This invention relates to coating and more particularly to vacuum deposition coating of the type wherein a metal such as aluminum is vaporized in a vacuum and the vapors thereof are condensed on a metallic base or surface.

A principal object of the present invention is to provide a vapor deposition coating process for producing thick, dense, strongly adherent metallic coatings on metallic surfaces which are susceptible to oxidation.

Another object of the invention is to provide a process of the above type whereby adherent metallic coatings having a thickness of at least 0.1 mil, and particularly between 1 and 5 mils can be obtained.

Still another object of the invention is to provide improved apparatus for accomplishing the above process.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others and the apparatus possessing the construction, combination of elements and arrangement of parts which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and the objects of the invention reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is a schematic, diagrammatic view of one form of apparatus embodying the present invention;

FIG. 2 is a schematic, diagrammatic view of another form of apparatus embodying the present invention;

FIG. 3 is a schematic, diagrammatic top view of still another form of apparatus; and

FIG. 4 is a schematic, diagrammatic view of still another form of apparatus embodying the present invention.

Heretofore vacuum deposited films of a metal, such as aluminum, upon a metallic surface such as iron have been very thin, generally having a thickness of less than about 0.1 mil. It is a well-known fact that such thin coatings are quite porous and as a result are not suitable for a great many applications. For example thin aluminum coatings do not in all cases adequately protect the coated metallic surface from corrosive influences and do not constitute good barriers against vapors and moisture. In order to obtain a coating of aluminum, for instance, which of itself possesses resistance to corrosion as well as protecting the metal surface or base from corrosion, it is necessary to vacuum deposit a dense, relatively heavy or thick aluminum coating. In the present invention strongly adherent dense metal coatings having a thickness above about 0.1 mil and particularly between about 1 and 5 mils can be provided.

The production of such thick, dense strongly adherent coatings is entirely unexpected in view of the fact that prior art workers have frequently reported that thick vacuum deposited films usually separated and flaked away from the surface being coated. It has been found that the non-adhesion of thick films has been in a great part due to inadequate cleaning of the metallic surface or base prior to coating. This is particularly true with regard to metallic surfaces which form thin surface oxide coatings, such as for example, aluminum, alloys thereof, iron, magnesium, zirconium, copper, and the like. In order to obtain a strong adherent bond between the thick coating and base, the oxide coating plus other surface contaminants must be removed as completely as possible prior to coating.

Many methods have been proposed for cleaning the surfaces of metals to be coated. However, these methods for the most part are not effective in removing surface oxides. For example, it is well known to wash or treat the surfaces to be coated with either water, bases, acids, an alcohol or other solvent for greases and oils, or combinations thereof. These methods are generally effective in removing only dirt, greases, oils, and the like. It is also known that improved adhesion can be achieved by subjecting the surfaces to be coated to elevated temperatures. This is effective in removing volatiles such as water from the surface. Moisture and monomolecular layers of oils and greases are also known to be removed by means of glow discharge or electron bombardment techniques. These means however do not remove oxide films or layers. Many of the above cleaning methods are conducted under atmospheric conditions, i.e., in an oxidizing environment. Thus, metals which are readily oxidizable, e.g., magnesium, even after being cleaned are subject to immediate reoxidation. It is therefore, necessary that the metallic surface to be coated be kept substantially oxide-free from the time of cleaning until the metal has been deposited thereon. In the present invention the readily oxidizable metal surface to be coated is cleaned of any oxide film under non-oxidizing conditions prior to coating.

The process of the present invention comprises removing substantially all of the oxide film from the metal surface to be coated, and thereafter, without subjecting the oxide-free metal surface to oxidizing conditions, vacuum depositing thereon a metallic coating having a thickness of at least 0.1 mil. In one preferred embodiment of the invention the metal surface to be coated is mechanically cleaned by means of abrasion. The mechanical abrasion can be achieved by grit or sandblasting, by means of rotating, flexible, contour-conforming abrasive flags, wire brush means, abrasive wheels, roughened surfaces such as sandpapers and the like. Included within the meaning of "mechanical abrasive means" are means for cutting or machining such as by milling the metal surface to be coated. This mechanical abrasion is conducted in a nonoxidizing atmosphere which can consist of a vacuum or protective gaseous atmosphere, such as nitrogen, argon, helium, carbon dioxide, and the like.

One form of apparatus for carrying out the above process comprises a vacuum tight chamber, means for positioning the metal surface or base to be coated within said chamber, means for providing said chamber with a non-oxidizing atmosphere, and means for mechanically cleaning the surface to be coated. The apparatus also in-
includes a source means for holding metal to be deposited on the mechanically cleaned metal surface, means for heating said source to melt and vaporize said metal, and means for imparting relative movement between said metal surface and said mechanical cleaning means and said source means to successfully clean and deposit on the metal surface a metal coating having a thickness of at least 0.1 mil. In one preferred embodiment of the invention, there is provided means for heating the cleaned metal surface prior to coating and means for imparting relative movement between said metal surface and said heating means.

The present invention will be described in connection with the vacuum deposition of thick dense films of aluminum and alloys thereof on various metal surfaces, it being understood that the invention is by no means limited to only aluminum coatings.

The process of the instant invention is set forth in the following non-limiting examples.

**Example I**

A 75-S alloy channel was mounted in a vacuum chamber on a rotatable arm so that it could be moved over a rotating wire brush and then positioned over two sources from which aluminum and zinc were respectively being vaporized. A 300 watt heater and a thermocouple were attached to the 75-S alloy channel for preheating and accurately measuring the substrate temperature. The temperature of the zinc source was measured by a thermocouple in contact with the crucible. The zinc evaporation temperature was held between 450-500°C during the coating operations.

Aluminum evaporation was controlled by monitoring the power input to the induction coil with a 6 kw, input to the source. This was equivalent to a temperature of approximately 1250°C for the aluminum.

The substrate was sand blasted and the system evacuated to 0.3 micron. The aluminum alloy was wire brushed for 30 seconds, then preheated to 375°F prior to coating. The substrate was then moved over the zinc and aluminum sources so as to have zinc and aluminum deposited thereon simultaneously. After exposure to the vapors for 2 minutes the coated substrate was then swung away and permitted to cool for a period of 5 minutes under vacuum.

The aluminum-zinc coating thickness was approximately 0.002 inch (2 mils). The adhesion was good and the coating appearance bright.

**Example II**

A ¾ inch thick sheet of rolled steel was sand blasted, cleaned with alcohol, etched lightly in sulfuric acid and mounted in a coating chamber on a rotatable arm. In order to preheat the sheet steel, a 280 watt heater was clamped onto the rear surface of the steel along with a thermocouple for measuring and monitoring the substrate temperature.

The rotating arm on which the steel was mounted permitted the steel sheet to be positioned first over a rapidly rotating conical wire brush driven by a ½ H.P. motor within the vacuum chamber. The steel strip was positioned so that part of the surface received abrasion from the wire brush and the remaining portion did not.

After wire brushing, the substrate was then rotated over an adjacent position where a carbon crucible was positioned. Aluminum was vaporized by inductively heating the crucible to approximately 1250°C. When the aluminum source at evaporation temperature prior to swinging the substrate over it, deposition of low energy aluminum onto the substrate is minimized.

The evaporation cycle involved evacuating the tank and contents to 0.09 micron, preheating the substrate to 260°C, wire brushing the substrate for 15 seconds, evaporating aluminum onto the substrate for 5 minutes, and cooling the coated substrate prior to venting the chamber. The coating thickness deposited was 0.002 inch (2.2 mils). Adhesion of the aluminum to the wire brushed area was excellent. The coating was bright in appearance and had a columnar structure. Adhesion of this thick coating on the unbrushed area was poor and could be readily peeled off. Thus much better bonding was obtained by use of heat and wire brushing under vacuum in comparison to heat alone.

In addition to aluminum, other coating metals such as copper, zinc, cadmium, silver, magnesium, alloys of aluminum, alloys of the aforementioned metals and the like can also be employed to give thick films. By thick films it is meant, vacuum deposited metal coatings having a thickness of at least 0.1 mil or greater. By the present invention, adherent coatings having a thickness of from 1 mil to about 5 mils can be obtained. Thus the thickness of the coating is dependent upon the time of exposure of the metal base to the coating vapors and the rate of metal evaporation, i.e., rate of metal vapor supplied to the coating zone. The rate of metal evaporation increases with increases of the temperature of the source. The rate of movement of the metal base determines the time of exposure of any unit area of surface to the metal vapors. By proper regulation of these factors thick coatings can be deposited on the metal base in an extremely short period of time. In addition to the deposition of a single metal film on an oxide free metal surface, a plurality of coatings of metals on the surface either simultaneously or successively. As shown in Example I, aluminum and zinc were both deposited simultaneously on the sheet consisting of the aluminum rich alloy, 75-S. The alloy 75-S (1.6% copper, 1.2% manganese, 2.5% magnesium, 5.6% zinc, 0.3% chromium, balance aluminum) can be extruded into aircraft wing panels, however, it does not possess the corrosion resistance of previous unnon-extrudable aluminum alloys. Corrosion resistance can be achieved by depositing thereon a thick, dense film of an aluminum-zinc alloy. As illustrated in Example I, aluminum and zinc were evaporated simultaneously in suitable proportions and deposited on the aluminum alloy base to form thereon an aluminum-zinc alloy. Aluminum-zinc alloys consisting of from 1 to 10% zinc and from 99 to 90% aluminum can be readily deposited.

The vacuum evaporation and deposition is preferably carried out at pressures below about 0.1 mm. Hg abs. and particularly below about 0.001 mm. Hg abs.

Referring now to FIG. 1 wherein 10 represents a vacuum coating device partitioned into two chambers 12 and 14. Each chamber is equipped with a pressure tight door for which hinges 16 are indicated. Within chamber 12 there is a suitably supported metal article 22 to be coated. Each of the chambers is maintained under a subatmospheric pressure, vacuum lines or conduits 18 and 20 leading to suitable pumping equipment (not shown) being provided for this purpose.

In chamber 12, the metal surface to be coated is contacted with mechanical abrading means 24, indicated here as revolving, flexible, contour-conforming abrasive flats. Either the metal article 22 or the mechanical abrading means or both can be moved so as to provide contact therebetween. The oxide-free surface is then preferably subjected to a vacuum pre-heat treatment by means of a heater 26 prior to entry into the coating chamber 14. The intensity and duration of the preheating depends upon the particular metal to be coated, the temperature which the metal is desired to possess during coating operations and the coating metal or metals. The preheating of the metal base is desirable since it enhances the formation of more adherent coatings. Chambers 12 and 14 are separated by a partition 28 and are provided with a vacuum tight passage 30 therethrough.

In chamber 14, the oxide-free metal surface is passed over source 32, heated by means of induction coil 34. The source serves to hold the metal to be melted and evaporated. A shield (not shown) can be positioned over
the source during the initial heat up period, this shield being removed when the proper high temperature of the metal vapors has been attained.

In the operation of FIG. 1, one or more preformed articles 22 such as wing sections are supported within chamber 12 such as by suitable suspension or conveying means. The source 32 is charged with a sufficient quantity of metal to be evaporated. Both chambers 12 and 14 are sealed from the atmosphere and each other and evacuated to a low free air pressure. The mechanical abrasing means 24 is then brought into contact with the metal surfaces to be cleaned. After the entire surface is thereby cleaned of oxide the article 22 is heated by means of an induction heating coil 26 and then advanced through vacuum seal 30 into the coating chamber 14 wherein it is subjected to the metal vapors emanating from crucible 32. After the desired thick coating has been deposited, the coating operations are stopped and the coated article removed from chamber 14 after the chamber has been brought to atmospheric pressure. While the coating operation is taking place, chamber 12 can be opened, and made ready for the next run.

Obviously, there can be variations of the above apparatus. For instance, instead of two chambers, a third chamber at the other side of chamber 14 can be employed for receiving a new vacuum article and thus provide for more continuous operations. Likewise, instead of multiple chambers, there can be provided but a single vacuum tight chamber such as illustrated in FIG. 2. Thus, there can be employed either a single chamber or a plurality of interconnected chambers.

In FIG. 2, whereas like numbers refer to like elements of FIG. 1, there is provided but a single chamber 36. The heating element 26 in this instance is illustrated as a resistance heater instead of an induction heater as shown in FIG. 1 although such can be used here equally well. In this embodiment, each of the articles to be coated 22, the mechanical abrasing means 24, the metal vapor source, or heating element or several of these can be suitably moved or advanced. For example, one method of operation is to have the article 22 remain stationary. In this case, the abrasing means 24 is moved over the article that is to be coated until it has been thoroughly cleaned. The abrasing means 24 is then moved away from the article and the article heated to a suitable high temperature. During the heating, the source 32 is advanced to a position (indicated by the dotted configuration) such that the vapor emanating therefrom will coat the oxide-free areas of the article. An alternative method of operation is to have the source 32 remain stationary and the article 22 suitably advanced as indicated by the dotted configuration.

Referring now to FIG. 3, which is a top view and wherein like numbers refer to like elements of FIG. 1 and other figures, there is provided a rotary jig 50 for holding a multitude of preformed articles 22, groove means 52 to enable cleaning and jiggling operations to be performed within chamber 12, and a means 54 for providing an inert or non-oxidizing atmosphere within chamber 12. After the jig 50 has been loaded with articles 22, it is moved to chamber 12 which is then sealed from the atmosphere and chamber 14 by means of vacuum seal 56. The air is evacuated from chamber 14 and chamber 12 and a protective or non-oxidizing atmosphere such as nitrogen is charged to chamber 12 from a suitable supply means 54. The operator inserts his hands through the glove ports (not shown) into the gloves 52. Each article is individually removed from the jig and each cleaned by mechanical abrasing means 58 here illustrated as a rotary wire brush or abrasive wheel. After each article 22 is cleaned it is placed on the jig. When the cleaning operations are completed, the non-oxidizing atmosphere is evacuated while at the same time, the heating means 26 is energized and the jig rotated so as to heat the articles 22 thereon. The jig 50 is then advanced through the seal 56 into the coating chamber 14. The source 32 is here shown as an elongated crucible supplied with suitable resistance heating means 34. The source, charged with metal, is heated to a suitably high temperature to vaporize the metal therein. The jig is rotated during coating operations so that each article will be completely exposed to the metal vapors emanating from the source 32.

The process is also applicable to the continuous treatment of wire, sheet, or strip in addition to preformed articles or lengths of material as shown in FIG. 4. Within compartment 12 there is suitably supported a feed roll 22 of the metal to be coated, e.g., steel articles or iron (often referred to as "tin plate"). The course of the sheet through the compartments 12, 13 and 14 is determined by rollers or idlers 70. Compartment 13 as 12 and 14 is provided with suitable pumping means (not shown) attached to vacuum conduits 19. Included within chamber 13 is a cutting means 72 for cutting off the coated sheet and a collecting means 74 for receiving the severed sections of the coated sheet. The operation of this apparatus is much the same as described above with the exception that it is carried out on a continuous basis and that the coated sheet at the end of its movement is severed into sections of suitable size by cutting means 72, which sections are deposited in collecting means 74.

Obviously there can be variations of the apparatus described in the above four figures. For example, the embodiment shown in FIG. 3 can also be employed in the other apparatus illustrated. Additionally, the metal articles can be introduced and removed from the chambers into the atmosphere through suitable vacuum seals so as to provide for continuous operations.

With regard to the mechanical abrasing means, it can be rotating, flexible, contour-conforming abrasion flaps, wire brush means, rotating wire brush means, suitably supported abrasive papers, abrasive wheels, sand blasting cutters and the like. Where conditions dictate, a plurality of such abrasive means can be employed, for example, where the metal to be coated is of such size as to require more than one mechanical abrasing means or where both surfaces or the metal are to be cleaned and coated.

When preformed articles with contours are to be coated, the flexible contour-conforming abrasive flaps are preferably employed. When preformed articles or lengths are to be coated, they can be moved or advanced into contact with the mechanical abrasing means or the abrasing means can be moved to the material or both can be movable. Likewise, when either preformed or lengths are employed, they can be advanced past the source of metal vapors or vice versa. Prior to coating, the cleaned surface to be coated is preferably heated to a suitably high temperature. This heating can be accomplished by means of induction heating, resistance heating or the like. The heating means can be moved to the material to be coated or it can be stationary and the material advanced to it or both means can be moved.

The source of metal vapors employed can be one of the many well known types which provides for high vaporization rates over long periods of operation. The source which can be of the crucible type can be heated by induction, resistance or electron bombardment, the heating means and the source must be such as to permit of high metal vaporization rates under the pressure existing in the vacuum coating chamber. For aluminum, the temperature of the source and vapors is maintained between about 1200° C. and 1600° C. Where crucible or cup type sources are employed, means can be provided therewith to feed additional metal thereto during coating operations. Where several coatings of a metal or metals or an alloy are desired on the metal base, or where the size thereof is large, a plurality of sources can be employed. Each of the sources carries therein a charge of the metal to be vaporized and the sources are so ar-
ranged or disposed with respect to the area of the surface to be coated and with respect to the contour thereof that the metal vapors are condensed on the metal base in a uniform manner. When a thick coating of a plurality of coatings is desired, the metal base can be successively advanced over several sources of metal vapors. Thus, as the metal base passes over one source, there is condensed thereon one metal. Passage over the next source deposits the same metal or a different metal on the first metal to make up a multi-layer coating. Alloys can also be deposited on the metal surfaces by evaporating two or more metals simultaneously from two or more sources and allowing the metal vapors to condense simultaneously upon the surface to be coated. Likewise, where it is desired to coat both surfaces or sides, two or more sources strategically positioned can be used.

Although not shown, before the metal surface to be coated is introduced into the chamber it is preferably subjected to the usual pre-cleaning operations for removing grease, oils, and other material of high vapor pressure. Likewise, the coated metal surface can be subjected to a post-heating in an oxidizing atmosphere such as air. The post heating treatment of the coated metal is not essential to the attainment of good adhesion. However, to enhance maximum adhesion of the coating, the coated metal can be heated to elevated temperatures for a suitable period of time.

Since certain changes can be made in the above process and apparatus without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of forming thick, dense, strongly adherent metal coatings on oxidizable metal surfaces which comprises mechanically abrading in a non-oxidizing atmosphere the metal surface to be coated to remove substantially all of the oxide film thereon, and thereafter without subjecting the oxide-free metal surface to oxidizing conditions, vacuum depositing thereon a metallic coating having a thickness of at least 0.1 mil.

2. The process of forming thick, dense, strongly adherent metal coatings on oxidizable metal surfaces which comprises mechanically abrading in a non-oxidizing atmosphere the metal surface to be coated to remove substantially all of the oxide film thereon, and thereafter without subjecting the oxide-free metal surface to oxidizing conditions, vacuum depositing thereon a metallic coating having a thickness of at least 0.1 mil.

3. The process of forming thick, dense, strongly adherent metal coatings on oxidizable metal surfaces which comprises mechanically abrading in a non-oxidizing atmosphere the metal surface to be coated to remove substantially all of the oxide film thereon, and thereafter without subjecting the oxide-free metal surface to oxidizing conditions, vacuum depositing thereon a metallic coating having a thickness of at least 0.1 mil, and then heating said coated metal surface to improve the adhesion of the coating.

4. The process of forming thick, dense, strongly adherent metal coatings on iron, steel and the like which comprises mechanically abrading in a non-oxidizing atmosphere the iron surface to be coated to remove substantially all of the iron oxides present thereon, thereafter without subjecting the oxide-free surface to oxidizing conditions, vacuum depositing thereon an aluminum coating having a thickness of at least 0.1 mil, said deposition being carried out at a pressure below about 0.1 mm. Hg abs.

5. The process of forming thick, dense strongly adherent aluminum-zinc alloy coatings on metal surfaces consisting of alloys rich in aluminum which comprises mechanically abrading in a non-oxidizing atmosphere the aluminum alloy surface to be coated to remove substantially all of the oxides present thereon, thereafter withoutsubjecting the oxide-free surface to oxidizing conditions, simultaneously depositing thereon aluminum and zinc to form an alloy coating having a thickness of at least 0.1 mil., said deposition of aluminum and zinc being carried out at a pressure below about 0.1 mm. Hg abs.

6. The process of claim 5 wherein the aluminum alloy surface to be coated has the nominal composition of 1.6 percent copper, 2.5 percent magnesium, 5.6 percent zinc, balance aluminum and the aluminum-zinc alloy deposited thereon consisting of from 1 to 10 percent zinc and 99 to 90 percent aluminum.

7. The process of forming thick, dense, strongly adherent aluminum coatings on magnesium surfaces which comprises mechanically abrading in a non-oxidizing atmosphere the magnesium surface to be coated to remove substantially all magnesium oxides present thereon, and thereafter without subjecting the oxide-free surface to oxidizing conditions, depositing thereon an aluminum coating having a thickness of at least 0.1 mil., said deposition being carried out at a pressure below about 0.1 mm. Hg abs.

8. An apparatus for producing thick, dense, strongly adherent metal coatings on oxidizable metal surfaces which comprises a vacuum tight chamber, means for positioning the metal surface to be coated within said chamber, means for providing said chamber with a non-oxidizing atmosphere, source means for holding metal to be deposited on the metal surface, means for heating said source means to melt and vaporize said metal therein, means for mechanically abrading the surface to be coated, while said surface is in said chamber, means for imparting relative movement between said metal surface and said mechanical abrading means, and means for imparting relative movement between said metal surface and said source to expose the abraded metal surface to the metal vapors to obtain a deposit of metal thereon having a thickness of at least 0.1 mil.

9. An apparatus for producing thick, dense, strongly adherent metal coatings on oxidizable metal surfaces which comprises a vacuum tight chamber, means for positioning the metal surface to be coated within said chamber, means for providing said chamber with a non-oxidizing atmosphere, source means for holding metal to be deposited on the metal surface, means for heating said source means to melt and vaporize said metal therein, means for mechanically abrading the surface to be coated, while said surface is in said chamber, means for heating the abraded metal surface, means for imparting relative movement between said metal surface and said mechanical abrading means, said heating means and said source to expose the abraded metal surface to the metal vapors to obtain a deposit of metal thereon having a thickness of at least 0.1 mil.

10. The apparatus of claim 9 wherein said mechanical abrading means comprises wire brush means.

11. The apparatus of claim 9 wherein said mechanical abrading means comprises abrasive wheels.

12. The apparatus of claim 9 wherein said mechanical abrading means comprises abrasive paper and cloths.

13. The apparatus of claim 9 wherein said mechanical abrading means comprises cutting means.

14. The apparatus of claim 9 wherein said mechanical abrading means comprises abrasive blasting means.

15. An apparatus for producing thick, dense, strongly adherent metal coatings on oxidizable metal surfaces which comprises a vacuum tight chamber with at least two chambers therein, a vacuum sealed passage between said two chambers, means for positioning the metal surface within said first chamber, means for providing first chamber with a non-oxidizing atmosphere, means for mechanically abrading the metal surface to be coated within said first chamber, means for evacuating said second chamber to a low free air pressure, source means for
holding metal to be deposited on the metal surface, and
means for heating said source means to melt and vaporize
said metal therein, within said second chamber, means
for imparting relative movement between said metal sur-
face and said mechanical abrading means to abraid the
metal surface, and means for advancing the abraded
metal surface through said vacuum passage and into said
second chamber to expose said abraded metal surface
to the metal vapors from said source to obtain a deposit
of metal thereon having a thickness of at least 0.1 mil,
and means for heating the abraded metal surface posi-
tioned between said mechanical abrading means and said
source means.

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