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ALUMINUM PLATING

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Fig. 1

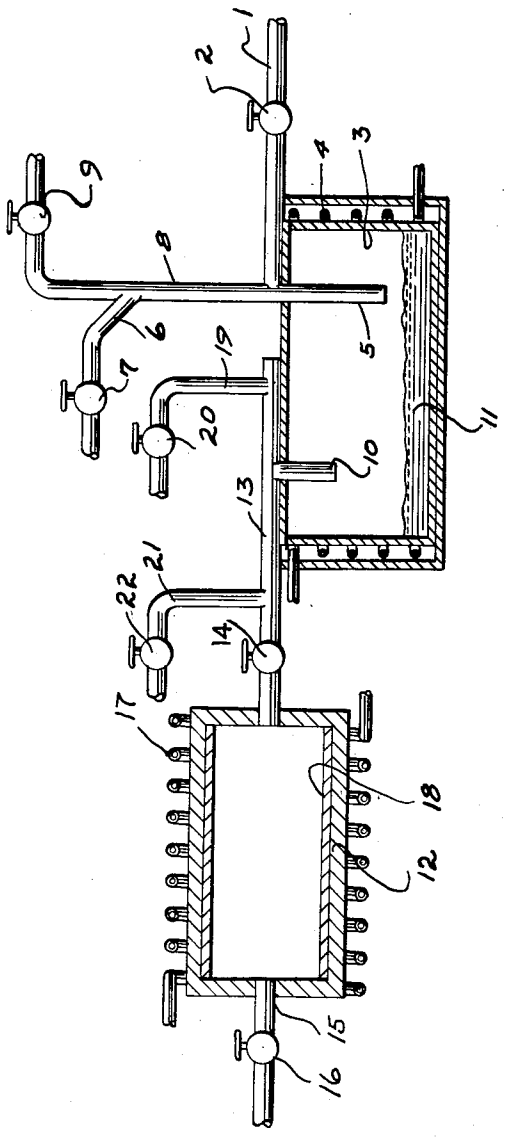
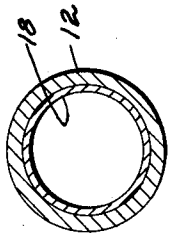


Fig. 2



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ALUMINUM PLATING

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15 Claims. (Cl. 117—107)

This invention relates to the deposition of aluminum from volatilizable, heat decomposable aluminum bearing compounds.

It has previously been suggested to utilize aluminum compounds in the gaseous state to procure deposits of aluminum metal and coatings of aluminum. Difficulties encountered have included the necessity for using relatively high temperatures to effect the decomposition of the aluminum compound; purity of deposit and thickness of deposit have also been limited and much effort has been expended to overcome these drawbacks.

It has now been found that a reactive additive olefinic gas may be introduced into the plating operation with the aluminum containing compound to provide for decomposition of the compound at lower temperatures and to materially improve film continuity in the case of aluminum coatings on articles of steel, copper and the like.

In a specific application isobutylene is provided as a reactive gas with aluminum tri-isobutyl as the plating gas. The function of the isobutylene is to react with hydrides of aluminum which tend to form when aluminum tri-isobutyl breaks down. The hydrides, which form either during the plating process itself or in storage of the aluminum tri-isobutyl include aluminum hydride, aluminum di-isobutyl hydride, and aluminum monobutyl hydride. The reaction of the isobutylene with these hydrides tends to reproduce the tri-isobutyl in accordance with the following exemplary reaction:

$$2(C_4H_8)+Al(C_4H_9)H_2=(C_4H_9)_3Al$$

Not only are impurities removed by the addition reactions but the concentration of the desired plating gas is actually increased.

Other unsaturated compounds useful as reactive additive gases with aluminum tri-isobutyl are: ethylene, propylene, and 3-methyl butene-1, for optimum plating—propylene gives directly comparable deposits to isobutylene. Unsymmetrical or symmetrical compounds, such as alpha butylene and beta butylene, are useful.

Films produced using these olefinic gas additives showed a refinement in the grain size of the aluminum deposit. This is believed to be due to the microscopic dissolution of the aluminum surface according to the equation previously cited.

Other aluminum containing compounds useful in conjunction with a reactive additive olefinic gas are: aluminum tri-isopropyl, aluminum tri-isoamyl, aluminum tri-isohexyl, and mixed aluminum alkyls such as diethyl isopropyl aluminum, propyl di-isobutyl aluminum, ethyl propyl isobutyl aluminum.

In general the object on which the aluminum is to be deposited in the practice of the invention need not be heated above 700° F. in order to attain adequate deposition of aluminum; preferably the object is at about 500° F. This is in contrast to processes wherein the olefin is not employed and temperatures well above 700° F. and frequently above 1000° F. are required to secure adequate plating rates.

The invention will be more fully understood by reference to the following detailed description and accompanying drawing wherein:

Figure 1 is a schematic view illustrating an apparatus arrangement useful in the practice of the invention; and

Figure 2 is a cross section of a tube metallized in accordance with the invention.

In the practice of the invention the substrate to be plated is suitably de-oxidized, cleaned and preferably degreased prior to commencing an operation; also, as noted hereinafter, the apparatus itself is evacuated by purging with an inert gas.

Referring to the drawing the numeral 1 designates a conduit having a valve 2 and through which the metallizing gas is fed to the vaporizer 3. In the present instance the metallizing gas is commercial aluminum tri-isobutyl and contains approximately 10 percent of aluminum tri-isobutyl hydride as used.

The vaporizer 3 is heated by means of an electrical coil 4 at a temperature of approximately 475° F. This metallizing gas enters the vaporizer in liquid form through a depending conduit 5. Simultaneously argon gas is introduced through conduit 6 having a valve 7 and is directed toward the vaporizer 3. As the argon passes toward the vaporizer it mixes with isobutylene gas passing through the conduit 8 having valve 9. The argon utilized is substantially oxygen free, testing less than 0.0005 percent oxygen by volume.

Within the vaporizer the argon and isobutylene mix with the aluminum tri-isobutyl which vaporizes and passes out through orifice 10. Aluminum tri-isobutyl hydride is a liquid and that portion of the liquid which does not react with the isobutylene remains in the bottom of the vaporizer as indicated at 11. The isobutylene, however, serves to react with the tri-isobutyl hydride to produce tri-isobutyl, as already noted. The argon with the aluminum tri-isobutyl passes outwardly through the orifice 10 towards the article to be plated, designated at 12.

As shown in Figure 1 this article is a tube of copper which is sealed at one end to a conduit 13 having a valve 14. At its other extremity the tube 12 is sealed to an exhaust conduit 15 having a valve 16. The aluminum tri-isobutyl flows through open valve 14 to the copper tube, which is itself maintained at a temperature of about 525° F. by any suitable heating means such as resistance heater 17. The aluminum tri-isobutyl decomposes, depositing aluminum on the interior of the copper tube as indicated at 18. Normally a thickness of 1¼ mil is readily achieved over the interior of the copper tube (3/16" I.D.) within 3 hours.

The gas flow rates at 70° F. and atmospheric pressure to achieve this deposition are about:

100 cc. per mintue of argon,
85 cc. per minute of isobutylene, and
42.7 cc. per minute of tri-isobutyl aluminum;

this isobutyl aluminum flow is equivalent to about 0.42

cc. per minute of the liquid tri-isobutyl. Suitably the carrier gas (argon) and the isobutylene are heated prior to their introduction to the system to a temperature of 200–220° F.

Gases of decomposition pass outwardly through valve 16 of the conduit 15 together with undecomposed aluminum tri-isobutyl.

For purposes of complete operation a by-pass conduit 9 provided with valve 20 is located in the conduit 14. For the purposes of initial purging the apparatus of air and moisture, prior to metallizing, an intermediate conduit 21, provided with a valve 22, is located in the conduit 14. Thus to purge the apparatus, through the vaporizer, it is merely necessary to close valve 14 and to open valves 22 and 7, and to pass a gas such as argon through the equipment. When the vaporizer and the lines leading thereto are sufficiently clear, valves 14 and 16 may be opened, with valves 20 and 22 closed, to completely purge the apparatus by permitting argon flow through valve 14, the copper substrate 12 and valve 16 also.

Suitably the operation of metallizing is effected at atmospheric pressure, although pressures as low as 5 mm. of mercury may be employed. As may be noted from Figure 2 the aluminum coating on the interior of the tube 12 is substantially uniform.

Other gases may be used as the carrier in the gas plating process, for example, nitrogen and helium.

By way of further example propylene may be substituted for the isobutylene and nitrogen for the argon under the same conditions as set forth hereinbefore. The nitrogen employed has less than 0.0005 percent oxygen by volume.

While liquids such as cyclopentadiene have characteristics rendering them useful as substitutes for isobutylene and propylene, they are less convenient to handle, requiring vaporization for admixing with the decomposable aluminum compound in the vaporizer.

It will be understood that this invention is susceptible to modification in order to adapt it to different usages and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

What is claimed is:

1. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: intermixing in the gaseous state a heat decomposable aluminum containing compound which tends to form hydrides of aluminum and an unsaturated compound capable of reacting with such hydrides to form the heat decomposable aluminum compound.

2. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: intermixing in the gaseous state a heat decomposable aluminum alkyl with an olefin.

3. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: intermixing in the gaseous state a heat decomposable aluminum alkyl and an alpha olefin.

4. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: the step of intermixing in the gaseous state a heat decomposable aluminum alkyl and isobutylene.

5. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable alumnium alkyl compound; the improvement which comprises: the step of intermixing in the gaseous state a heat decomposable aluminum alkyl and propylene.

6. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: the step of intermixing in the gaseous state a heat decomposable aluminum alkyl and ethylene.

7. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: the step of intermixing in the gaseous state a heat decomposable aluminum alkyl and 3 methyl-butene-1.

8. In an aluminum deposition process, wherein a substrate is heated in the presence of a heat decomposable aluminum alkyl compound; the improvement which comprises: the step of intermixing in the gaseous state a heat decomposable aluminum alkyl and cyclopentadiene.

9. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature sufficient to decompose a gaseous aluminum alkyl, contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and a gaseous olefin capable of reacting with such alkyl to form a heat decomposable compound to thereby occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

10. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature sufficient to decompose a gaseous aluminum alkyl, contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and isobutylene with a carrier gas to occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

11. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature sufficient to decompose a gaseous aluminum alkyl, contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and propylene with a carrier gas to occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

12. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature sufficient to decompose a gaseous aluminum alkyl, contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and isobutylene with argon to occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

13. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature sufficient to decompose a gaseous aluminum alkyl, contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and propylene with nitrogen to occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

14. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature of between about 500° F. to about 700° F., contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and a gaseous olefin capable of reacting with such alkyl to form a heat de-

composable compound to thereby occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

15. A process for the deposition of aluminum which comprises the steps of heating an object on which the aluminum is to be deposited in an evacuated atmosphere to a temperature of about 525° F., contacting the heated object with a gas flow containing a heat decomposable aluminum alkyl and a gaseous olefin capable of reacting with such alkyl to form a heat decomposable compound

to thereby occasion deposition of the aluminum on the heated object, continuing the gas flow to the heated object to build up a continuous film of aluminum on the object, and thereafter removing the object from the gas flow.

References Cited in the file of this patent

UNITED STATES PATENTS

2,619,433	Davis et al.	Nov. 25, 1952
2,847,320	Buffoff	Aug. 12, 1958