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ART OF BONDING OF VACUUM METALLIZED COATINGS TO METAL SUBSTRATES

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This application is a continuation-in-part of my co-pending application Serial No. 836,145, filed August 26, 1959, now U.S. Patent No. 3,123,493, issued March 3, 1964.

This invention relates to the preparation of coatings upon metal substrates by vacuum deposition of metal thereon from metal vapors, and is particularly connected with the production of securely bonded coatings.

The method of this invention leads to the production of a composite product having the advantage of a substrate of a physically strong, cheap and easily fabricated metal but with the substrate metal having disadvantages such as low corrosion or other chemical resistance, with an adherent thin coating of a metal which is nobler and more costly than the substrate but which acts to provide the composite with the requisite chemical properties.

It has been proposed to vaporize a metal in vacuo, and effect deposition thereof on a metal sheet as a substrate. In practice, a heating is employed to regularize the coating and improve the bonding effect. With certain pairs of metals for the substrate and the coating, the bonding is accomplished with an interalloying effect at the interface. When steel is coated with deposited aluminum vapor, for example, there is interalloying of body-centered cubic iron and face-centered cubic aluminum. The two metals are so dissimilar electrochemically and in interatomic spacing that such alloying is not a simple intersolution but rather a new phase or phases, i.e., intermetallic compounds, must form. The iron-aluminum alloys such as $FeAl_3$ and Fe_2Al_5 are hard and brittle so that while bonding can be accomplished in form effective if no mechanical stresses are later to be exerted upon the coated sheet, the relatively thick alloy layers formed cause fractures along the alloy interface when stresses are exerted, with resultant separation along the interface between the iron base and the aluminum coating deposit.

According to the instant invention, an interalloying is produced for an interface thickness of only a few atoms diameters, e.g. 3 to 10 atoms diameters, that is, it is not detectable by microscopic inspection or by cleavage between substrate and coating during fabrication. Therewith, controls are provided for the presentation of a completely clean and non-gassing substrate surface, for the temperature at which coating is being effected, and competent to receive and effect a bond with the coating metal which is resistant to severe chemical corrosion influences without obstruction of the bond.

It has previously been proposed to clean the surface of a ferrous sheet in various ways. For example, in galvanizing, a steel strip is heated in air or oxygen to burn off oils, and then it is heated at 900 to 1,200 degrees F. in hydrogen to reduce surface oxides back to elemental iron. Therewith, the reducing chamber contains hydrogen at super-atmospheric pressure, and the sheet is advanced therefrom to a zinc-coating bath, noting that the hydrogen is not then of great harm to the plating but may assist in keeping the bath low in zinc oxide. When this proceduce of cleaning by hydrogen is employed at super-atmospheric pressure, the seal between the chamber for such cleaning operation and the deposition chamber must be able to resist penetration of the vapors of the first or high pressure chamber into the second or high-vacuum deposition chamber: and any hydrogen within the substrate as it

passes into the deposition chamber can cause the formation of gases as a blanket at the substrate surface which interferes with deposition of the metal vapor thereon.

According to this invention, a hydrogen removal of surface oxygen is effected by storing hydrogen within the body of the substrate, and later withdrawing this hydrogen through the surface under a temperature condition at which hydrogen is effective to reduce surface oxides: and includes the employment of this hydrogen-withdrawing step as a means of also riding the substrate of chemisorbed oxygen, air adsorbed oxides, carbonates, hydroxides, and other volatile or evaporable impurities. Therewith the withdrawal of the hydrogen from the substrate by low pressure or vacuum, prior to the advancement of the substrate into the vacuum deposition chamber, reduces the load upon the evacuation equipment for this deposition chamber and acts to prevent the development of a gas blanket at the surface of the substrate during the deposition.

An object of the invention is the employment of a surface cleaning operation for the purpose of introducing and storing hydrogen within the metal substrate, followed by a preliminary evacuation for withdrawing the hydrogen through the surface of the substrate, with a heating during the withdrawal, and then by a deposition of metal upon the substrate after cooling to a temperature lower than that of the hydrogen withdrawal.

Another object of the invention is the surface cleaning of a metal substrate with storage of hydrogen in the substrate stoichiometrically capable of removing surface oxygen present as the substrate is advanced to a first evacuation zone, the effecting of this cleaning and the removal of the stored hydrogen in the first evacuation zone by heating to promote the escape of the hydrogen, and effecting the deposition of metal from its vapor in a second evacuation zone at a temperature below that in the first zone and at which the deposited metal has a low diffusion rate into the substrate effective to produce adhesion with the interfacial alloy thickness restricted to not exceeding ten atom diameters.

A further object is a procedure in which a primary atmospheric cleaning accomplishes the storage of hydrogen within the substrate, followed by subjection of the heated substrate to evacuation whereby to withdraw the hydrogen and effect thereby a removal of surface oxygen, and followed in turn by the vacuum deposition of metal vapor upon the cleaned surface for a time and temperature period during which alloy formation is restricted.

A further object is a process of preparing a metal coated metal sheet by cleaning the surface of the metal sheet and storing hydrogen in the body of the sheet, with a subsequent heating and evacuation to cause the stored hydrogen to evolve and be effective for a surface preparation of the sheet, and with a final vacuum deposition of metal thereon at a lower temperature of insignificant diffusion effects between the metals.

Illustrative of the practice of this invention is:

Example 1

A succession of commercially clean sheets of blackplate steel about 0.009 inch thick were treated with perchloroethylene to effect de-greasing and removal of rolling lubricant: this was by dippings or by spray. They were next given a 30 second dip in 5 percent hydrochloric acid solution, rinsed in water, given a 5 second dip in 1% sodium hydroxide solution, rinsed in hot water, dried with a clean cloth towel and placed in a batch-type vacuum metallizing chamber connected to a pump system which could maintain a vacuum of ½ micron pressure in the sealed chamber. The substrates thus prepared had 1 to 3 parts per million of hydrogen in the surface layers thereof. The specimens were about

17 to 4 inches in size: each was bent into U-shape with 5 inch legs which were in vertical position in the chamber, with a 7 inch horizontal connection between them at the top. After evacuation of the chamber, electric current was caused to flow through the strip; and its temperature was raised to 650 degrees F. in about 2 minutes. The pressure when the heating of the specimen began was about ½ micron. During the heating, gas was evolved and the pressure rose to about one micron with the pump system in continuous operation. It was notable that the gas evolution became more rapid at a specimen temperature of about 600 degrees F., indicated by a pressure change to above one micron. When the pressure began to drop again with the temperature then at 650 degrees F., due to cessation of gas evolution from the specimen, the heating current was cut off and the specimen allowed to cool: during the cooling to about 400 degrees F., no further gas evolution was noted, and the pressure returned to the ½ micron capability of the pump system.

The chamber had vaporizing equipment in the form of two tungsten coils located about 5 inches below the horizontal portion of the specimen: the tungsten wires had a charge of aluminum. When the specimen reached the temperature of 400 degrees F., the coils were heated conductively by electricity so that the aluminum evaporated therefrom and was deposited on the specimen, largely on the inner surface thereof, that is, the surfaces facing the coils. A coating thickness of 30 micro-inches was obtained in about 20 seconds. The specimen was allowed to cool in the vacuum chamber to below 250 degrees F., e.g. to 200 degrees F.: the seal was broken, and the coated specimen removed.

The sheets were subjected to fabrication, i.e. bending of the aluminum coated product; and were employed as ends for containers. The containers were filled with non-sterile luncheon meat by standard procedure. Containers with ends of the same substrate, which had been coated with aluminum after like cleaning but with the vacuum deposition at less than 250° F., were likewise filled as controls. The cans were held at 40° F., and specimens examined at 3 days, 7 days, 2 weeks and 3 weeks. The ends coated at temperatures below 250° F., e.g. at room temperature, showed deterioration at 7 days and were progressively worse at 2 and 3 weeks, with 10 to 60% of the aluminum film adhering to the meat product and indicating separation of the coating from the base metal: sulfide staining was from slight to moderate. Comparably the ends coated at about 400° F. by the instant process showed excellent adhesion, no cleavage, and from a trace to very slight sulfide staining. When the ends were removed, and washed with carbon tetrachloride for removing adherent fat so the specimens could be photographed, the remainder of the aluminum coating came off from some of the metal which had been coated at below 250° F., and about 90% was detached from the other specimens of such metal with low temperature coatings. In comparison, the ends made from metal coated at 400° F., there was no detachment or appearance of inter-face corrosion: that is, the aluminum remained in place as a sacrificial protection anodically for the underlying steel plate.

The adhesion of a coating to a substrate involves the interface condition. Specimens of the various materials were examined by electron microscope as to this condition. The steel substrate was dissolved away by dilute nitric acid, thus leaving the coating film of aluminum; and this film was picked up on an electron microscope grid and examined by the electron microscope at enlargement of 25,500 times. The specimens coated at room temperature showed a fine grain structure, with grain sizes of 0.1 to 0.25 micron for one lot of specimens, with no sub-grain network apparent except for dislocation bands. Another lot had a grain size from 0.2 to 0.4 micron, with minor fine sub-grain networks: in this lot, there was difficulty in removing the steel substrate, and the electron microscope test revealed small dark spots from the incomplete removal. Comparably, the specimens coated at 400° F. showed a larger grain size, from 0.4 to 1.0 micron: a great amount of sub-grain structure was observed when the electron beam was first directed on the film, this structure shifting and disappearing during the observation due to the energy effect of the beam thereon. The larger grain size of the product of Example 1, compared to those with coatings at temperature below 250° F., demonstrates a difference of product by which the adhesion and absence of interface corrosion are exhibited under the critical luncheon meat test.

The several types of specimens showed ability to be fabricated, except for specimens where the vacuum deposition was made upon a substrate heated to 650° F. or above. In the latter, the diffusion was so rapid under conditions otherwise as in Example 1, that the brittle interfacial alloy developed to a detectable thickness, and caused cleavage and separation during fabrication. The ability of the material produced under the present invention to withstand the corrosion test is of great commercial significance.

The procedure is applicable with metal substrates having a body-centered cubic habit, for facilitating the bonding of later-applied metal coatings thereto: for examples, bodies of carbon irons and steels and alloyed irons and steels having a major matrix component of ferritic structure, including molybdenum and chromium steels. Likewise, the substrate need not be a sheet or web of such metal because separate articles, e.g., castings of the metal, can be treated as in Example 1 to store hydrogen therein, and then heated in vacuum for effecting the removal of surface oxygen-containing films by batch or conveyor operations. Further, coatings other than aluminum, including titanium, chromium and cadmium, may be vacuum deposited upon such substrates cleaned by this procedure, to attain adherent coatings.

In the practice according to Example 1, the rate of evolution of gas from the base plate was such that no blistering or increase of porosity was apparent, and the cleaned base plate received the deposited aluminum smoothly. The deposition of this coating at 400 degrees F. resulted in no detectable amount of interface alloy: fabrication did not result in cleavage, which occurs with films of the brittle alloy at thicknesses of about 10 atom diameters or over.

The invention is not restricted to the illustrative embodiment, and can be practiced in many ways within the scope of the appended claims.

What is claimed is:

1. The method of preparing an aluminum-coated steel substrate, which comprises degreasing the surface layer of the metal substrate with a cleaning liquid, treating the degreased surface for about 30 seconds with an acid solution having the approximate strength of a 5 weight percent hydrochloric acid solution whereby hydrogen is stored in said metal surface in an amount of from 1 to 3 parts per million, thereafter treating the surface layer of the steel substrate with an alkaline solution having the approximate strength of a 1 weight percent sodium hydroxide solution for about 5 seconds, rinsing the metal surface containing the hydrogen with water, drying the metal surface, placing the substrate in vacuo and therein heating to a temperature of 500 to 650 degrees F. whereby to cause the stored hydrogen to come forth from the substrate until evolution of hydrogen therefrom essentially ceases, cooling the substrate to a temperature below 500 degrees F. while preventing the access of oxidizing gases thereto, and thereafter effecting deposition of aluminum on the surface of the substrate under vacuum and at a sheet temperature of 250 to 500 degrees F., and thereafter cooling the coated substrate in vacuo to a tem-

perature below 200 degrees F. before a detectable inter-alloy film has been formed.

2. The method of claim 1, in which the substrate is heated in vacuo with constant pumping for removal of evolved gases until initial pressure increase ceases and the pressure falls essentially to the pressure prior to the heating.

3. The method of claim 1, in which the heating is to a temperature of 600 to 650° F., the vacuum deposition is conducted with the substrate at about 400° F., and the coated substrate is cooled to below 200° F. in about 2 minutes.

4. The method of preparing a substrate having a metal surface of a major portion of ferritic structure with a metal coating, which comprises degreasing the metal surface of the substrate with a cleaning liquid, treating the degreased surface for about 30 seconds with an acid solution having the approximate strength of a 5 weight percent hydrochloric acid solution whereby hydrogen is stored in said metal surface in an amount of from 1 to 3 parts per million, thereafter treating the metal surface of the substrate with an alkaline solution having the strength of a sodium hydroxide solution of about 1% concentration, rinsing the metal surface containing the hydrogen with water, drying the metal surface, placing the substrate in vacuo and therein heating to a temperature of 500 to 650° F. whereby to cause the stored hydrogen to come forth from the substrate until evolution of hydrogen therefrom essentially ceases, cooling the substrate to a temperature below 500° F. while preventing the access of oxidizing gases thereto, and thereafter effecting deposition of a metal selected from the group consisting of aluminum, titanium, chromium and cadmium on the surface of the substrate under vacuum and at a sheet temperature of 250 to 500° F., and thereafter cooling the coated substrate in vacuo to a temperature below 200° F. before a detectable inter-alloy film has been formed.

5. The method of claim 4, in which the heating is to a temperature of from 600 to 650° F., the vacuum deposition is conducted with the substrate at about 400° F., and the coated substrate is cooled to below 200° F. in about 2 minutes.

6. The method of preparing a chromium-coated steel substrate, which comprises degreasing the surface layer of the steel substrate with a cleaning liquid, treating the degreased surface with a hydrochloric acid solution of about 5% concentration for about 30 seconds whereby

hydrogen is stored in the surface layer of the steel substrate in an amount of from 1 to 3 parts per million, thereafter treating the surface with an alkaline solution having the approximate strength of a 1 weight percent sodium hydroxide solution for about 5 seconds, rinsing the metal surface containing the hydrogen with water, drying the metal surface, placing the substrate in vacuo and therein heating to a temperature of 500 to 650° F. whereby to cause the stored hydrogen to come forth from the substrate until evolution of hydrogen therefrom essentially ceases, cooling the substrate to a temperature below 500° F. while preventing the access of oxidizing gases thereto, and thereafter effecting deposition of chromium on the surface of the substrate under vacuum and at a sheet temperature of 250 to 500° F., and thereafter cooling the coated substrate in vacuo to a temperature below 200° F. before a detectable inter-alloy film has been formed.

7. The method of claim 6, in which the heating during the placing step is to a temperature of 600 to 650° F., the vacuum deposition is conducted with the substrate at about 400° F., and the coated substrate is cooled to below 200° F. in about 2 minutes.

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