Nov. 29, 1960 P. ALEXANDER 2,962,538

VAPORIZING HEATER FOR VACUUM DEPOSITION AND METHOD OF EMPLOYING THE SAME

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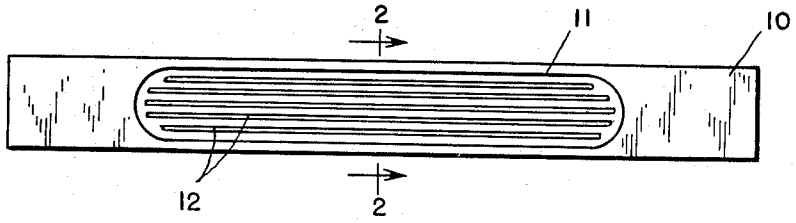

FIG. 1.

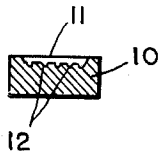

FIG. 2.

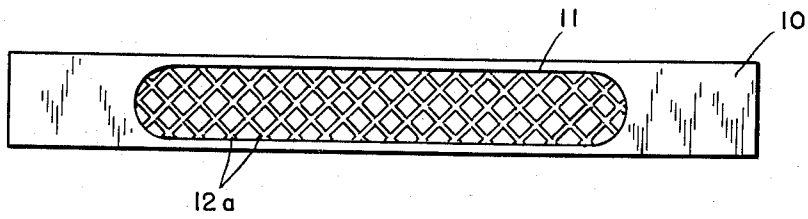

FIG. 3.

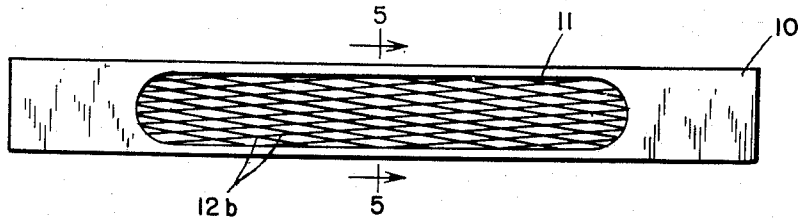

FIG. 4.

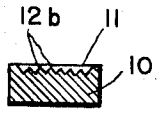

FIG. 5.

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VAPORIZING HEATER FOR VACUUM DEPOSITION AND METHOD OF EMPLOYING THE SAME

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10 Claims. (Cl. 13—25)

This invention relates to the vaporization of high boiling metals and deposition of the metal vapor upon a substrate, and is particularly concerned with a vaporizing element or heater for such purpose, and methods of making and using the same.

It has been proposed in the art to employ a body of electrically conductive material, such as carbon or metals or metal compounds, which is refractory and remains solid at the temperature of operation, to heat the body by its electrical resistance to current flow through it, and to bring the deposit metal to the body so that the deposit metal is melted and spreads out on the body; with employment of a body temperature at which the metal will evaporate. Such work is customarily done in vacuum to secure the uninhibited spreading of the metal vapor, to reduce the temperature for vaporization, and to protect the deposit metal against oxidation.

For regular vaporization of the molten metal, it is desirable that such metal be present on the surface of the heater as a continuously replenished thin film, and that it be protected against contamination by materials such as the carbide formed when molten aluminum acts upon carbon. Hence carbon is not a satisfactory material for contact with the molten deposit materials; and surface coatings of protective material have been employed, or a non-carbon element is provided. For example, materials such as tungsten metal, tungsten carbide, and tungsten silicide, zirconium metal and zirconium carbide, titanium metal and titanium carbide have been employed as protective coatings on carbon as set out in my prior patents and patent applications: these give a far longer operational life than unprotected carbon. It has also been proposed to employ refractory borides and nitrides: and these have been found satisfactory in many cases. However, such bodies, or bodies having such surfaces, change in their behavior during operation. At first, the deposit metal does not form an extended regular film upon the bodies, but later the spreading occurs more regularly: so that there is an initial operational stage of conditioning the element, and if one of several vaporizer elements has to be replaced, it must be conditioned regardless of the operational status of the other elements. This initial behavior is more pronounced when the surface, e.g. of a titanium boride element, is smooth. Titanium boride is highly resistant to molten aluminum; and when a smooth freshly prepared surface thereof receives molten aluminum, it is not readily wetted even at temperatures as high as 1500 degrees C. When an element having an effective surface of about 1400 square millimeters has been operated for about an hour, and about 150 to 200 grams of aluminum evaporated from it, the heater receives the aluminum more smoothly and a thin film is formed because the molten aluminum will then spread over the surface. This preconditioning effect appears permanent; as the element may be cooled and reheated as an incident of a continued operation, without requiring a further conditioning at each re-heating.

The failure to produce a regular film by the spreading of the deposit metal is disadvantageous, because the molten metal may collect in beads or pools which are deep and in which a high temperature gradient or differential exists between the bottom, which is at the temperature of the vaporizer element, and the top, which is being cooled by the loss of the latent heat of evaporation of the metal. When this differential is high, so that the vapor pressure of the aluminum adjacent the element is greater than the hydrostatic pressure of the metal above it, bubbles of vapor form at the bottom of the pool or bead and rise rapidly to the surface, often exploding and projecting globules of metal instead of exclusively issuing as a vapor of molecular particles. If such globules reach the substrate to be coated, they damage the coating and often pierce holes in a plastic film or paper present as the substrate. In addition, the pre-conditioning does not proceed regularly, as the presence of molten aluminum in the illustrative case is necessary in contact with the area: hence the preconditioning effect first occurs at the area which is receiving the replenishment supply, and then spreads over the rest of surface. Therewith etching or corrosion during the life of the element is irregular and a substantially uniform film thickness is not maintained.

Such pre-forming or pre-conditioning of a vaporizer element may be performed in the absence of a substrate. When a coating operation is being started with the vaporizer elements all fresh, a substrate may be introduced; but care must be taken to feed the deposit metal very slowly, so that the molten metal does not exceed one millimeter in depth at any point and to keep the temperature of the heater correspondingly low: therewith the rate of evaporation is very low, and the rate of feed of a continuous substrate must be reduced until the specified thickness of deposit is effected because unless this is done, the substrate is excessively heated and may be damaged. and the production is uneconomical.

Wettability of the vaporizer element surface by the molten deposit material may be effected, as stated above, by employing a suitable refractory substance as a coating or covering layer; but the property of wettability appears connected with the property of solubility: that is, when the coating material is relatively soluble, the molten material spreads readily; whereas if the coating material has a vanishingly small solubility, the molten material fails to spread on a smooth surface thereof. For example, tungsten metal can be employed, but in course of time, it is dissolved in molten aluminum and the resultant liquid demands a higher operating temperature. As the molten deposit metal evaporates from the mixture, the tungsten remains behind at the vaporization surface, and at the margins it is deposited upon the body of the element beyond the area orginally occupied, so that the coating appears to creep out over the vaporizer surface and toward its edges. Since the precipitated metal is wettable, it thus acts as a wick to draw the molten aluminum toward and over the edges of the vaporizer. The vaporized metal establishes a zone over the vaporization area, with the particles tending to move in directions normal to the surface unit at which the evaporation occurred. Thus, aluminum evaporated from a fresh heater element can be directed so that most of it encounters the substrate; but after the creepage has occurred, aluminum being evaporated from upright edges will not be directed toward an overlying substrate, and efficiency is lost.

It has been found that vaporizer elements may be made of substances, which are refractory and otherwise satisfactory for employment except for not being wetted by the molten deposit material when the same is first applied thereto, by providing the area from which the metal is to be evaporated with a number of narrow and shallow grooves. These can form parallel lines placed longitudinally in the top surface or they can cross each

other forming a diamond pattern on the surface. The molten metal spreads over the surface along these lines apparently in capillary fashion due to the action of physical forces at the interface regions, and forms a thin film over all the intended operating surface without contracting into comparatively deep pools or beads of limited area.

A further feature is the provision of a vaporizing element having a deep body with shallow ribs on its top, to provide a shallow basin for the molten metal with thick sections of material at its bottom and sides, whereby the heating is maintained at a regular level without excessive local chilling due to presence of thin sections of the body adjacent molten metal which is being cooled by evaporation therefrom.

Illustrative forms of vaporizer elements, according to this invention, are shown on the accompanying drawings, in which:

Fig. 1 is a top view of such an element;

Fig. 2 is a cross-section substantially on line **2—2** of Fig. 1;

Figs. 3 and 4 are top views of modified structures;

Fig. 5 is an enlarged section on line **5—5** of Fig. 4.

The vaporizer elements shown in Figs. 1 to 5 may be made of refractory materials such as the carbides, borides, nitrides and silicides of the transitional metals belonging to groups IV, V and VI of the periodic system of the elements. Titanium diboride, TiB_2, is a specific example. Such elements may be made by molding under high pressure; and the bodies then subjected to a pre-sintering heating. At this stage the bodies are machinable and can be given the desired final shapes.

In the structure of Fig. 1, the general body **10** has a depression **11** in its upper surface. The bottom or floor of the depression has multiple spaced grooves **12** therein; which are exaggerated in size in the drawing, for clearness.

Illustratively the body **10** may have a length of 150 millimeters, a width of 18 millimeters, and a thickness of 7 millimeters, with the depression **11** having its floor one millimeter below the general top plane of the element. The depression thus has a depth of one millimeter with a width of 14 millimeters, and a length of 100 millimeters, the ends being semi-circles of 7 millimeter radius. The grooves **12** in this illustrative form are for example 0.010 to 0.050 inch wide and 0.005 to 0.060 inch deep, with flat crests therebetween providing the floor level and having widths of 0.020 to 0.100 inch, for example each groove can be about 0.020 inch wide, 0.010 inch wide and with flat crests 0.0625 inch wide. In such a structure, the depression **11** has a floor at a depth less than one-fourth, being about one-seventh in the illustrated form, of the vertical thickness of the body mass beneath it; and the minimum horizontal dimension of the upstanding portions around the depression **11** is twice the depth of the depression itself.

A number of the grooves should be present to facilitate distribution of the metal to be deposited over the length and width of the depression floor, from the point at which it is momentarily being melted during its delivery into the depression; noting that the preferred practice is to employ a wire which is being continually advanced with its end brought into the depression and there melted, the end of the wire being traversed back and forth along the length of the depression **11**.

The grooves need not be in the nature of hairline cracks; and it is preferred to have each groove not less than 0.010 inch wide and not less than 0.005 inch deep. Therewith, each groove should coordinate in width with the intervening and marginal crest regions; and it is preferred in practice to have the width of each groove not greater than one-tenth of the width of the depression floor, and its depth not greater than one-tenth of the vertical distance from the depression floor to the bottom surface of the element body. Therewith, the spacing of the grooves, from center to center in Figs. 1 and 2, should not be less than one-fifteenth nor more than one-fourth of the width of the depression, the specific number of grooves being determined by such selected spacing and by having the individual grooves within the stated ranges of related width and depth. The grooves can terminate within the top area, e.g. the floor in the illustrative showing.

The grooves may be cut in the body while it is in the pre-sintered state; and the final sintering then accomplished. It is also feasible to provide the distributing grooves during the initial pressure molding by providing a forming punch which is a matrix for the intended top conformation of the vaporizer body, e.g. by having ribs on the punch for forming the grooves in the mass being pressed. The mass is then heated to produce the final sintered structure.

When a fresh element of this type is heated in a vacuum chamber, and aluminum wire fed so its end maintains contact with the vaporizing element, the aluminum melts and spreads readily along the surface without forming local comparatively deep pools or beads; and the element may be operated from the beginning, without requiring pre-conditioning, under operating conditions and without exhibition of "spitting" or "sputtering" of globules. A further advantage of such an element is that it maintains during its entire operational life a better and more even spreading of the aluminum film than an element without grooves. This fact again results in a longer useful life of the element, because the corrosion is more evenly distributed over the whole vaporizing surface.

In Fig. 1, the grooves **12** are shown as parallel and extending along the length of the vaporizing surface of the heater element.

In Fig. 3, the grooves **12*a*** are shown as parallel lines in two groups which intersect in a diamond pattern, the grooves being exaggerated in width and spacing, for clearness.

In Fig. 4, the grooves **12*b*** in each of two groups are shown closer together than in Fig. 1, and at a smaller angle between the groups than in Fig. 2, so that the bottom of the depression **11** is forming of a number of long needle-like elevations having sharp upper edges, as shown in Fig. 5, adjacent the intersections. In Fig. 4, the grooves are shown as single lines.

The refractory carbide, boride, nitride and silicide material are often referred to as "hard metals," and have been used as abrasives and cutting tools because of their hardness.

In each example, a thin film of volatilizable metal is being exhibited in a shallow trough above a thick body of resistively heated material. In heating by electrical resistance, the same amperage is present at each successive transverse cross-section along the length of the body. Therefore, assuming homogeneity, a portion with a large cross-section will have a lesser current intensity of amperes per unit area, as compared with a section which is smaller and thus has more amperes per unit area. This same principle applies to the individual portions of a cross-section. When a large amperage is flowing, the wattage effect is greater, and there is greater heating and thus a higher temperature is present.

The illustrative practices are not restrictive, and the invention may be utilized in many ways within the scope of the appended claims.

What is claimed is:

1. A vaporizing element for the deposition of metals, composed of a refractory material selected from the class consisting of the carbides, borides, nitrides and silicides of the transitional metals belonging to groups IV, V, and VI of the periodic system and having a body with a top depression, the depth of the body beneath the floor of the depression being at least four times the depth of the depression, the walls bounding the depression having a

greater horizontal dimension than the depth of the depression.

2. A vaporizing element as in claim 1, in which the body is composed of a sintered mass of a refractory hard metal material, and in which the depression has a depth of about one millimeter and the depth of the body beneath the floor of the depression is about seven times the depth of the depression.

3. A vaporizing element as in claim 1, in which the floor of the depression has a roughened surface.

4. A vaporizing element as in claim 1, in which the floor of the depression has grooves therein.

5. A vaporizing element as in claim 4, in which the grooves are in parallel sets intersecting one another.

6. A vaporizing element in claim 4, in which the grooves are defined by long needle-like elevations.

7. A vaporizing element for the deposition of metals, composed of a refractory material resistant to wetting by the molten metal to be vaporized, and having a body with a top area having a plurality of grooves with widths of 0.010 to 0.050 inch and depths of 0.005 to 0.060 inch, with intervening crests located substantially in a horizontal plane, said grooves terminating within the said area.

8. A vaporizing element as in claim 7, in which the grooves are parallel and are spaced 0.020 to 0.100 inch apart.

9. A vaporizing element as in claim 7, in which the top of the element has a flat area and the grooves are about 0.020 inch wide, 0.010 inch deep, and are spaced about

0.0625 inch; each groove being no wider than one-tenth of the width of the flat top area and no deeper than one-tenth of the vertical distance from the said top area to the bottom surface of the element body, and the grooves being spaced from center to center a distance between one-fifteenth and one-fourth of the width of said top area.

10. A vaporizing element for the deposition of metals, composed of a refractory material resistant to wetting by the molten metal to be deposited, and having a body of generally rectangular section at its ends for the conduction of electric current thereto, and a top depression intermediate the ends, said depression having a depth of about one millimeter and having in its floor a plurality of grooves with widths of 0.010 to 0.050 inch and depths of 0.005 to 0.060 inch, the depth of the body below the floor of the depression being at least four times the depth of the depression and at least four times the depth of the grooves.

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