United States Patent Office 2,860,098 Patented Nov. 11, 1958

2,860,098

METAL COATING

Frederick Fahnoe, Morristown, and James J. Shyne, Arlington, N. J., assignors to Vitro Corporation of America, Verona, N. J.

No Drawing. Application March 31, 1954 Serial No. 420,200

9 Claims. (Cl. 204—181)

Our invention is directed toward improved metal to metal coatings and structures resulting from same.

In many industrial applications, it is desirable to apply a metal coating to a metal member by methods other than electrolytic deposition and then subsequently form the coated member into various shapes. Conventional techniques such as spraying, dipping, and painting have not proved completely successful for one or more of the following reasons: the coating is porous and is subject to corrosion as well as to the attack of various chemical agents often used during the forming process; the coating is poorly bonded to the metal member and tends to separate therefrom; if the coating is bonded by sintering, the temperatures required are high enough to soften or melt the metal member and thus adversely affect the composite metallurgical properties of the coated member; and the coating is not as ductile as the metal member itself and therefore tends to crack and chip during the forming process.

We have discovered a non-electrolytic process which obviates these disadvantages and which results in an improved coated body.

Accordingly, it is an object of the present invention to provide new and improved processes and structures of the character indicated.

It is a further object to provide a new process for applying an impermeable ductile metal coating of uniform thickness to a metal member.

Yet a further object is to provide an improved metallic member which comprises a base metal member to which is bonded a ductile impermeable metal coating.

Still another object is to provide an improved metal body of the character indicated which is free from internal stresses or strains.

In our copending application S. N. 388,119, filed October 26, 1953, we disclosed processes utilizing electrophoretic deposition. This phenomenon occurs when an electrostatic field is established between two electrodes immersed within a colloidal or gross dispersion of charged particles, thus causing the migration of the suspended particles toward one of the electrodes and producing the deposit of an adherent coating on that electrode. Exceptional uniformity of coating thickness and compacting (with an attendant relatively high coating density) are obtained as compared with dipping, spraying, brushing and other more conventional methods of application. Irregularly shaped objects of a desired contour can be coated with excellent uniformity and reproducibility of coating. Further details of this process will be found in the above-mentioned application.

In the present invention of reducible or decomposable metallic compound or mixture of such compounds is electrophoretically deposited on a base member. This member is generally formed from a metal or alloy, although any material having a conductivity at least equal to a semi-conductor can be used. The coated member is then heated at a relatively low temperature, if necessary

in an inert or reducing atmosphere, to reduce or decompose the compound to metal. The coated body is then heated further at a higher temperature (which is always below the melting or softening temperature of the base member) to sinter the metal coating and form a ductile non-porous coating of uniform thickness well bonded to the base member. Alternatively, the electrophoretically coated member may be heated at this higher temperature initially and thus concurrently sinter and reduce or decompose the deposited coating.

It is to be emphasized that the reduction and sintering temperatures required for this process are much lower than conventionally used. In conventional powder metallurgy, the sintering temperature employed is at least ⅔ of the melting temperature (expressed in the absolute scale) of the lowest melting component. For example, the sintering temperature of chromium is generally on the order of 1500° C. This temperature is higher than the melting temperature of stainless steel (on the order of 1400° C.) so that conventional techniques of the type discussed previously cannot be used. In our process chromium is sintered at a much lower temperature, on the order of 1050 to 1150° C., and thus can be applied directly to stainless steel without melting same.

While it is not our intention to be bound by theory, it is believed that this sharp reduction in sintering temperature is obtained through use of the Van der Waal forces of attraction established between adjacent particles in the electrophoretically deposited coating. These particles are so small (micron or sub-micron size), and the deposit density is so high, that these forces of attraction are believed much higher than are conventionally obtainable. Through action of these forces, the particles exhibit intergranular growth (sintering) at much lower temperatures than has been observed in the prior art.

The mechanism by which this type of coating is bonded to its base member is not fully understood. However, cross-sectional analysis has established that as these coated members are heated, the metals codiffuse into each other across the coating-member interface and the end result of this codiffusion is a strong permanent bond.

The following examples set forth certain well defined instances of the application of this invention. They are, however, not to be considered as limitations thereof, since many modifications can be made without departing from the spirit and scope of this invention.

Example I

A 5 micron layer of chromic oxide was deposited out of a gross dispersion containing 2% by weight of chromic oxide particles in isopropyl alcohol onto a steel plate in the manner described in the aforesaid copending application.

The coated plate was then heated in a hydrogen atmosphere to a temperature of 1150° C. for a period of 1 minute. Subsequent cross-sectional analysis revealed that the oxide had been completely reduced to metallic chromium. Further tests established that this coating had good adherence and excellent ductility.

The firing temperature required to produce this chromium minimum coating is a function of the water vapor-hydrogen partial pressure ratio. Thus, this ratio must not exceed 0.001 in the above process, otherwise reduction will not take place.

Example II

A 10 micron layer of nickel oxide was deposited on a steel plate in the manner described previously.

The coated plate was then heated in a hydrogen atmosphere to a temperature of 200° C. for a period of one minute. Cross-sectional analysis revealed that the nickel oxide had been completely reduced to metallic nickel; the

coating however was very soft, spongy and possessed poor adherence.

This process was repeated with various firing temperatures within the range 200–400° C. for periods ranging between 1 to 30 minutes. The results were the same as before.

This process was repeated with various temperatures within the range 600–1000° C. for periods of one minute. These coatings were much tougher, highly ductile and possessed good adherence. Coatings produced at the lower temperatures within the 600–1000° C. range were somewhat porous; those produced at temperatures between 900–1000° C. were substantially non-porous with excellent surface continuity.

Increases in the firing period beyond one minute had no appreciable effect.

Example III

A 4 micron layer comprising a mixture of substantially 40% by weight of chromium oxide and substantially 60% by weight of nickel oxide was deposited on a molybdenum plate.

The coated plate was then fired in hydrogen at a temperature of 1000° C. for a period of one minute. Cross-sectional analysis revealed that both oxides had been completely reduced to form a chromium-nickel coating. This coating was well bonded, extremely ductile and only slightly porous.

Additional chrome-nickel layers were built up on this coated plate by repetitive steps of deposition and reduction to a thickness of 30 microns. This layer was found to have the same properties as the original 4 micron layer.

Example IV

A 6 micron layer comprising a mixture of substantially 78% by weight of nickel oxide, 15% by weight of chromium oxide, and 7% by weight of iron oxide was deposited on a molybdenum plate.

The coated plate was then fired in hydrogen at a temperature of 1000° C. for a period of one minute. A well bonded, ductile, non-porous nickel-chromium-iron coating was formed.

Example V

A 3 micron layer of copper oxide was deposited on a steel plate.

The coated plate was fired in hydrogen at a temperature of 250° C. for a period of one minute. The copper oxide was completely reduced to metallic copper but the coating was spongy and possessed poor adherence.

The coated plate was then fired in hydrogen at a temperature of 600° C. for a period of one minute. The coating thus produced was much tougher and well bonded.

It was found that the same quality coating could be obtained by initially firing the coated plate at 600° C.

Example VI

A 5 micron layer of silver oxide was deposited on a steel plate.

The coated plate was fired in hydrogen at a temperature of 150° C. for a period of one minute. The silver oxide was completely reduced to metallic silver but the coating was porous and possessed poor adherence.

The coated plate was then fired in hydrogen at a temperature of 900° C. for a period of one minute. The coating thus produced was only slightly porous and was well bonded.

It was found that the same quality coating could be obtained by initially firing the coated plate at 700° C.

Example VII

A 4 micron layer of chromic fluoride was deposited on a copper plate.

The coated plate was fired in hydrogen at a temperature of 900° C. for one minute.

It was found that the fluoride had been completely reduced to metallic chromium and that a strong, well-bonded coating had been formed.

Example VIII

A 4 micron layer of zirconium hydride was deposited on a molybdenum plate.

The coated plate was fired in helium at a temperature of 1200° C. for one minute.

It was found that the hydride had been completely decomposed to metallic zirconium and that a strong, well-bonded coating had been formed.

This process is generally applicable to the use of any reducible or decomposable metallic compound which can be electrophoretically deposited on a base metallic member in the manner outlined in the aforesaid copending application and can be reduced or decomposed at temperatures below the melting or softening temperature of the base member.

By means of this process, corrosion-resistant coatings can be applied to low melting metals to produce structures not hitherto obtainable. Moreover, ductile and non-porous coatings can be applied to metals in this manner thus obtaining coated members possessing unique structural properties.

While we have described and pointed out various embodiments of the present invention, many modifications within the scope and sphere of this invention will be apparent to those skilled in the art and it is our intention not to be limited except as indicated in the claims which follow.

We claim:

1. The method of applying and bonding a metal coating to a selected surface of a metallic base member of the group consisting of steel, molybdenum and copper, comprising the steps of electrophoretically depositing particles of a metallic compound of the group consisting of the oxides of chromium, nickel, iron, silver and copper, chromium fluoride and zirconium hydride out of liquid media onto said surface, the selected coating material being capable of being converted to the metal and sintered at temperatures below the melting temperature of the selected base member, and heating said coated member at a temperature high enough and in an atmosphere to convert said particles of metallic compound to metal and to sinter said metal and to bond said metal to said member by metal-member codiffusion at their common interface.

2. The method of claim 1 wherein a layer of chromium oxide is deposited on said metallic base and thereafter heated in a hydrogen atmosphere to reduce said chromium oxide to metallic chromium.

3. The method of claim 1 wherein a layer of nickel oxide is deposited on said metallic base and thereafter heated in a hydrogen atmosphere to reduce said nickel oxide to metallic nickel.

4. The method of claim 1 wherein a layer of copper oxide is deposited on said metallic base and thereafter heated in a hydrogen atmosphere to reduce said copper oxide to metallic copper.

5. The method of claim 1 wherein a layer of silver oxide is deposited on said metallic base and thereafter heated in a hydrogen atmosphere to reduce said silver oxide to metallic silver.

6. The method of claim 1 wherein a layer of chromium fluoride is deposited on said metallic base and thereafter heated in a hydrogen atmosphere to reduce said chromium fluoride to metallic chromium.

7. The method of claim 1 wherein a mixture of 40 percent chromium oxide and 60 percent nickel oxide is deposited on said metallic base and thereafter heated in a hydrogen atmosphere to reduce said oxides to metal.

8. The method of claim 1 wherein a mixture of 78 percent nickel oxide, 15 percent chromium oxide, and 7 percent iron oxide is deposited on said metallic base

and thereafter heated in a hydrogen atmosphere to reduce said oxides to metal.

9. The method of applying and bonding a coating of zirconium to a selected surface of a molybdenum base member, comprising the steps of electrophoretically depositing particles of zirconium hydride out of liquid media onto said surface, and heating said coated member in a helium atmosphere at a temperature high enough to decompose said zirconium hydride to metallic zirconium and to sinter said zirconium particles and bond said zirconium metal to said member by metal-member codiffusion at their common interface.

References Cited in the file of this patent

UNITED STATES PATENTS

2,036,667	Williams	Apr. 7, 1936
2,233,622	Lytle	Mar. 4, 1941
2,307,018	Cardell	Jan. 5, 1943
2,442,863	Schneider	June 8, 1948
2,462,125	Oakes	Feb. 22, 1949
2,474,038	Davignon	June 21, 1949
2,570,248	Kelly	Oct. 9, 1951
2,708,726	Atherton	May 17, 1955
2,711,390	Childers	June 21, 1955

FOREIGN PATENTS

1,044,212	France	June 17, 1953