilitate formation of the sheet. Alternately a self-supporting sheet of the coating material can be formed by mechanically working the mixture, for example, by ball-milling for a period of time of about 30 minutes a mixture of the powdered coating material mixed with 1–15 percent, by volume, of powdered polytetrafluoroethylene followed by a calendering step to form a self-supporting sheet of the described thickness. Other methods of mechanical working including cross-rolling, indenting, mix-mulling, pressing, calendering, or a combination of these described in our co-pending application Ser. No. 818,781, filed Apr. 23, 1969. The powdered polytetrafluoroethylene used as a binder is prepared as described in U.S. Pats. Nos. 2,593,582 and 2,586,357.

As stated above, a laminate of various layers of a powdered metal or alloy and binder or a powdered metal or alloy mixed with abrasive or mixtures thereof can be used in this process.

The thickness of the coating layer used in this process can vary greatly and still provide a flaw-free metallic



coating of this invention. For example, the thickness of the layer and the resulting coating can be 0.0005 inch or less to 0.25 inch or greater. Preferably the coating layer used in our process and resulting coating is about 0.002 to 0.100 inch.

The time required to form a coating metallurgically bonded to the substrate is very short and consists of 0.1 to about 20 seconds. The rate of heating selected should preferably result in the decomposition and volatilization of the binder and adhesive before the solidus temperature of the coating metal is achieved to produce a void- and flaw-free, metallurgically bonded coating. The second electrode which is in contact with the coating layer reaches a temperature near the solidus temperature of the coating metal or alloy and thereby provides additional heat to fuse the matrix material.

A preferred embodiment of our invention is shown in FIG. **1** wherein the metallic substrate **1** is coated with a coating layer **2** of a mixture of powdered metal, powdered abrasive and an organic binder. The metallic substrate is in electrical contact with a first electrode **3** made of a metal such as copper. The first electrode is electrically connected to a power source **10** by an electrically conducting cable **11**. The first electrode is a combination of the substrate and support member holding same. The power source **10** can be a power transformer, an electric generator, either of the alternating or direct current type which is capable of producing a high amperage-low voltage electrical current. An electrode support member **4** made of a metal such as copper is in electrical contact with a second grooved electrode **5** made of graphite, tungsten and the like wherein the groove **6** is positioned opposite said coating layer **2**. The electrode support is connected by an electrical cable **9** to the power source to give a closed circuit. A timer switch **8** located in cable **9** controls the flow current. A prime mover **7** powered by a solenoid system, a hydraulic pump and the like is used to move the electrode support and the second electrode which are arranged such that the prime mover moves the second electrode to a position wherein the grooved portion of said second electrode is in contact with the coating layer. The prime mover causes the second electrode to subject the coating layer to a moderate pressure of 1 to 5,000 psi or higher. Electric current from the power source is conducted through the metal substrate through the coating layer through the electrodes with the formation of sufficient heat to decompose the binder and melt the coating metal. Preferably, the coating layer is subjected to a moderate pressure of 5 to 100 psi pressure although higher or lower pressures can be used. In the formation of metal coatings which do not contain abrasive, it is preferable to provide a stop which limits the movement of the electrode in contact with the coating layer. Without the use of a stop, molten metal can be forced from the coating layer with the formation of a thinner metal coating than desired.

The pressure applied to the coating layer during the heating steps decreases the electrical resistance of the coating layer. Normally the coating layer has high electrical resistance. When the metallic particles in the coating layer are brought closer together under pressure there results a decrease in the electrical resistance of the coating layer.

FIG. **2** shows the metal coated substrate resulting from FIG. **2**. In FIG. **2** the substrate **1** is coated with a void-free, abrasive-filled metal coating **12** which is attached to the substrate by a metallurgical bond **13.** The metallurgical bond consists of a thin layer between the substrate and the coating where alloying of the substrate and metal coating has occurred.

In FIG. **3,** which shows another preferred embodiment of the process of this invention, the metal substrate **14** is in electrical contact with an electrode **16** which is connected to a power source **10** by means of a cable **11** which is an electrical conductor. The coating layer **15** is a mixture of a powdered metal and powdered abrasive bonded together by an organic polymeric binder such as polytetrafluoroethylene, polymethyl methacrylate, shellac and the like. The coating layer can be held in place by means of an adhesive (not shown) such as shellac or rubber cement. The use of an adhesive permits the use of the process to coat non-horizontal position. The electrode support member **17** is in electrical contact with a second electrode **18** positioned opposite the first electrode, the substrate and the coating layer. The prime mover **7** moves said electrode support member and said second electrode into electrical contact with the coating and subjects the coating to a moderate pressure described above. The electrode support member is in electrical contact by means of cable **9** with a timer switch **8** which in turn is in electrical contact with the power source **10** by the same cable **9.** Cable **9** is an electrically conducting cable.

FIG. **4** shows the coated substrate of FIG. **3** wherein the substrate **14** is partially coated with a powdered abrasive filled metal coating **19** said coating being attached to the substrate by a thin metallurgical bond **20.**

The electrode in contact with the coating layer can provide a portion of the heat which causes fusion of the metal in the coating layer and therefore it is preferable that this electrode is constructed of a material such as graphite or tungsten which has sufficient electrical resistance such that the passage of an electrical current through it heats the electrode at the heating rates described above.

The portion of the second electrode which makes electrical contact with the coating layer can be sculptured to match a surface of an intricately shaped metallic substrate.

The source of electricity can be any high amperage, low voltage electrical power source of either the direct or alternating current type. Such electrical current can be provided by a power transformer which converts electrical current to the desired amperage and voltage or a generator.

The coating produced is metallurgically bonded to the substrate. The metallurgical bond is a thin layer between the substrate and the coating where alloying of the coating metal and substrate metal has occurred. The occurrence of the metallurgical bond is essential for producing a strongly bonded metal coating or an abrasive-filled coating free of porosity and occlusions on the substrate. The formation of a pore-free coating with said continuous metallurgical bond from a metallic powders mixed with a binder by or a mixture of a metallic powders a powdered abrasive and a binder the rapid process of our invention, was highly unexpected. The coated metal objects produced by our process are useful in applications where they are subjected to extremes of wear, impact, temperature and abrasion. Without the metallurgical bond, these objects would not be suitable in these applications.

The coatings produced by our invention can be void and flaw-free and are strongly metallurgically bonded to the substrate. The absence of binder in the final coating was demonstrated by sectioning of the coated area followed by microscopic examination. It was highly unexpected that the organic binder used to hold the particles of the coating composition in position on the substrate could be decomposed and volatilized in the short period of time of the heating step.

The abrasive-filled coating can contain up to 90 percent, by volume, of the abrasive such as a metal carbide, a metal nitride, a metal boride, a metal silicide and the like. The abrasive can have an average particle diameter of 0.1 to −150 microns or mixtures thereof; however, coarser or finer material can be used. The coating produced has extreme resistance to wear. However, the embodiments of this invention are included in the formation of an abrading surface by the use of large particles of abrasives.

A modification of this invention which provides metal alloy, abrasive-filled metal and abrasive-filled alloy articles of manufacture of controlled porosities comprises the steps described above for coating a substrate except that a non-adhering substrate is used. For example, the substrate can be replaced with an electrode composed entirely of graphite or tungsten or other electrically conducting substance. The molten coating metal or alloy does not bond upon cooling to tungsten or graphite. Further examples of non-adhering substrates include metals which have been treated to make them non-adhering, for example, a low carbon steel which has been coated with a slurry of an electrically conducting parting agent or chilled metal surfaces.

The articles of manufacture produced by this modification of the coating process can be void-free and have good physical and mechanical properties. These articles of manufacture can be used as inserts at points of wear of objects such as gears, tools, blades, saws and the like. The articles can be attached to a substrate by brazing techniques or with an adhesive such as an epoxy cement. The abrasive-filled articles are particularly useful to prevent or retard wear at points of friction of gears, tools, blades, saws and the like.

The following examples further illustrate the invention. In the examples, percentages are expressed by volume unless otherwise specified and temperature is in degrees Centigrade unless otherwise specified.

## EXAMPLE I

On a ¼ inch thick stainless steel (type 316) plate a piece of metal loaded film 0.015 inches thick containing 95 percent, by volume, 1–325 mesh of a powdered nickel based alloy American Metal Standard (AMS) 4775 contain, by weight, 5 percent silicon, 3.5 percent boron, 15 percent chromium, 4 percent iron, 0.6 percent carbon and the balance nickel, and 5 percent by volume powdered polytetrafluoroethylene resin prepared as described below were placed. Over this a piece of steel shim 0.005 inches thick was placed. Circular copper electrodes having a ¼ inch diameter contact surface were pressed against the upper and lower surfaces of this sandwich. Pressure was applied to the film by means of a mechanical system connected to the electrodes to reduce the electrical resistance of the metal loaded film. Approximately 8,000 volt-amps was conducted through the steel plate and metal filled film for one second using a Miller Electric Company spot welder Model 10 T as a source of electrical power.

The result was the formation of a fused circular disc coating of the AMS 4775 alloy having a ¼ inch diameter in the area of the plate between the electrodes. The 0.005 inch steel shim was welded to the top of the fused disc. The steel shim was removed by grinding to give a steel wear plate having wear- and corrosion-resistant disc metal coating composed of AMS 4775 alloy. Cross-sectioning followed by microscopic examination proved that the disc was void and flaw free and metallurgically bonded to the plate.

The metal loaded film was produced by ball-milling for about 30 minutes a mixture of 95 percent, by volume, of powdered AMS 4775 (−325 mesh) and 5 percent, by volume, of powdered polytetrafluoroethylene (produced as described in U.S. Pats. Nos. 2,586,357, 2,593,582, 2,670,417 and 2,685,707. A porcelain grinding medium was used. The ball-milled mixture was pressed into a film by means of pressure rolls or calender rolls.

EXAMPLE II

Over an 0.060 inch thick steel substrate the following described laminate was placed. A film produced as described in Example I using polytetrafluoroethylene as binder, containing 0.010 inch thick of −325 mesh tungsten carbide in juxtaposition with a second film 0.015 inch thick of powdered 4775 nickel base alloy (−325 mesh) was made by rolling both the two films together. The polytetrafluoroethylene resin content in both films was 5 percent by volume.

The arrangement for heating consisted of a copper electrode in contact with the 0.060 steel sheet. On this was the above-described laminate with the AMS 4775 alloy in contact with the steel. A graphite electrode with a ¼ inch diameter contact area was pressed against the tungsten carbide surface of the laminate. Ten thousand volt amps for one half second was applied to the layer. The assembly was allowed to cool.

The result was a well-fused coating metallurgically bonded over the ¼ inch diameter area which was in contact with the graphite electrode. The coating had excellent wear resistance. In this and other coatings containing abrasive, it is believed that the metal acts as a matrix for the abrasive.

EXAMPLE III

The procedure of Example I was repeated except that the metal filled film used was formed by ball-milling a mixture of 25 percent, by volume, of powdered tungsten carbide (−325 mesh), 70 percent, by volume, of AMS 4775, and 5 percent, by volume, of powdered tetrafluoroethylene followed by calendering. The product was a steel plate having a void and flaw-free abrasive filled metal wear resistant disc metallurgically bonded thereto.

EXAMPLE IV

The procedure of Example I was repeated except that for the 0.060 inch steel substrate a ⅛ inch thick graphite plate was used.

A circular disc of the solid AMS 4775 and tungsten carbide was obtained. The disc was shown to be void-free by grinding and microscopic inspection.

EXAMPLE V

The procedure of Example IV was repeated except that a metal filled film formed by ball-milling a mixture of 25 percent, by volume, of powdered tungsten carbide (−325 mesh), 70 percent, by volume, of AMS 4775 nickel based alloy, and 5 percent, by volume, of powdered tetrafluoroethylene followed by calendering was used instead of the metal filled film used in Example IV.

The product was a void- and flaw-free abrasive filled AMS 4775 disc.

The coating process of our invention is useful for providing a metal coating which is corrosion resistant on a metallic article. Likewise, the process is useful for providing a wear resistant metallic coating or an abrasive-filled metallic coating, on a metallic article. Corrosion and wear resistance is an essential property for metallic articles such as turbine blades which are subjected to friction and corrosive atmospheres.

The coating process of this invention is useful for coating the working or wearing area of various tools, bits, shafts and the like.

The articles of manufacture produced by the process using a non-adherent substrate are useful as inserts for tools, bits, gears, shafts and the like, and as porous filters, seals and the like. These can be brazed or glued to the tool, bit, gear, shaft, etc. with an epoxy adhesive.

The foregoing detailed description has been given for clarity of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

**1.** A process for coating a metallic substrate with an essentially void-free, metallurgically bonded coating comprising:

a. overlaying the substrate with a preformed, flexible, uniform, self-supporting layer comprising an organic binder having dispersed therein a material selected from the group consisting of (1) a powdered metallic matrix and (2) a mixture of a powdered metallic matrix and powdered abrasive; said metallic matrix being characterized as having a solidus temperature lower than the solidus temperature of the substrate and in the molten state being further characterized as wetting the substrate;

b. uniformly pressing the self-supporting layer and substrate together with an electrode which is not wetted by said molten matrix metal;

c. passing without arcing an electrical current through said self-supporting layer and substrate for resistance heating of said self-supporting layer to a temperature above the solidus temperature of said matrix and below the solidus temperature of said substrate; and then

d. cooling to a temperature below the solidus temperature of said matrix.

**2.** The process of claim **1** wherein from about 1 to 25 percent, by volume, of the self-supporting layer is an organic binder selected from the group consisting of a polymethacrylate, a polyacrylate and polytetrafluoroethylene.

3. The process of claim 1 wherein from about 1 to 15 percent, by volume, of the self-supporting layer is polytetrafluoroethylene as binder.

4. The process of claim 1 wherein from about 1 to 10 percent, by volume, of the self-supporting layer is polytetrafluoroethylene as binder.

5. The process of claim 1 wherein the abrasive is selected from the class consisting of an oxide, a carbide, a nitride, a boride, a silicide and diamond.

6. The process of claim 1 wherein the coating metal is a braze alloy selected from the class consisting of iron-based, nickel-based, cobalt-based, copper-based, and silver-based alloys.

7. The process of claim 1 wherein the self-supporting layer comprises up to 90 percent of the powdered abrasive, by volume.

8. The process of claim 1 wherein the self-supporting layer is pressed under pressure in the range of 1 to 5,000 psi.

9. A process for producing an essentially void-free article of manufacture comprising

a. placing a preformed flexible, uniform, self-supporting layer comprising an organic binder having dispersed therein a material selected from the group consisting of a (1) powdered metallic matrix and (2) a mixture of a powdered metallic matrix and powdered abrasive, on an electrically conducting substrate which is not wetted by molten metallic matrix;

b. uniformly pressing the self-supporting layer and substrate together with an electrode which is not wetted by said molten matrix metal;

c. passing without arcing electrical current through said self-supporting layer and substrate for resistance heating of said self-supporting layer to a temperature above the solidus temperature of said matrix, and then

d. cooling to a temperature below the solidus temperature of said matrix.

10. The process of claim 9 wherein from about 1 to 25 percent, by volume, of the self-supporting layer is an organic binder selected from the group consisting of a polymetharcylate, a polyacrylate and polytetrafluoroethylene.

11. The process of claim 9 wherein from about 1 to 15 percent, by volume, of the self-supporting layer is polytetrafluoroethylene as binder.

12. The process of claim 9 wherein from about 1 to 10 percent, by volume, of the self-supporting layer is polytetrafluoroethylene as binder.

13. The process of claim 9 wherein the abrasive is selected from the class consisting of an oxide, a carbide, a nitride, a boride, a silicide and diamond.

14. The process of claim 9 wherein the self-supporting layer comprises up to 90 percent of the powdered abrasive, by volume.

15. The process of claim 9 wherein the self-supporting layer is pressed under pressure in the range of 1 to 5,000 psi.

16. The process of claim 9 wherein the coating metal is selected from the class consisting of iron-based, nickel-based, cobalt-based, copper-based, and silver-based alloys.

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