United States Patent Office 3,131,049 Patented Apr. 28, 1964

3,131,049

PRODUCTION OF CHROMIUM LAMELLA ON A MOLTEN SUPPORTING VEHICLE

Bruno R. Miccioli, North Tonawanda, N.Y., assignor to Union Carbide Corporation, a corporation of New York

No Drawing. Filed Jan. 24, 1963, Ser. No. 253,756
7 Claims. (Cl. 75—.5)

This invention relates to chromium lamella in general and to the methods of production of the lamella.

Lamella of many metals are commercially known and extensively used in a multitude of applications.

Metal lamella of varied thickness and area are used in wrapping, electronic apparatus, paints, corrosion protection, light reflecting pigments and abrasives.

Chromium lamella have been unavailable for commercial use because of the inability to produce the lamella with a small cross sectional area and the desired physical properties required by the electronics, paint, etc., industries. This results from the characteristic hexagonal close packed crystal structure of chromium which permits a minimum absorption of distortional energy before the lattice ruptures.

Foils of many metals are mechanically produced by processes essentially based on rolling of fillets and ingots or swagging on accurately machined surfaces. In all of these mechanical processes the decrease in thickness of the element is accompanied by a storing of distortional energy which manifests itself as stresses within the material. Chromium is not readily amenable to treatment by mechanical means because the slight ability of the metal to absorb distortional stress without fracture is completely exploited before the cross-section is reduced to a dimension small enough for commercial value.

Prior to the inception of the present invention, chromium lamella could not be manufactured in thickness of less than 0.015 inch. This minimum thickness was accompanied by brittleness and consequently the surface area of the lamella was very small.

It is an object of the present invention to provide thin chromium lamella having a thickness of less than 5 mils and of large surface area.

It is further an object of the present invention to provide thin powered chromium lamella having thickness less than 2 mils.

It is another object of this invention to provide a process whereby chromium lamella are produced.

The above-mentioned objects are achieved by introducing a chromium metallo-organic compound which is in a gaseous state into intimate contact with a molten supporting vehicle for a time sufficient to cause thermal decomposition of the chromium metallo-organic compound, the molten support being maintained at a temperature sufficient to cause thermal decomposition of the metallo-organic compound and being chemically inert and not wetting with regard to the chromium metal which nucleates and deposits on the molten support, and subsequently removing the chromium metal which is in lamella form from the molten support.

A typical metallo-organic compound suitable to the invention process is chromium dicumene, although any compound which decomposes freeing chromium in the elemental state is amendable to the process. Other preferred metallo-organic compounds fufilling the chemical and physical requirements are chromium acetylacetonate

(volatization temperature 100° C. and decomposition temperature 350° C.), chromium carbonyl (volatization temperature 100° C. and decomposition temperature 140° C.). Chromium dicumene is preferable with respect to the acetylacetonate and the carbonyl because: the chromium acetylacetonate, being originally bonded to oxygen, tends to form oxy-compound impurities and in the carbonyl, the chromium being originally bonded to carbon, tends to precipitate chromium carbide impurities. Contamination of the chromium hexagonal close packed latice by carbon, oxygen, or nitrogen tends to decrease the metal's inherent inability to withstand distortional stress thereby rendering the metal slightly more brittle. Additional chromium metallo-organic compounds which are amendable to the process of the invention include dicyclopentadienyl chromium, dibenzene chromium, tricyclopentadienyl chromium hexamine, and cyclopentadienyl chromium carbonyl hydride.

Supporting vehicles employed in the process should have low melting points, boiling points higher than the decomposition temperature of the particular chromium metallo-organic compound which is being employed, should not alloy with or react with the elemental chromium which is deposited, nor wet it in any way. Examples of the preferred supporting vehicles are pure indium; Wood's metal which consists of 50 weight percent bismuth, 25 weight percent lead, 12.5 weight percent tin, and 12.5 weight percent cadmium, and Rose metal which consists of 50 weight percent bismuth, 27.1 weight percent lead, and 22.9 weight percent tin. Additional supporting vehicles which may be employed include mercury and tricresyl phosphate.

A procedure embodying the proces of this invention and illustrating the method of obtaining novel forms of chromium is conducted as follows:

The chromium metallo-organic compound (chromium dicumene, for example) is heated in one vessel to a temperature sufficient to volatize said compound (approximately 120° C. for chromium dicumene) and transported in the gaseous state, either alone or by means of an inert gas carrier such as argon, to the entrance orifice of a second vessel in which a suitable supporting vehicle (Wood's metal, for example) is maintained in a molten condition at a temperature at least equivalent to the thermal decomposition temperature of the metallo-organic compound (approximately 300° C. in the case of chromium dicumene) but below the boiling point of the molten supporting vehicle.

Beginning from the above-mentioned entrance orifice, two alternate techniques may be employed each one of which results in a different novel chromium product.

Alternate (1).—The gaseous metallo-organic chromium compound is permitted to enter the vessel containing the molten supporting vehicle. At the interface between the smooth, mirror-like surface of the molten vehicle and the thermally decomposing gaseous molecules of the metallo-organic compound, the liberated elemental chromium nucleates and deposits as a thin lamella and the dicumene and inert gases remaining are permitted to leave the vessel to be recovered elsewhere. When a sufficiently thick foil of chromium metal having a large surface area has deposited on the vehicles surface, cooling and solidification of the entire mass is accomplished to stabilize and retain its physical appearance. The deposited layer of chromium may, subsequently, be separated from the solidi-

fied mass by remelting the supporting vehicle in a suitable inert liquid (for example, boiling toluene), thus recovering the uncontaminated material for further use and withdrawing the chromium metal in the form of a thin uniform foil. With proper care, the chromium foil may be withdrawn directly from the molten supporting vehicle without cooling and subsequent remelting.

Alternate (2).—The gaseous metallo-organic chromium compound is conducted from the entrance orifice of the vessel containing the molten supporting vehicle to an exit within the molten vehicle and thermally decomposing the gaseous molecules of the metallo-organic compound therein, thus liberating elemental chromium which nucleates and deposits as powdered lamella. Introduction of the gaseous metallo-organic compound under pressure produces a finer lamellar powder. After sufficient decomposition the vehicle is cooled and caused to solidify. Subsequent remelting in a liquid (for example, boiling toluene which is inert to the solid intermediate) permits recovery of the product and the uncontaminated vehicle.

The adaptation of the present process to continuous deposition and recovery of lamella is feasibile when common engineering knowledge is employed and is well within the realm of a person skilled in the art.

Following are examples of the novel processes and products.

Example I

Approximately 100 ml. of chromium dicumene were heated to 120° C. in a vessel, and the gaseous compound was transported by means of an argon stream into a separate vessel in which about 1000 grams of Wood's metal was maintained in the molten state at about 300° C. The gaseous molecules of chromium dicumene were forced to impinge, without substantial mixing, on the surface of the molten supporting vehicle, whereon the chromium dicumene thermally decomposed, leaving a thin foil of chromium metal on the vehicle surface. Decomposition of the metallo-organic compound in other parts of the vessel other than the proximity of the supporting vehicle surface was prevented by maintaining the upper surface of the vessel below 300° C. by means of external cooling. The dicumene component of the decomposed chromium dicumene compound was collected in a separate trap. When a sufficient and uniform layer of chromium metal was deposited on the alloy, the mass was cooled, solidified, removed and immersed in boiling toluene, thus remelting the supporting vehicle and recovering the foil of chromium metal. The foil was found to average about 0.002 inch in thickness and approximately 98% pure chromium. The surface area was approximately 3 square inches.

Example II

Approximately 100 ml. of chromium dicumene were heated to 120° C., in a vessel, and the gaseous compound was transported by means of an argon stream into a second vessel, in which about 1000 grams of Wood's metal was maintained in the molten metal state at about 300° C. The gaseous molecules of chromium dicumene were forced into the molten Wood's metal by means of a pipe, where the chromium dicumene thermally decomposed, leaving a multitude of thin chromium flakes dispersed in the molten metal. The dicumene component of the decomposed chromium dicumene was allowed to bubble through the molten Wood's metal together with the carrier gas and was collected in a separate trap. The agitation caused by the escaping gases further improved the formation and dispersion of chromium lamella flakes in the Wood's metal. When the chromium dicumene decomposition was terminated, the vehicle and lamella were cooled, thus solidifying the entire mass, which, after removal, was immersed in boiling toluene, thus remelting the Wood's metal and recovering the metallic chromium flakes. In this manner, powdered chromium lamella of less than 1 mil in thickness and substantially stress free were produced.

From the description of the invention, it can readily be seen that chromium foil and powdered chromium lamella of various areas, minute thicknesses and essentially free of internal stress can be produced by this novel process.

This application is a continuation-in-part of U.S. Serial No. 852,949, filed November 16, 1959, and now abandoned.

What is claimed is:

1. A process for the production of chromium lamella comprising introducing a chromium metallo-organic compound which is in the gaseous state into intimate contact with a molten supporting vehicle, and said molten supporting vehicle being characterized as possessing a boiling point higher than the decomposition temperature of said chromium metallo-organic compound and chemically inert and non-wetting to chromium metal; and maintaining said supporting vehicle at a temperature sufficient to cause thermal decomposition of said gaseous chromium metallo-organic compound; and maintaining said intimate contact between said molten supporting vehicle and said chromium metallo-organic compound for a time sufficient to cause thermal decomposition of said chromium metallo-organic compound, whereby said thermal decomposition of said chromium metallo-organic compound produces elemental chromium metal which nucleates to form a lamella on said molten supporting vehicle; and removing said lamella.

2. A process for producing chromium foil by the thermal decomposition of a chromium metallo-organic compound which is in the gaseous state as delineated in claim 1, wherein said compound is brought into intimate contact with the surface of said molten supporting vehicle and whereby said thermal decomposition produces elemental chromium which nucleates and deposits as a foil on said molten supporting vehicle.

3. A process for producing lamellar chromium powder by the thermal decomposition of a chromium metallo-organic compound which is in the gaseous state as delineated in claim 1, wherein said compound is brought into intimate contact with the body of said molten supporting vehicle from within and whereby said thermal decomposition produces elemental chromium which nucleates and disperses throughout the molten supporting vehicle as said lamellar chromium powder.

4. A process for the production of chromium foil as delineated in claim 2 wherein said metallo-organic compound is chosen from the group consisting of chromium dicumene, chromium acetylacetone, chromium carbonyl, dicyclopentadienyl chromium, dibenzene chromium, tricyclopentadienyl chromium hexamine, and cyclopentadienyl chromium carbonyl hydride, and said molten supporting vehicle is chosen from the group consisting of Wood's metal, Rose metal, pure indium, mercury and tricresyl phosphate.

5. A process for the production of lamellar chromium powder as delineated in claim 3 wherein said metallo-organic compound is chosen from the group consisting of chromium dicumene, chromium acetylacetone, chromium carbonyl, dicyclopentadienyl chromium, dibenzene chromium, tricyclopentadienyl chromium hexamine, and cyclopentadienyl chromium carbonyl hydride, and said molten supporting vehicle is chosen from the group consisting of Wood's metal, Rose metal, pure indium, mercury and tricresyl phosphate.

6. A process for the production of chromium foil as delineated in claim 4 wherein said metallo-organic compound is chromium dicumene, and said molten supporting vehicle is Wood's metal.

7. A process for the production of lamellar chromium powder as delineated in claim 5 wherein said metallo-organic compound is chromium dicumene, and said molten supporting vehicle is Wood's metal.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 24,821	Stauffer	May 3, 1960
1,759,661	Muller et al.	May 20, 1930
2,729,190	Pawlyk	Jan. 3, 1956
2,732,292	Jordan	Jan. 24, 1956
2,807,532	Hahn	Sept. 24, 1957
2,816,826	Brennan	Dec. 17, 1957
2,834,690	Marvin	May 13, 1958
2,913,333	Eaton et al.	Nov. 17, 1959

FOREIGN PATENTS

683,459	Great Britain	Nov. 26, 1952

OTHER REFERENCES

Newton: Introduction to Metallurgy, 2nd Edition, John Wiley & Sons, New York, 1948, page 355.

Handbook of Chemistry and Physics, 41st Edition, Chemical Rubber Publishing Company, Cleveland, Ohio; page 344.