Zinc and Magnesium Vapor Generators in a Steel Strip Coating System

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ABSTRACT

Investigation in the field of generation of sublimating metal vapors in vacuum allowed to create high-capacity devices for thermal evaporation of zinc and magnesium. Experiments with prototype generators for steel strip coating have been conducted. We studied the possibility of simultaneous deposition of various metal vapors with high repeatability at relatively simple monitoring and control over the process.

At the same time we investigated the operation capability of the vapor generators combined with ion sources. Due to ion pre-treatment the strip temperature was significantly reduced, while producing sufficient adhesion.

Thermodynamic basics of vapor generation and design of prototype vacuum machine to produce corrosion-resistant coatings on metal substrates are under discussion.

INTRODUCTION

Vapor pressure of some metals, for example, magnesium, zinc, cadmium, antimony, tellurium and others at boiling temperature essentially exceeds pressure in the vacuum chamber. That is why these metals are usually evaporated from the surface of material remaining in solid phase (sublimation). Sublimation rate, as a rule, turns out to be essentially below theoretical and fluctuates in time. This is basically due to contamination of the evaporation surface with oxide films. Besides, when conducting intensive sublimation process, entrainment of microparticles with vapor into the deposit and formation of the structures, deranging the deposit continuity and deteriorating its mechanical properties, were observed. In order to evaporate sublimating metals at liquid phase a number of devices [1] named vapor generators have been created. To ensure competitiveness of the process it is necessary to provide minimum power consumption and maximum vapor utilization (close to 100% is desirable) of the metal evaporated. These purposes may be achieved in the systems under discussion.

Mixtures of various metals, e.g. Zn+Mg, Mg+Hg, Sn+Cd and others, can be obtained in the vapor generators relatively simply. These features of the vapor generators are very attractive when considering evaporation methods not only for sublimating metals, but also for other metals and compounds. These devices have essential advantages compared to other types of evaporators, e.g. those for evaporation of MgF_2, Mn, ZnS etc. The vapor generators can be utilized for the coatings, where concentration of the deposited ingredients should vary through the layer.

Some results of the investigation of the vapor generators designing are presented below.

THEORY

The conception of the vapor generators operation includes evaporation of sublimating materials conducted at increased pressure and temperature above the triple point with subsequent transportation of dry vapor to the deposition surface, pressure decrease and deposition in the area, where both solid and vapor phases exist. For magnesium, as an example, this process can be seen in i – p (enthalpy-pressure) diagram (Figure 1).

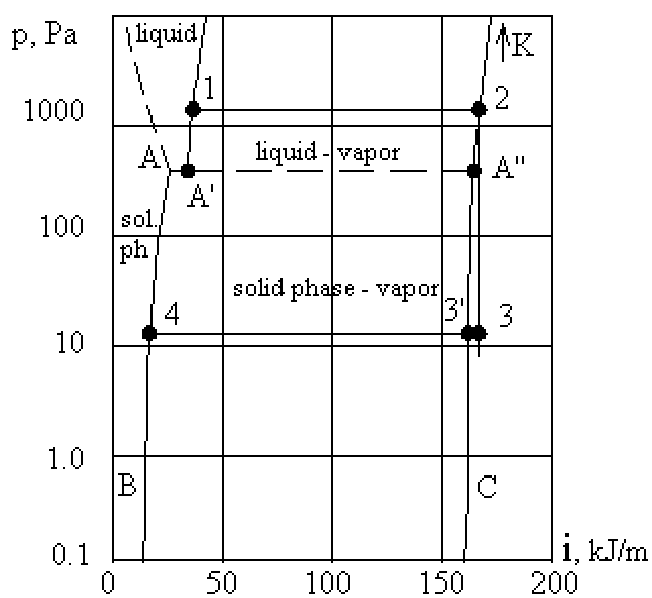

Figure 1. Section of thermodynamic process diagram for magnesium.

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At initial warming the material state changes along saturation line BA. The process is conducted below the triple point, while solid phase and saturated vapor of the vaporized material are in the crucible at corresponding temperature and pressure. Then the loaded material is melted and brought up to the evaporation temperature. In the diagram, line AA' corresponds to the triple point. In point A' all material is melted, there are liquid and vapor phases. Line A'1 in the diagram corresponds to overheating. The valve is opened and the material is evaporated (transition 1-2 in the diagram). Point 2 corresponds to the saturated vapor state in the quasi-closed vessel at set temperature Ts, to which certain pressure *p* (line 1-2 in the diagram) corresponds. There is only the vapor phase to the right from line KC.

In order to avoid appearance of liquid or solid phase in the vapor flow the vapor parameters should correspond to the points on the right from KC line. This is achieved by conducting the transportation process and vapor expansion along the line, close to isenthalpy, i.e. down the line 2-3 in the diagram. Line 3-4 illustrates the material deposition on the substrate. Thus, theoretical possibility of by-passing the zone below the triple point and liquid-vapor interfacing line and on the right from the dry saturated vapor line is shown.

It should be noted, that theoretically only vapor generation process (1-2) is power-consuming, transportation and throttling do not demand heat supply. The power costs are defined only by the necessity to support the preset temperatures of the vapor duct and vapor distributor and are determined by heat loss of these devices at operating temperatures. It seems that creating such a device is a simple task. Having some kind of a heated vessel, it is necessary to selected proper throttles to provide the melt temperature above the triple point at a preset flow. However, there are some essential limits.

It is clear that the vapor generators are applicable only for evaporation of substances, for which resistant constructional materials could be selected to endure their evaporation and transportation temperatures. This natural condition essentially restricts applicability of the method. However, after an attentive analysis its application remains comparatively broad.

For preventing ejection of the melted substance droplets into the vapor duct and further into the vapor distributor and on the substrate, bubble and film boiling in the heated wall-melt system should be excluded. Heat transfer from the wall to the vaporized material under film boiling conditions is essentially impeded and at a specific power can lead to intolerable growing of the wall temperature. To avoid such conditions, it is suggested to "suppress" boiling by the pressure of liquid material column. The calculation has shown that minimal height *H min* of the liquid column over the intensive heating zone, preventing boiling, is determined by the formula:

$$H\ min = (Pv - Ps)/\rho g,$$

where Pv—saturated vapor pressure at wall temperature Tv,
Ps—saturated vapor pressure of the vaporized material Ts (line 1-2 in p-i diagram),
ρ—density of melted material,
g—intensity of gravity.

The difference Tv - Ts is determined by heat flow through the wall, by the level of heat exchange between the wall, including by arranging convective streams in the melt.

In this respect creation of a vapor generator with inside ribbing of the heat conductive wall is extremely interesting. This will not only allow to essentially decrease the temperature difference, but also to solve the problem of crucible rewarming. It is clear that the cycle has to be ended when the melt height over the wall heated part is not less than *H min*. Solidifying material, as it is being chilled, tears off from the wall. Its subsequent heating in the following cycle will be difficult due to the gap appeared between the wall and solid material. Special ribs are designed [2] to provide continuous thermal contact with the solidified material.

The method of pressure reduction and vapor transportation to the distribution device is an essential problem in the vapor generators application. The calculation shows that adiabatic (isoentropic) vapor expansion in the throttle or vapor duct leads to significant oversaturation of the vapor (line 1-3' of p-i diagram). Practically it means gas-phase condensation of the droplets and solid particles in the vapor and is unacceptable for a qualitative process. A conclusion may be made that for ensuring dry state of the vapor it is necessary to create irreversible conditions in the flow by increasing hydraulic resistance and, consequently, necessary energy level for overcoming the friction forces. In practice this would mean that to provide dry vapor it is necessary to decrease the speed of the vapor flow significantly below sonic level and provide conditions, close to isothermal. The calculation shows that polytropic factor of the process should not exceed 1.07 ($n < 1.07$).

EXPERIMENT

On the basis of made calculation a number of vapor generators were manufactured for evaporation of various metals and compounds. Thermodynamic processes of vapor generation were investigated primarily for magnesium and zinc. Figure 2 shows the layout of the vacuum pilot machine for coating steel strips utilizing the vapor generator designed on the basis of the above calculation. The evaporation rate for the present system is determined by only one coefficient-saturated vapors temperature (and corresponding pressure) in the crucible.

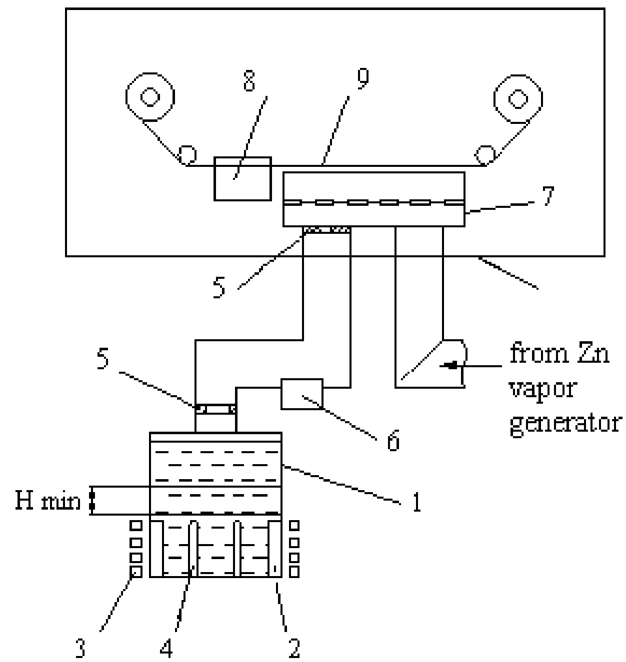

Figure 2. Layout of the Mg and Zn deposition machine. 1-magnesium crucible; 2-ribs; 3-inductor; 4-capsules with thermocouples; 5-throttles; 6-device of vapor pressure measurement; 7-vapor distributor; 8-plasma device for strip treatment; 9-steel strip; 10-vacuum chamber.

Capability of precise measurement of the melt temperature is the main issue here. Figure 3 shows the relation, registered during the vapor generator testing.

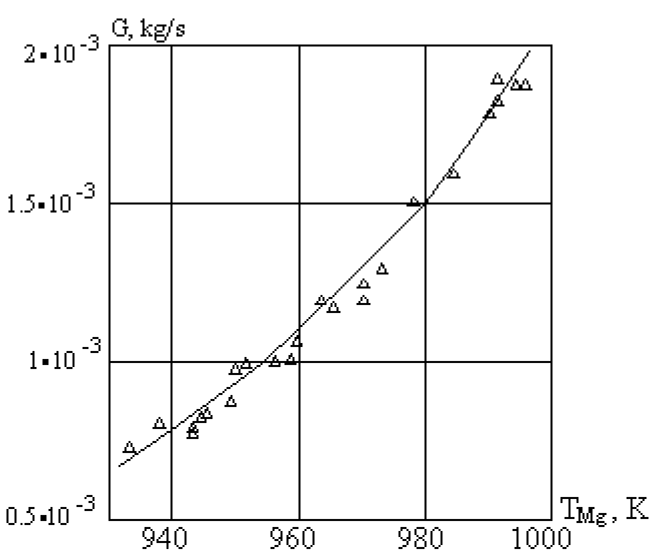

Figure 3. Deposition rate versus magnesium melt temperature.

Temperature was measured by thermocouples inserted in special ampoules, which were dipped in the melt. The temperature field of the crucible and its conformity to the melt temperature were investigated. Essential differences were found: under some conditions of power supply, apparently accompanied with the melt boiling, the temperature difference between the heat conductive wall and the melt exceeded 300 °K.

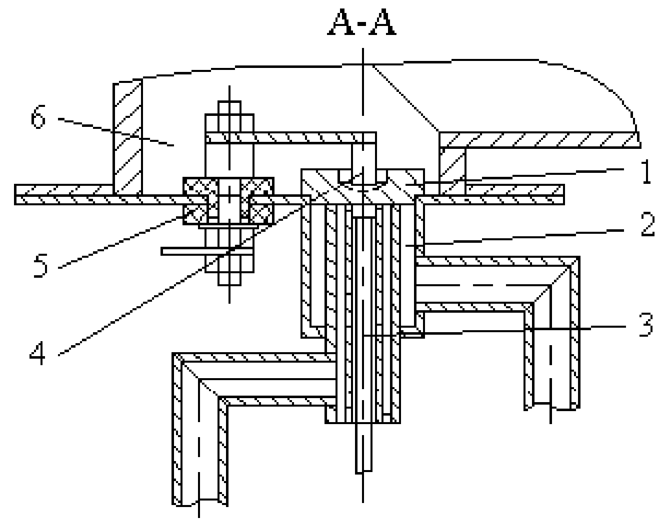

Figure 4. Device for measurement of magnesium vapor pressure. 1-condensate collector; 2-cooling system; 3-thermocouple; 4-contact heater; 5-ceramic insulator; 6-magnesium vapor duct.

The device shown in Figure 4 was used for measuring metal vapors pressure in the duct or vapor distributor. The principle of pressure measurement by corresponding saturated vapors temperature was used as the measurement basis. Since the metal vapor in the vapor duct is already quite far from saturation, there is no sense to measure its temperature. For saturation temperature estimation a plate with changeable surface temperature is placed into the investigated cavity, and as the temperature changes periodically, growth or evaporation of the metal deposit are measured. The average temperature at constant deposit thickness corresponds to the temperature of the saturated vapors, from which pressure in the cavity can be determined. Both stationary and transition processes have been investigated using the described system. Optimal operation conditions were found for the devices of cleaning and preparing the steel strip surface prior to coating. Just as it was preliminarily estimated, deposition rate of each metal is determined according to the parameters of the corresponding vapor generator and their influence on each other is insignificant.

CONCLUSION

Theoretical principles of calculation and engineering of the system for generation of vapors, sublimating and evaporating at relatively low temperatures of metals and compounds, have been developed. The pilot system with controlled vapor generators for various metals has been created, providing capability for broad technological investigations of combined layers deposition onto roll materials. It was shown that optimization of the vapor generators design for specific metals and targeted capacity is necessary.

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