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PREVENTION OF SPLATTERING DURING VAPORIZATION PROCESSING

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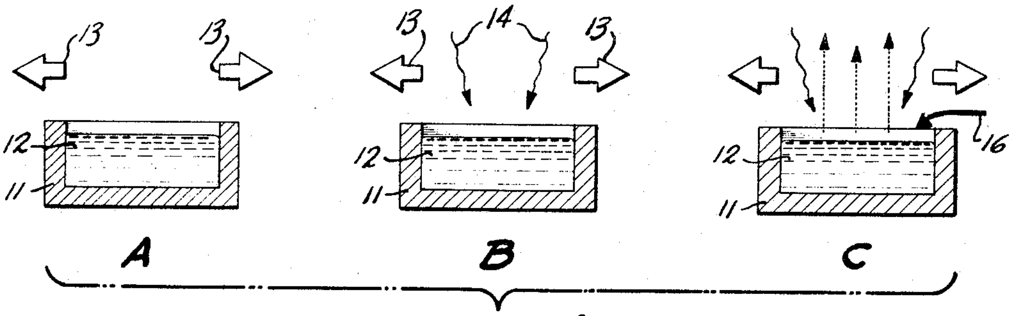

FIG. 1

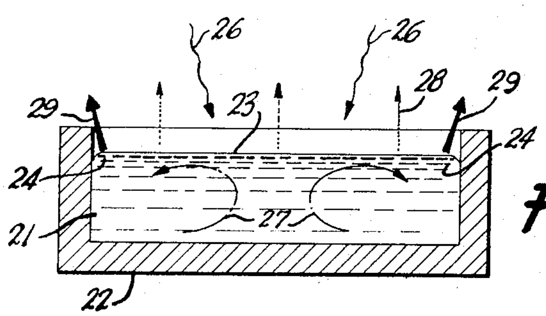

FIG. 2

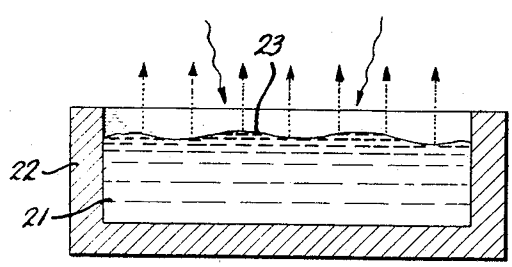

FIG. 3

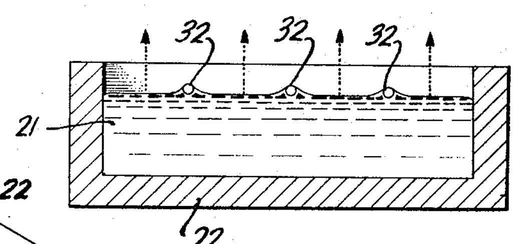

FIG. 4

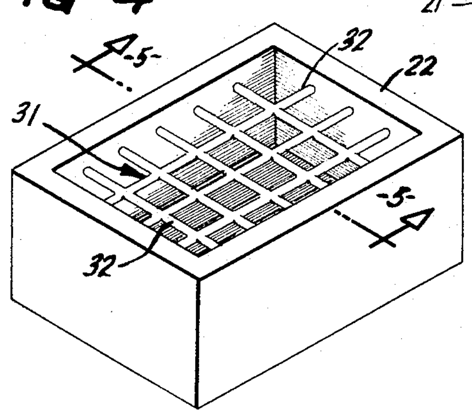

FIG. 5

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PREVENTION OF SPLATTERING DURING VAPORIZATION PROCESSING

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The present invention relates to the prevention of splattering during the vacuum evaporation of materials and is particularly useful in connection with very rapid rates of vaporization.

In vacuum evaporation processing it has been observed that a substantial amount of explosive vaporization or splattering is often experienced. In all instances this splattering is undesirable, and in many circumstances it is wholly unacceptable. Observation shows that the amount of splattering increases with increasing vaporization rates, and this has actually precluded the utilization of vacuum vaporization in many commercial applications. The problem of splattering, which is present even at low vaporization rates and which is magnified at higher vaporization rates, is overcome by the present invention.

Although the present invention is applicable to improve all vacuum vaporization processes, it is primarily important in the vacuum vaporization of metals or metal alloys having low or intermediate melting temperatures. For most materials, such as metals, the surface tension thereof is appreciable at vaporization temperatures and this causes explosive vaporization from points of decreased surface tension, such as may be provided by slag or impurities floating upon the surface of the molten material, or the meniscus about the edge of same. In accordance with the present invention, it is provided that the surface tension of at least a substantial area of a molten pool of material to be vaporized is reduced in the manner and for the purposes set forth below.

The present invention is illustrated and described as to the method and apparatus thereof in the accompanying drawings, wherein:

FIGURE 1 schematically illustrates at A, B, C, thereof successive steps in the method of the present invention;

FIGURE 2 is a sectional view of a container filled with a molten material undergoing conventional vacuum vaporization;

FIGURE 3 is a sectional view similar to FIGURE 2, and illustrating one solution to the problem of splattering as provided by the present invention;

FIGURE 4 is a perspective view of a crucible adapted to contain material for vacuum vaporization, and illustrating one embodiment of the apparatus of this invention; and

FIGURE 5 is a sectional view taken in the plane **5—5** of FIGURE 4.

Careful consideration of the phenomena of explosive vaporization or splattering of droplets from a molten pool of material, such as metal, during vacuum evaporation, shows that this splattering occurs from particular points upon the pool surface. In the presence of floating impurities upon the pool, it is found that splattering occurs about these impurities atop the pool. In the instance of vacuum evaporation of extremely pure metal, for example, it is found that splattering occurs from the meniscus at the pool edges. It may be postulated that in the application of heat to a molten pool of material for evaporation of such material, there is unavoidably produced a superheating of at least some portions of the molten material. Convection currents in the molten material move these superheated molecules about in the pool, and they preferentially depart from the pool surface at points of

lowest surface tension. Under the circumstance wherein very pure material is being operated upon so that no floating impurities are present upon the pool thereof, it is found that this explosive vaporization then occurs at the curved pool surface formed by the meniscus between the molten material and the container. It is provided by the present invention that splattering of vacuum vaporized material shall be prevented by lowering of the surface tension of a substantial area of a molten pool of material being vaporized. This lowering of the surface tension over a substantial area of the pool is herein accomplished by additions to the pool. In the instance of metal vaporization, there is added to the pool a dissimilar metal, i.e., one which does not have substantially the same characteristics. In particular, this dissimilar metal has a substantially different surface tension than the material being evaporated. As a further limitation upon the material added to the pool, it is necessary for such added material to have a very low vapor pressure in comparison to the pool material in the percentage of material added thereto. It will be appreciated, of course, that combinations of material may be evaporated, if this is the desire; however, under most circumstances it is not intended to evaporate any appreciable amount of the added material.

Referring to FIGURE 1, there is illustrated at A thereof, a crucible **11** containing a material **12** that is to be vacuum evaporated. Evacuation of the volume above the material **12** is indicated by the block arrows **13**. Heat is applied to the material **12**, as indicated by the arrows **14** in FIGURE 1B, so as to thereby melt this material **12**. It has been found that advantageous heating for melting and vaporization may be accomplished by the utilization of bombarding electron beams directed onto the upper surface of the pool. In accordance with the present invention, there is added to the molten material **12** an additional and dissimilar material, as indicated by the arrow **16** in FIGURE 1C. With regard to the identity of the added material, it is provided hereby that there shall be employed an additive material that reduces the surface tension of at least a substantial area of the molten pool. The material added may either dissolve in the molten material of the pool to thereby form an alloy therewith, or, alternatively, may remain in solid form but disposed so as to deform the upper pool surface. At any rate, the added material should be substantially dissimilar to the material in the pool, and should have a low vapor pressure at the evaporation temperature of the pool material, at least in the concentration of additive material employed. Particular examples of suitable additive materials are set forth below.

Considering further the present invention, reference is made to FIGURE 2, wherein there is illustrated a molten pool **21** of metal, such as copper or the like, contained within a crucible **22**. It will be seen that the upper surface **23** of this pool **21** is generally planar under normal circumstances, but at the edges thereof there is formed a curved pool surface defining a meniscus **24**. This curvature may, of course, extend either upwardly or downwardly, depending upon the relative properties of the material of the crucible and the metal of the pool. If the molten pool of material or metal wets the crucible material, as in the case of molten copper contained within a tungsten crucible, the meniscus will curve upward, contrary to the showing of FIGURE 2. Application of heat to the pool as, for example, by electron beam bombardment or some other suitable manner, as schematically illustrated by the wavy arrows 26, unavoidably causes a certain amount of superheating of molten metal. There are established within the pool certain convection currents, as indicated by the light arrows **27** within the pool, which serve then to generally move superheated metal outwardly of the pool under the circumstances wherein heating is accomplished as indicated, and this superheated metal is released at the meniscus of the pool surface. The curvature of the pool surface at the meniscus **24** provides a reduced surface tension area as the surface tension of a liquid is minimized at a region of curvature of the liquid. In the vaporization of metal from a liquid pool thereof, there is unavoidably present some limited areas of reduced surface tension upon the pool surface, for some type of meniscus must be present. With a very limited area of decreased surface tension, there is then produced an explosive evaporation of superheated metal from this limited area, so as to splatter droplets of molten metal from the pool. Normal vaporization of the metal is indicated by the dotted arrows **28** and the heavy arrows **29** indicate splattering from the meniscus.

As briefly noted above, this splattering is highly disadvantageous in many applications, and in particular, it has been found to almost preclude the utilization of vacuum vaporization processes with certain metals. The foregoing is particularly true when extremely pure metals are being operated upon to produce high-quality vapor-deposited films. In FIGURE 3, there is illustrated a manner of overcoming the difficulty discussed above in connection with FIGURE 2. In accordance with the present invention, there is provided in FIGURE 3 for the disturbing of the upper pool surface **23**, so as to thereby produce curves thereon, and consequently to establish a plurality of areas of reduced surface tension. By the provision, in accordance herewith, of a sufficient area of reduced surface tension, the superheated material within the pool then readily escapes therefrom without concentration at minute areas and does then not explosively release from the pool to cause splattering.

One form of apparatus suitable for disturbing the upper pool surface to prevent splattering is illustrated in FIGURES 4 and 5. As shown therein, a grid **31** is disposed within the crucible **22**. This grid may be stamped from a sheet of material or formed of rods or wires joined together. The individual elements or portions **32** of grid **31** are comprised of high-temperature metals, at least with respect to the evaporation temperature of material to be evaporated from the crucible. In this instance, and in accordance with the method of the present invention, the additive material is comprised of the grid itself. Under these circumstances, wherein the additive metal or material remains as a solid within the pool, it is necessary for this material to be disposed substantially at and, in fact, slightly above the upper pool surface. In this manner of carrying out the present invention, the added metal must not only have the above-identified properties, but in addition, must be capable of being "wetted" by the molten material of the pool. The grid **31** is disposed above the upper surface of the molten material of the pool so that it touches this upper surface and, consequently, the pool surface curves up and over the grid.

As an example of the present invention, in accordance with the above-described manner of carrying out same, there may be utilized a tantalum or molybdenum grid with a molten pool of copper evaporant. This grid may, for example, be stamped or otherwise formed of a tantalum sheet, for example. The grid is immersed in the molten copper and the level of the molten copper is then adjusted to be disposed slightly below the top of the grid. Inasmuch as copper wets tantalum, there thus appears from the top of the crucible a complete copper surface, but with a pattern of disturbed surface tension wherever the grid provides a curvature of the copper surface. It is particularly noted that both tantalum and molybdenum, identified above as suitable materials for the grid in this instance, are essentially insoluble in molten copper, and furthermore have a very low vaporization rate at the temperature of a molten copper pool. In one instance of operation of the present invention, the grid was disposed no more than ¼" above the free horizontal surface of molten copper in the pool, so that the copper entirely covered the grid to form a plurality of curved surfaces atop of the pool. Vaporization of the copper at copper vapor pressures of about 5–10 mm. of mercury at the pool surface produced no observable splatter of the copper.

This manner of carrying out the present invention requires relatively careful location of the pool surface relative to the grid. If the grid becomes unduly exposed above the surface of the molten material in the pool, a bombarding electron beam utilized to vaporize the material, will actually melt the upper surface of the grid and splatter will occur. On the other hand, if the grid is entirely submerged in the pool so that there is no observable ripple upon the pool surface, it is found that the grid has substantially no effect in eliminating splatter. There is thus provided by the present invention for the addition to a molten pool of material being vaporized of a partially submerged grid of insoluble material that is wet by the molten evaporant in order to thereby substantially entirely preclude explosive evaporation. The foregoing example of the present invention relating to the evaporation of copper is noted to be particularly significant, inasmuch as prior art attempts to evaporate copper at commercially feasible rates have proven wholly unsatisfactory because of the problem of splattering. This same problem appears to be of minimal importance in the evaporation of aluminum, and it may be postulated that splattering of aluminum is inherently minimized because of the exceptionally low surface tension of aluminum at temperatures required for substantial evaporation rates. Apparently, aluminum does not superheat to any great extent because of the inherent relationship between normal surface tension and vapor pressure as functions of temperature. It is furthermore noted that in the vacuum evaporation of so-called "high temperature" metals, the problem of splattering does not appear particularly significant, possibly because of radiation losses from the molten pool at the temperatures required for vaporization. In the vapor deposition of copper, for example, heat is released from the molten pool by conduction, convection and evaporation, while at higher temperatures these same effects are present with the addition of radiation losses. Investigation has indicated that vaporization processes proceeding at a temperature of 3000° F. or lower, are particularly susceptible to the problems overcome by this invention, inasmuch as substantial superheat apparently occurs because of the minimization of radiation losses. The present invention, as described above, overcomes the problem of splattering by providing a sufficient area of low surface tension for the steady release of superheat without explosive evaporation, as would otherwise occur.

It is additionally provided by this invention that splattering may be eliminated through the addition of a material which dissolves in and, in fact, alloys with the molten material of the pool, i.e., the evaporant. The properties of this added material are those set forth above, i.e., such material shall be substantially dissimilar to the material being evaporated, and furthermore shall have a very small evaporation rate at the process temperature. With regard to this latter limitation, it is noted that the critical evaporation rate is that of the material in the proportion employed. The process hereof requires only the addition of very minute amounts of alloying materials which dissolve in the evaporant and, for example, 1 to 10% of additive material may be employed. With regard to the degree of dissimilarity between the evaporant and the added material, it is noted that the effect upon surface tension increases with increasing dissimilarities between the materials. As a general proposition, and speaking only of pure metals at this point, all alloys have lower surface tensions than do the constituents of the alloys. The addition of tantalum to columbium could be expected to produce but very little difference in surface tension, inasmuch as these two metals are quite similar, while the addition of zirconium to beryllium or copper produces a very marked difference in surface tension.

The present invention thus provides, in addition to the previously described manner of prevention splatter, for the addition to the molten evaporant of a dissimilar material which dissolves in the evaporant. This added material, in the proportion employed has a very low vapor pressure at the process temperature. As an example of the foregoing, a small amount of zirconium was added to a molten pool of copper heated to establish a suitable vapor pressure thereof for vapor processing. This addition provided a material reduction in the surface tension of the molten pool, and was observed to prevent splattering of the copper. As regards further examples of the present invention, either tungsten or tantalum in a very small proportion may be added to a molten pool of iron to prevent splattering of the iron during vaporization. In the evaporation of zirconium, a tungsten additive may be utilized to prevent splattering. With tungsten added to zirconium evaporant in an amount of 5% of the zirconium, there is produced a zirconium vapor containing about ten parts per million of tungsten. Under most circumstances this minute contamination of the vapor is not critical and does not limit its utilization. In each of the foregoing examples the additive material will be seen to dissolve in the evaporant and to have a very low vapor pressure in the proportion added.

Although, as noted above, the present invention is particularly advantageous in the prevention of splattering during vapor processing on a commercial scale, it is also advantageous in precluding splattering at lower vaporization rates. In this respect it may be considered that vapor pressure of the order of 0.1 mm. of mercury of the evaporant provides a low evaporation rate, a vaporization pressure of about 1 mm. of mercury is representative of a generally typical evaporation rate, and a vapor pressure of 10 mm. of mercury provides a commercially feasible evaporation rate for very large-scale operations. In all of the foregoing situations, the present invention provides a material advancement in the art. Inasmuch as the surface tension of pure metals is substantial at the melting point thereof, it is highly important that means be provided for the release of superheat from a molten pool of this material during evaporation. Of the common metals, only aluminum appears to have such a low vapor pressure in the temperature range of substantial surface tension that the problem of superheat at high vaporization rates does not occur. Even in the instance of aluminum, however, there may be particular circumstances wherein reduction in the surface tension thereof, in accordance herewith, will be found to be advantageous.

There has been described above particular preferred steps of the process of this invention together with preferred apparatus in accordance herewith. It is believed to be clear that the present invention provides a marked and important advancement in the art which substantially extends the utility and applicability of vacuum vaporization. It is not intended to limit the present invention by the terms of the foregoing description but instead reference is made to the appended claims for a precise delineation of the present invention.

What is claimed is:

1. An improved vacuum vaporization method for vaporizing a metal from the surface of a molten pool of significant depth comprising, heating a metal to be vaporized within a crucible with an electron beam to form a molten pool, said crucible including an open topped container having a plurality of rod-like members extending at least partially across the open top of the crucible in a generally horizontal plane, said rod-like members being formed from a metal having a negligible vaporization rate at the condition necessary for vaporization of said metal and having the characteristic of being wet by said metal, heating the surface of the molten pool to vaporize said metal, and controlling the level of the molten pool within the crucible so that the surface of the molten pool lies just below the upper surface of said rod-like members, whereby the metal may be rapidly vaporized from the areas of reduced surface tension adjacent the rod-like members.

2. An improved vacuum vaporization method for vaporizing a metal from the surface of a molten pool of significant depth comprising, heating a metal to be vaporized within a crucible with an electron beam to form a molten pool, said crucible including an open topped container having a horizontal grid at least partially spanning the open top of the crucible, said grid being formed from a metal having a negligible vaporization rate at the conditions necessary for vaporization of said metal and having the characteristic of being wet by said metal, heating the surface of the molten pool to vaporize said metal, and controlling the level of the molten pool within the crucible so that the surface of the molten pool lies just below the upper surface of said grid, whereby the metal may be rapidly vaporized from the area of reduced surface tension adjacent the grid.

3. An improved vacuum vaporization method for vaporizing a metal from the surface of a molten pool of significant depth comprising, heating a metal having a vaporization temperature below 3000° F. with an electron beam to form a molten pool of said metal, said crucible including an open topped container having a horizontal grid at least partially spanning the open top of the crucible, said grid being formed from a metal having a negligible vaporization rate at the conditions necessary for vaporization of said metal and having the characteristic of being wet by said metal, heating the surface of the molten pool to vaporize said metal, and controlling the level of the molten pool within the crucible so that the surface of the molten pool lies just below the upper surface of said grid, whereby the metal may be rapidly vaporized from the areas of reduced surface tension adjacent the grid.

4. A method in accordance with claim **3** wherein the metal is copper, beryllium, iron or tantalum or mixtures thereof.

5. A method in accordance with claim **3** wherein the grid is zirconium, tungsten or tantalum or mixtures thereof.

6. A method in accordance with claim **3** wherein the metal is copper and the grid is zirconium.

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