Deposition of Coatings or Free Foils of Sublimating Metals

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ABSTRACT

Various methods of intensive deposition of metals, having low vapor generation temperature (mainly, metals sublimating under heating in vacuum), are considered. On the basis of thermodynamic diagram analysis a conclusion was drawn about possible methods of overheated vapor generation and supply to a moving substrate. Vaporization sources of sublimating metals for web coating and free metal foils production are described. Vacuum systems were developed and manufactured for the production of thick two-layer free copper - magnesium foils. Magnesium deposition rate was up to 500 g/min. A vacuum system for the deposition of cadmium layer 15 µm thick onto long metal tubes is also described.

INTRODUCTION

Physical properties of a number of metals (zinc, cadmium, magnesium ...) are such that under pressure of the order of 1.3×10^{-2} Pa in a vacuum chamber, necessary for deposition processes, these metals have no liquid phase. In this case the vaporization (sublimation) process is usually carried out from solid phase. The sublimation rate thus becomes considerably (by some orders) below the theoretical value at given temperature and not constant in time. It is caused by contamination of the vaporization surface with the films of the compounds, formed by the metals and air components. Forcing vaporization rate by increase of supplied power density and temperature of sublimating metal results in microparticles detachment from its surface and their inclusion into the deposit.

Let us consider the thermodynamic i - p diagram (enthalpy - pressure) to analyze possible processes of conversion of sublimating metals into vaporous state [1]. Figure 1 shows the typical i-p diagram for the sublimating substance, whose pressure in triple point (P_t) is higher than pressure (P_k) in the vaporization zone. The metal in the chamber is under pressure P_k. During heating the process is going along line 5-4 or even 5-4', which is preconditioned by a large number of transferred solid microparticles.

The possibility of metal conversion into vaporous state with its preliminary transformation into liquid state in a vessel, separated from the vacuum chamber (condensation compartment)

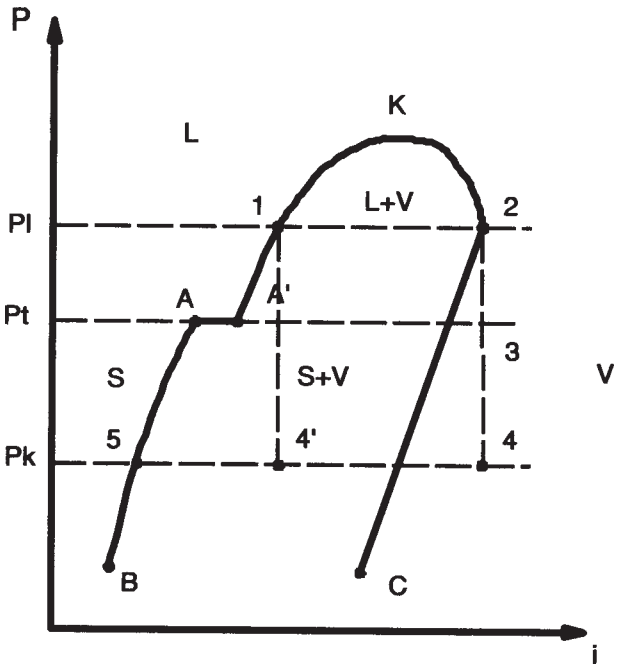

Figure 1. Processes of sublimating metal vaporization in i - p diagram

with some throttling devices, has been investigated. For the sake of simplicity it is possible to speak in this case about three of possible processes:
a) Metal conversion into liquid state under pressure of inert gas (P_i) and throttling of the liquid without sufficient heat supply to metal during throttling, line 1 - 4';
b) Same as in a) but with sufficient heat supply to metal during throttling of the liquid, line 1 - 4;
c) Metal conversion in the vessel into liquid state under pressure of saturated vapors of the metal itself, its conversion into vapor in the same vessel and then throttling of the vapor, lines 1 - 2- 3 - 4.

The process a) goes by isenthalpy and at pressure P_k comes to point 4' into the zone solid body - vapor. That practically provides not only detachment of the liquid metal droplets, which go into solid state though partially evaporating, but also the possibility of vapor-phase deposition at significant flows. In case of heat supply during throttling the process b) goes by polytrope and comes at pressure Pk into point 4, the position of which depends on the amount of supplied heat. If point 4 is

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in the zone of overheated vapor on the right of curve K - C, the process runs normally, the vapor is dry, there are no solid or liquid particles. Here there is a certain complexity in organization of the heat supply and its regulation at optimum level. Metal conversion in a quasi-enclosed space from liquid into vaporous state (process c) is possible when temperature of the liquid vapor T_L and corresponding pressure of saturated vapors P_L are located above the triple point A'. For example, parameters of sublimating metals state in the triple point are the following: Magnesium - T_t = 650 °C, P_t = 360 Pa; Zinc - T_t = 420 °C, P_t = 18.7 Pa; Cadmium - T_t = 321 °C, P_t = 14.7 Pa.

It is necessary to carry out the heat supply and conversion of the liquid into the state of a dry saturated vapor (line 1 - 2) at precisely calculated parameters (for a given vaporization rate) of the melt temperature, pressure of saturated vapors at this temperature, temperature of heat-exchange wall and the melt level above the heat-exchange surface, having sufficient hydrostatic pressure of evaporated metal to eliminate bubbling [2].

Line 2 - 3 in i - p diagram shows the throttling process in the zone between quasi-enclosed space and vapor-line. The throttle cross-section area is selected so that at preset vapor rate to ensure sufficiently large pressure fall and "drift" to the right of line K -C, i.e. vapor overheating with elimination of liquid and solid phases. On the other hand, excessive decrease of pressure would result in undesirable increase of the vapor-line diameter to provide the vapor flow rate below sonic value. Before input into the vapor distributor, located in direct affinity of the substrate, the second throttle 3 - 4 is mounted. Both throttling processes are run by isenthalpies, which here coincide with isotherms. It means that heat supply to the vapor on the entire way to the substrate is not necessary and temperature of all parts contacting with the vapor should not be below T1.

It should be noted that the arc vaporization method is convenient in case of the deposition of small amounts of sublimating materials when for various reasons a high adhesion should be provided without the substrate heating and the surface roughness is acceptable.

EXPERIMENTAL DETAILS

For realization of process b) (line 1 - 4 in i - p diagram) a magnesium vaporization source has been created. It is shown schematically in Figure 2.

Magnesium melting furnace (1), heated liquid metal line (3) for the metal supply into the vacuum chamber and tubular heated throttling vaporization element (5), placed under the condensation zone and enclosed with hot and cold shields (6), are

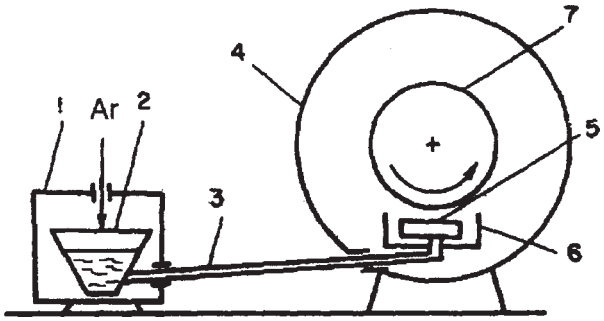

Figure 2. Layout of the source for magnesium vaporization from liquid phase
1 - magnesium melting furnace; 2 - crucible; 3 - liquid metal line; 4 - vacuum chamber; 5 - vaporization element; 6 - hot shield; 7 - substrate

main assemblies of the vaporization source. Detachment of magnesium melting and vaporization zones has allowed to reduce response time of the system essentially as an object of regulation. Thus, magnesium cleaning of oxides and other contaminants takes place outside of vaporization zone. That has allowed to bring vaporization rate nearer the theoretical value. All constructive elements in contact with liquid magnesium are made of titanium. Titanium has good constructive and technological properties. It is practically not dissolved with magnesium and its wetting angle with magnesium in the working temperature range is close to zero [3]. Throttling vaporization element is made of porous tubes, sintered of titanium powder. Open porosity of the tubes is about 30 %, diameter of the pinholes is about 30 μm. That allows to create a quasi-enclosed cavity for liquid magnesium inside the material.

Liquid magnesium is fed into the vaporization element under pressure of argon over the melt surface in the furnace crucible. Magnesium is throttled in the pinholes of the vaporization element with simultaneous heating and converted into vapor. Heating of the vaporization element is carried out with direct supply of electrical current about 2500 A, frequency 8 kHz through the element. Usage of high-frequency current has allowed to increase the vaporization rate at the expense of power concentration in the affinity of outside surface and stabilize intensive vaporization by elimination of shunting effect of liquid magnesium.

Figure 3 shows dependence of magnesium vaporization rate on heating current of the vaporization element. It is visible that this dependence is practically linear. The argon pressure value over the melt was sustained constant at an optimum level.

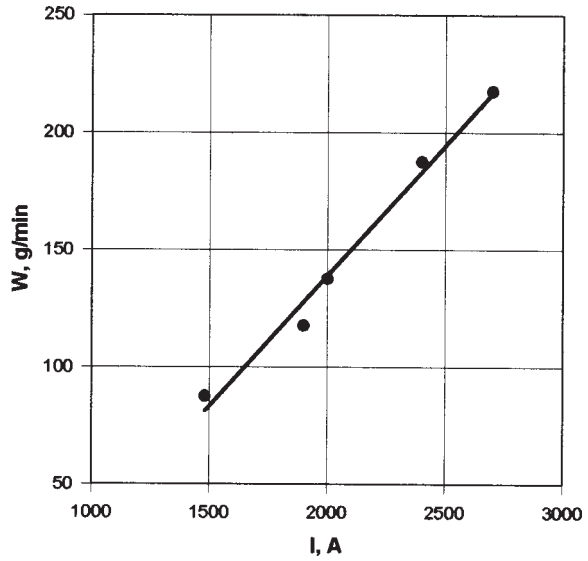

Figure 3. Magnesium vaporization rate of Figure 2 device versus heating current of the vaporization element

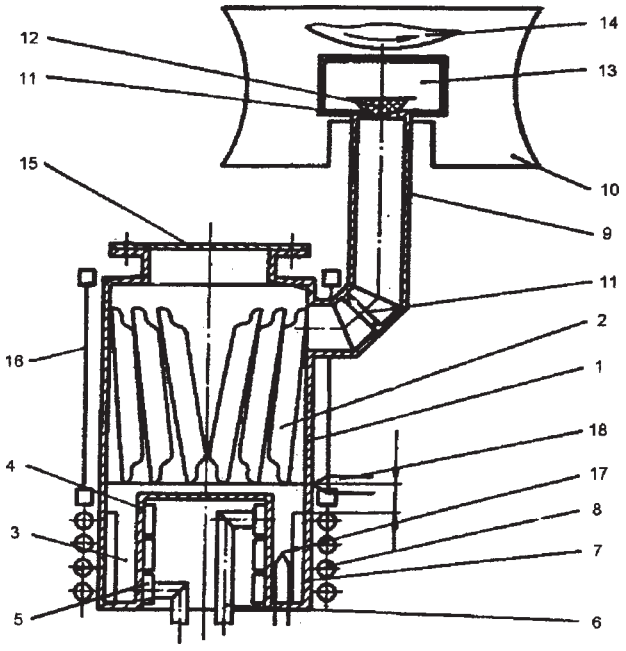

Figure 4. Layout of throttling vaporization source
1 - vaporization device; 2 - magnesium ingots; 3 - magnesium residual after previous melting cycle; 4 - cooling barrel; 5 - cooling channels; 6 - compressed air ducting; 7 - walls; 8 - inductive heater; 9 - vapor-line; 10 - vacuum chamber; 11 - throttle; 12 - check valve; 13 - vapor distributor; 14 - substrate; 15 - loading hatch; 16 - additional resistive heater; 17 - thermocouple; 18 - minimum level sensor

To study process c) (lines 1 - 2 - 3 - 4 of i - p diagram) a throttling vaporization source (vapor generator) has been created. It is shown schematically in Figure 4. The vapor generator incorporates a cylindrical vaporization device (1). Barrel (4) is placed in the bottom part of the device. There are channels (5) in the barrel for blowing of cooling air in the cooling modes. At the lower part of outside cylindrical surface induction heater (8) is located. The vaporization source is connected to vacuum chamber (10) with vapor-line (9), provided with throttles (11) at the input and output of the vapor. Check valve (12) is mounted at the vapor output into vapor distributor (13). Executed testing has confirmed serviceability of the device and feasibility of creation of a vapor generator with productivity up to 500 g/min. and more. Qualitative coatings were deposited at vaporization rates from the melt surface up to 9 g/min. per cm^2.

Figure 5 and 6 show dependencies of productivity of the magnesium vapor generator on the temperature at various throttle diameters and on the throttle diameter at constant temperatures, correspondingly. On the basis of shown curves it is possible to select the throttle diameter depending on necessary vaporization rate at optimum temperatures range of 720 ... 760 °C. Adjustment of the vaporization rate during deposition is provided by changing temperature of the liquid magnesium in the specified range ensuring the rate range P max./P min. = 2 ... 4.

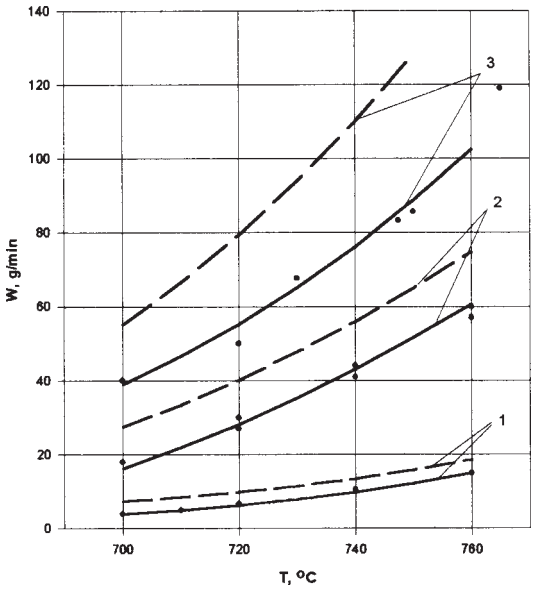

Figure 5. Magnesium vaporization source productivity versus temperature T_L for different throttle sizes (1 - 1 cm^2, 2 - 4 cm^2, 3 - 8 cm^2)

Comparison of operation of the devices, realizing processes b) and c), shows that the first device is characterized by a smaller response time during operation and shorter start and stop time, however the vaporization element has limited life. The vapor generator is characterized by versatility relative evaporated metals, possibility to increase productivity in a rather simple way and combine simultaneous vaporization of various metals easily.

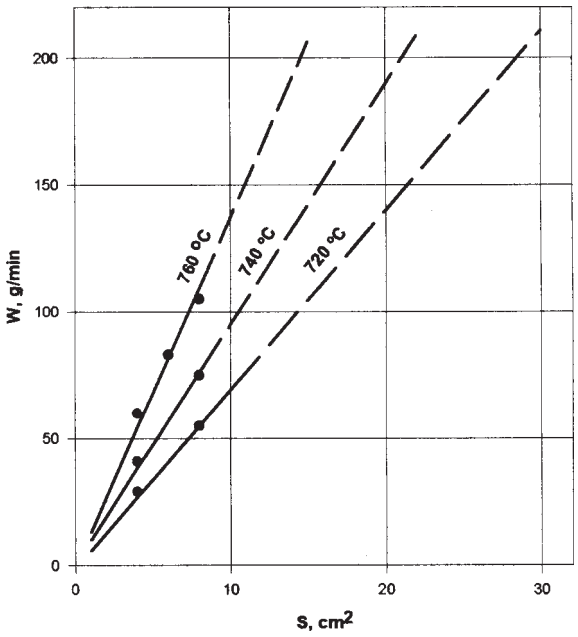

Figure 6. Magnesium vaporization source productivity versus throttle size

As a result of the research works several web coaters were created with vaporization sources of sublimating metals and alloys. In the machine for vacuum production of free multi-layer foil Cu + Mg + Hg (3 %) thickness of the magnesium layer was 250 µm, speed of the deposition drum rotation was 1 ... 3 m/min., magnesium vaporization rate was up to 50 g/min., vapor utilization factor was higher than 85 %.

The method of arc vaporization is used in the vacuum machine for cadmium coating nickel foil for batteries. The same method is used for the deposition of cadmium as a corrosion-resistant coating on helicopter spars up to 16 meters long. The vaporization compartment is a ring of 6 planar circular arc vaporization sources, inside which the spar tube is advances. Thickness of the magnesium layer is about 15 µm. Selection of the vaporization method is preconditioned by the necessity to provide good adhesion without heating the steel tube (substrate) and by relatively short deposition cycles.

CONCLUSION

Theoretical background has been developed, designs of high rate vaporization sources of vacuum sublimating metals have been elaborated and investigated. Feasibility of sublimating metals vaporization at high rates free of droplet and/or solid phase and with high vapor and power utilization factors is shown.

The data received as a result of the research works allowed to create a number of vacuum machines for coating roll materials.

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