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PRODUCTION OF DUCTILE FOIL

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This invention relates generally to a process for the manufacture of dense, ductile metallic foil, and more particularly it relates to the manufacture of dense, ductile metallic foil utilizing a vacuum evaporation process. This application is a continuation-in-part of application Serial No. 283,532 filed May 27, 1963, and now abandoned.

It is generally known that metallic foils may be manufactured by depositing a thin metallic coating on the surface of a substrate, and thereafter stripping the coating from the surface of the substrate in the form of a thin continuous foil sheet. As used herein, the term "metal" includes pure metals and metal alloys, including alloys of metals and non-metals. Foil, as distinguished from strip or plate, may be defined as a sheet of material having a thickness of not more than about 6 mils.

Metallic foil may be manufactured by spraying droplets of molten metal on the surface of a substrate and allowing the metal to slidify in the form of a thin coating which is then stripped from the surface of the substrate in the form of a foil. This process is generally referred to as "flame spraying." Metallic foil may also be manufactured by decomposing a gaseous metallic compound, for example, a metallic carbonyl compound, and depositing the liberated metal on the surface of a substrate in the form of a coating which is then removed from the substrate in the form of a foil. Flame spraying and decomposition processes may be utilized to form foils of a limited number of metals, and foils produced by flame spraying and decomposition processes are generally ductile. A "ductile" foil, for purposes of this invention, may be defined as a foil which may be folded over and creased twice along the same line without fracturing or breaking.

However, flame spraying and decomposition processes are generally limited and cannot be employed to form foils of many metals and alloys. For example, the decomposition process cannot be employed to form foils of metals which do not form a readily decomposable gaseous compound, and cannot be employed to form foils of alloys. Flame spraying processes are not desirable for the manufacture of foils of high melting point metals and alloys since at the temperature necessary to flame spray the metal, the substrate may be impaired or destroyed. Further, flame spraying and decomposition processes do not generally provide metallic foils at sufficiently high rates to be economical in large scale operations. In addition, it is difficut to provide foils which have a high density and which are substantially free from pin holes and other imperfections in the foil when using flame spraying and decomposition processes.

Metallic foils may also be manufactured by vacuum evaporation processes, for example, as disclosed in United States Patents Nos. 3,181,209 and 3,183,563. Metallic foil manufactured by vacuum evaporation processes are substantially free from pin holes and other imperfections, and the foil may be manufactured at a desirable rate. Vacuum evaporation processes are particularly attractive in that foil may be formed from substantially all metals and alloys, in substantially any desired thickness. The freedom from pinholes and imperfections makes foils which are manufactured employing vacuum vaporization techniques particularly desirable for uses such as electrical capacitors where the physical properties of the foil are important. Foils suitable for such operations, however, must have good ductility, that is, the foil must be able to be manipulated and bent during manufacture of the capacitor.

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Heretofore, vacuum evaporation processes for the manufacture of foil were somewhat complicated by the fact that it was not generally understood how to obtain ductile foil. While it was possible to obtain ductile foils of some metals and alloys using vacuum evaporation processes, other metals and alloys could not be formed into ductile foil using conventional vacuum evaporation techniques.

It is a principal object of the present invention to provide a method for the manufacture of metallic foil by a vacuum evaporation process. A further object is to provide a method for the manufacture of dense, ductile metallic foil employing a vacuum evaporation process which may be utilized to form ductile foils of metals which have heretofore not been able to be manufactured in ductile form utilizing vacuum evaporation processes.

Other objects and advantages of the present invention will become apparent from a study of the following detailed description.

Very generally, the present invention is directed to a method of manufacturing ductile metallic foil by vacuum evaporation which includes vaporizing a coating material in a vacuum and condensing the vaporized coating material upon a substrate within the vacuum while maintaining the substrate at a minimum temperature of at least about 25 percent of the melting point of the coating material in degrees Kelvin, and thereafter removing the coating material from the substrate in the form of a thin self-supporting foil sheet. The minimum temperature at which the substrate is maintained in order to obtain a ductile foil falls within the range of between about 25 percent and about 50 percent of the melting point of the coating material in degrees Kelvin, depending upon the particular coating material.

It has been discovered that, in a vacuum evaporation process, when the substrate is maintained at a minimum temperature that is at least 25 percent of the melting point of the foil material in degrees Kelvin, the foil obtained when the deposited coating material is removed from the substrate will have good ductility, that is, the foil will be able to withstand folding and creasing along the same line at least twice without breaking or fracturing. The minimum temperature at which the substrate is maintained in order to provide a foil product of good ductility may be as low as 25 percent of the melting point of the coating material in degrees Kelvin, or may be as high as 50 percent of the melting point of the coating material in degrees Kelvin. The precise minimum substrate temperature will be different for each metal, but for most metals will be between about 30 percent and about 40 percent of the melting point in degrees Kelvin. The upper limit of the substrate temperature is not critical, and so long as the substrate is not adversely affected by the temperature, a ductile foil may be obtained at substrate temperatures up to the melting point of the coating material. It is not generally necessary to exceed about 90 percent of the melting point of the coating material, particularly for those metals which have relatively high melting points, and it is usually preferred to maintain the substrate at a substrate temperature slightly above the minimum substrate temperature, for example, between about 25 degrees Kelvin and about 300 degrees Kelvin above the minimum substrate temperature.

The precise reason why foil obtained by a vacuum evaporation process wherein the substrate is maintained above the minimum substrate temperature has desired ductility is not altogether understood. It is generally believed, but it is not intended that the present invention be limited thereto, that metals and alloys vaporized from the surface of a melt and deposited on a substrate have several lattice stages, depending on the temperature of the surface upon which they are deposited, in which the arrangement of atoms within the lattice is slightly different. It is thought that at substrate temperatures below the described minimum substrate temperature the lattice structure of the deposited metal is strained to some degree, thereby causing the foil to be brittle. This may be readily demonstrated by vaporizing and depositing a metal on the surface of a substrate maintained at a temperature below the desired minimum of 25 percent of the melting point of the coating material. In such instances, the foil may be difficult to remove from the surface of the substrate and, in many instances, disintegrates or flakes apart upon removal. If the foil is such that it can be removed from the substrate in the form of a sheet, the sheet will fracture or break when folded over and creased once or twice. Such a foil has but limited utility and is not sufficiently ductile for most uses.

However, in accordance with the present invention, when the substrate is maintained at a minimum temperature falling within the range of 25 percent and 50 percent of the melting point of the coating material in degrees Kelvin, or higher, the lattice structure of the deposited metal is believed to be more stable than the lattice structure of the metal deposited at lower temperatures and a ductile foil may be readily obtained.

A dense ductile copper foil may be obtained utilizing a minimum substrate temperature of about 25 percent of the melting point of copper in degrees Kelvin, while dense ductile aluminum foil may be obtained at a minimum substrate temperature of about 45 percent of the melting point of aluminum in degrees Kelvin. At the present time, it is not understood why ductile copper foil may be obtained at substrate temperatures as low as about 25 percent of the melting point of copper in degrees Kelvin, whereas aluminum should be condensed at a substrate temperature of at least about 45 percent of the melting point of aluminum in degree Kelvin in order to obtain a ductile aluminum foil. There does not appear to be any correlation between the boiling point, melting point, or molecular structure of the various metals and the minimum substrate temperature necessary to obtain ductile foil. With the exception of copper and aluminum and their alloys, ductile foils of substantially all remaining metals and alloys may be obtained at a minimum substrate temperature within the range of between about 30 percent and about 40 percent of the melting point of the metal in degrees Kelvin.

The method of the invention may be carried out in a conventional vacuum evaporation chamber. The coating material from which it is desired to form a dense ductile foil is placed within a crucible or container within the vacuum chamber and is heated to a temperature at which the coating material vaporizes at an appreciable rate. The vacuum chamber is desirably maintained at a pressure below about one millitorr, preferably below about .1 millitorr in order to provide for a suitable flow rate of vaporized coating material. The vacuum chamber may be evacuated utilizing conventional vacuum diffusion pumps, and the coating material may be vaporized by a suitable heat source. One form of heat source that is particularly suited for use in vacuum evaporation processes is an electron beam gun, such as is more fully described in United States Letters Patent No. 3,177,535.

A substrate is positioned above the crucible containing the coating material and the vaporized coating material is deposited upon the surface of the substrate in the form of a thin uniform coating. For batch operations the substrate may be stationary, and for continuous operation the substrate may be in the form of an endless belt, or the like, which is moved slowly over the open mouth of the crucible. It is also possible to form the substrate in the form of a cylindrical drum which may be mounted in the wall of the vacuum chamber as disclosed in Patent No. 3,183,563. Any suitable material may be employed as a substrate. A desired substrate is one that has a nonporous smooth surface, for example, stainless steel. The coating material is then removed from the surface of the substrate in the form of a foil. It is generally desirable to apply a parting agent to the substrate prior to deposition of the coating material thereon in order to insure that the foil may be readily removed from the surface of the substrate. Suitable parting agents which may be used include NaCl, Al_2O_3, Teflon, polyethylene and other metal salts and oxides.

The substrate may be heated to above the minimum temperature desired in order to obtain ductile foil by a suitable heat source positioned adjacent thereto. It is possible to employ induction heating adjacent the back surface of the substrate, or the surface of the substrate may be exposed to a radiant heater or an electron beam gun at a point just prior to the point at which the substrate enters the vapor cloud of foil material generated above the surface of the crucible. In some instances it may also be desirable to provide means for cooling the substrate should the temperature of the substrate exceed the desired amount.

The foil may be removed from the surface of the substrate within the vacuum chamber, or the substrate containing the coating material deposited thereon may be passed out of the vacuum chamber and the foil removed from the substrate exterior of the vacuum chamber. The foil may be removed from the substrate by pulling the foil under tension from the surface of the substrate. This may be accomplished by means of a takeup roll or drum angularly spaced from the substrate about which the foil is wound, and which is rotated at a slightly greater linear velocity than the velocity of the substrate, causing the foil to be lifted tangentially from the surface of the substrate. It is also contemplated to utilize a doctor blade or the like in order to aid in the separation of the foil from the surface of the substrate.

In a particular embodiment of the invention, it is contemplated to remove copper foil from the surface of the substrate without utilizing any separating means, that is, in the absence of a parting agent, and without using a doctor blade or the like. It has been discovered that copper foil may be removed from a substrate without using any separating means when the substrate temperature is maintained below about 505 degrees K. Since 25 percent of the melting point of copper, 339 degrees K., the minimum substrate temperature required to obtain ductile copper foil, is below 505 degrees K., it is possible to obtain ductile copper foil without the necessity of utilizing a parting agent. The ductile copper foil may be stripped from the substrate using the described takeup roll.

The present invention may be employed to form dense ductile foil of substantially all metals which may be deposited in the form of a thin coating upon the surface of a substrate, and which are stable at ambient conditions. An exemplatory list of materials which may be employed within the scope of the invention, but not considered to be limiting upon the described invention, includes: copper, aluminum, nickel, lead, chromium, iron, magnesium, manganese, molybdenum, silver, gold, platinum, tin, tungsten, zinc, niobium, tantalum, titanium, zirconium, vanadium and alloys and mixtures thereof. Common alloys which may be formed into dense ductile foils in accordance with the present invention include brass, stainless steel, aluminum-silicon alloys, aluminum-copper alloys, titanium-aluminum-vanadium alloys, and titanium-aluminum-tin alloys. It is apparent that other alloys and metals may be employed within the scope of the invention.

The coating material is heated to a suitable elevated temperature at which an appreciable vaporization of the foil material occurs, while at the same time the substrate is maintained above the minimum temperature necessary to attain a dense ductile foil. The temperature of the substrate is measured and controlled by suitable temperature sensing devices, such as thermocouples. However, it is difficult to obtain accurate temperature readings of the substrate, particularly where the substrate is moving and where the substrate and the coating material are heated by means of electron beam guns. The temperatures set forth hereinafter as being examples of the practice of the present invention are not considered to be accurate to greater than plus or minus 25 degrees K. Accordingly, in some instances, it may be possible to deposit a coating material upon the surface of the substrate at temperatures slightly less than, for example, 25 to 50 degrees K., than the temperature recited with respect to the respective coating materials. This is particularly true where the temperature is indicated as being a threshold temperature below which the coatings are not considered to have sufficient ductility for the purpose of the invention.

Example I

Pure copper, which has a melting point of 1356 degrees K. was heated by electron bombardment from an electron beam gun within an evacuated chamber maintained at a pressure of 0.1 millitorr. The copper was heated to a temperature of about 1900 degrees K., at which temperature an appreciable vaporization of the copper took place. An endless stainless steel substrate was positioned above the pool of molten copper and was slowly moved through the copper vapors to deposit the copper vapors upon the surface of the substrate in the form of a thin uniform coating. The temperature of the stainless steel substrate was maintained between about 408 degrees K. and 428 degrees K.

The deposited copper coating was removed from the surface of the stainless steel substrate without using any separating means and without employing a parting agent on the surface of the substrate. The thickness of the deposited coating was varied by varying the vaporization rate of the copper, in order to provide coatings having a thickness of from 1 mil to 100 mils. The copper foil obtained upon removal of the copper coating from the substrate was analyzed and found to have all of the properties of an annealed foil, including a greater ductility than would normally be expected. In this connection, the copper foil had sufficient ductility so that it would be creased and folded along the same fold line eight times before failure occurred. The density of the foil was substantially greater than that normally encountered in vacuum vaporization operations for the manufacture of copper foil.

Example II

A copper foil was prepared in accordance with Example I except that the temperature of the substrate was reduced to 435 degrees K. The foil obtained exhibited good ductility. The temperature of the substrate was then reduced to about 325 degrees K., at which temperature the foil had substantially decreased ductility and failed when folded and creased twice.

Copper foil was also prepared in accordance with Example I utilizing substrate temperatures of 700 degrees K. and 800 degrees K., and in each instance the copper foil product was considered to have a high density and excellent ductility. However when the copper foil was deposited on the substrate maintained above a temperature of 505 degrees K. it was necessary to utilize an Al_2O_3 parting agent in order to insure that the copper foil coating could be readily removed from the surface of the stainless steel substrate.

Example III

Substantially pure aluminum, which has a melting point of 933 degrees K. was vaporized and deposited upon a substrate utilizing the apparatus of Example I. The aluminum was heated to a temperature of 2000 degrees K in order to obtain a satisfactory vaporization rate, and the temperature of the stainless steel substrate was varied in order to determine the appropriate minimum substrate temperature in order to attain good ductility of the aluminum foil. The substrate temperature was incrementally increased from ambient, i.e., 300 degrees K., until a substrate temperature was reached at which the aluminum foil was considered to be ductile. It was determined that the substrate should be maintained at a minimum temperature of about 450 degrees K. in order to attain good ductility of the aluminum foil or approximately 47 percent of the melting point of aluminum in degrees K.

Example IV

A series of aluminum alloys were vaporized in accordance with the preceding examples and deposited upon the surface of a stainless steel substrate. An aluminum alloy containing 7 percent silicon, an alloy containing 4 percent copper, and an alloy containing 3 percent silicon and 2 percent copper were vaporized and deposited as a uniform coating on the surface of the substrate. In each instance, it was determined that when the substrate was maintained at a minimum temperature of about 45 percent of the melting point of the respective alloy, the alloy foils removed from the substrate exhibited good ductility.

Example V

A nickel foil was prepared by vaporizing nickel, which has a melting point of 1728 degrees K., in a vacuum chamber in accordance with the preceding examples. The nickel was heated to a temperature of 2300 degrees K. and the substrate was maintained at a temperature of 710 degrees K. The deposited nickel coating was removed from the surface of the substrate in the form of a foil which exhibited superior ductility when compared to nickel foils prepared in accordance with previously known vacuum evaporation processes. Further experiments showed that nickel foils prepared at minimum substrate temperatures below about 700 degrees K. did not have good ductility and it was generally determined that the minimum substrate temperature in order to obtain nickel foils of good ductility was about 41 percent of the melting point of nickel in degrees K.

Example VI

A pure lead foil was obtained by vaporizing lead, which has a melting point of 600 degrees K. and depositing the lead on the surface of a substrate at ambient conditions. The lead foil was extremely ductile and had good density. The minimum substrate temperature necessary in order to obtain ductile lead foils was not determined inasmuch as ambient temperatures are higher than 50 percent of the melting point of lead in degrees Kelvin.

Example VII

A common high brass, containing 65 percent copper and 35 percent zinc was vaporized by heating to a temperature of 1400 degrees K. and depositing the brass vapors on the surface of a substrate maintained at a temperature of 425 degrees K. The brass had a melting point of about 1205 degrees K. No attempt was made to determine the minimum substrate temperature in order to obtain ductile brass coatings inasmuch as the selected temperature, which was 35 percent of the melting point of the brass, provided brass foils having superior ductility.

Example VIII

Niobium, which has a melting point of 2770 degrees K. was vaporized in an evacuated chamber and deposited on a surface of a stainless steel substrate. The niobium was heated to a temperature of 3000 degrees K. and the substrate was maintained at a temperature of 925 degrees K. The niobium foil obtained by removing the niobium coating from the surface of the substrate exhibited good ductility and had a good density. Experiments showed that when the niobium was deposited upon the surface of a substrate which was maintained at a temperature below about 925 degrees K. the foil obtained did not have as good ductility as those foils obtained when the substrate temperature was maintained above 925 degrees K.

Accordingly, niobium foils are preferably prepared with a substrate temperature of at least about 33 percent of the melting point of niobium.

Example IX

A stainless steel foil was prepared by vaporizing an 18 percent chromium, 8 percent nickel stainless steel at a temperature of about 2200 degrees K. and depositing the stainless steel vapors on a substrate maintained at a temperature of about 800 degrees K. The stainless steel foil was of good density and had excellent ductility. No attempt was made to establish a minimum substrate temperature for obtaining ductile stainless steel.

Example X

A tantalum foil was prepared in accordance with the preceding examples by vaporizing tantalum, which has a melting point of 3300 degrees K. and depositing the tantalum upon a substrate maintained at a temperature of 1100 degrees K., or about 33 percent of the melting point of tantalum. A dense and ductile tantalum foil was prepared. No attempt was made to determine the minimum substrate temperature in order to obtain a ductile tantalum coating.

Example XI

A titanium foil was prepared in accordance with the preceding examples by vaporizing titanium, which has a melting point of 1900 degrees K., and depositing the titanium vapors on a surface of a substrate maintained at a temperature of about 920 degrees K. or approximately 47 percent of the melting point of titanium. A dense highly ductile titanium foil was obtained. No attempt was made to determine the minimum substrate temperature necessary to obtain ductile titanium foils.

Additionally, titanium alloys containing 6 percent aluminum and 4 percent vanadium, and 5 percent aluminum and 2½ percent tin, were vaporized and deposited on the surface of a substrate maintained at about 40 percent of the melting point of the respective alloy compositions. In each instance, the titanium alloy foil obtained exhibited a superior density and had good ductility.

Foils of chromium, iron, magnesium, manganese, molybdenum, platinum, gold, silver, tin, tungsten and zinc were prepared by vaporizing the respective metals in an evacuated chamber in accordance with the preceding examples and depositing the vaporized metals upon the surface of a substrate maintained at a temperature which varied between about 30 percent and about 40 percent of the melting point of the vaporized metal. In each case, the foil obtained exhibited good ductility and had increased density.

It can be seen that a method has been provided whereby the guess-work and empirical determinations have been substantially eliminated from the vacuum evaporation process of manufacturing ductile foil. Although certain features of the invention have been set forth with particularity to describe the invention, various alternatives and embodiments within the skill of the art are contemplated.

Various of the features of the invention are set forth in the following claims.

What is claimed is:

1. A process for the manufacture of dense ductile metallic foil by vacuum evaporation comprising, vaporizing a metal bearing coating material within a vacuum, condensing at least a portion of the metallic content of the vaporized coating material upon a substrate within the vacuum, maintaining the temperature of the substrate above a minimum substrate temperature of at least about 25 percent of the melting point of the condensed mate-

rial in degrees Kelvin, and removing the condensed material from the substrate in the form of a dense ductile metallic foil.

2. A process for the manufacture of dense ductile metallic foil by vacuum evaporation comprising, vaporizing a metal bearing coating material within a vacuum, condensing at least a portion of the metallic content of the vaporized coating material upon a substrate within the vacuum, maintaining the temperature of the substrate above a minimum substrate temperature of between about 25 percent and about 50 percent of the melting point of the condensed material in degrees Kelvin, and removing the condensed material from the substrate in the form of a dense ductile metallic foil.

3. A process for the manufacture of dense ductile metallic foil by vacuum evaporation comprising, vaporizing a metal bearing coating material within a vacuum, condensing at least a portion of the metallic content of the vaporized coating material upon a substrate within the vacuum, maintaining the temperature of the substrate between a minimum substrate temperature of between about 25 percent and about 50 percent of the melting point of the coating material in degrees Kelvin and a maximum temperature of the melting point of the condensed material in degrees Kelvin, and removing the condensed material from the substrate in the form of a dense ductile metallic foil.

4. A process for the manufacture of dense ductile metallic foil by vacuum evaporation comprising, vaporizing a metal bearing coating material within a vacuum, condensing at least a portion of the metallic content of the vaporized coating material upon a substrate within the vacuum, maintaining the temperature of the substrate above a minimum substrate temperature of between about 30 and about 40 percent of the melting point of the condensed material in degrees Kelvin, and removing the condensed material from the substrate in the form of a dense ductile metallic foil.

5. A process for the manufacture of dense ductile copper and copper base alloy foil by vacuum evaporation comprising, vaporizing a coating material selected from copper and copper base alloys within a vacuum, condensing the vaporized coating material upon a substrate within the vacuum, maintaining the temperature of the substrate above a minimum substrate temperature of about 339 degrees Kelvin, and removing the coating material from the substrate in the form of a dense ductile foil.

6. A process for the manufacture of dense ductile aluminum and aluminum base alloy foil by vacuum evaporation comprising, vaporizing a coating material selected from aluminum and aluminum base alloys within a vacuum, condensing the vaporized coating material upon a substrate within the vacuum, maintaining the temperature of the substrate above a minimum substrate temperature of about 420 degrees Kelvin, and removing the coating material from the substrate in the form of a dense ductile foil.

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