

Improvement of Web Heat Condition by the Deposition Drum Design

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ABSTRACT

The tendency of PVD processes towards increasing deposited layers thickness and consequent growth of thermal load onto the substrate are evident. For this reason the substrate heat transfer enhancement becomes necessary. The paper is focused on the roll substrate cooling during its exposure on the deposition drum. Sources of heat-transfer substances in the form of gases or polymer-released moisture are available in a polymer substrate. Apart from that, the polymer substrate has a good contact with the drum surface due to its mechanical properties, at least at the initial stage. Metal roll substrates (metal foils) have much heavier problems of cooling. Insufficient or non-uniform cooling of metal substrates causes occurrence of permanent wrinkles, corrugation, ribbed structure etc. Technique of intensification of the substrate heat transfer on account of forced feeding inert gas into the gap between the substrate and drum (“the drum venting”) with simultaneous spreading the substrate in the deposition zone is a universal means of intensive cooling any roll substrates. The results of investigation of the substrate – “venting” drum heat transfer are presented in the paper. Temperatures of PET film 12 microns thick and copper foil 10 microns thick during deposition of lithium layers 20 ... 25 microns thick were directly measured. Effective heat transfer coefficient of the substrate has been determined based on a simplified heat transfer model by experimental measurement of the foil section temperature change in passing the deposition zone. It was equal to 100 ... 250 $W/m^2 \cdot K$. The feasibility of using the offered method of intensive substrate cooling for increasing PVD processes productivity in order to produce materials for rechargeable batteries and solar cells is discussed.

INTRODUCTION

Generally, a PVD process consists of two stages. The first stage is the deposited substance atomizing by one or another method (for example, by heating or sputtering). The second stage includes atoms transfer from a coating source to the substrate and atoms condensation on the substrate with energy release to form the coating. For more convenient different materials deposition data comparison we use a specific characteristic: energy of transferring of one gram of the deposited substance [1]. It is quite evident that total amount of energy, transferred to the substrate, depends first of all upon the deposition process productivity. In practice, it is possible to reach only such

process productivity, which is determined by the substrate capability to admit the transferred energy.

In recent years, the market of power supply materials takes interest to vacuum processes for one-run depositing the layers 10 and more microns thick. Relatively thick copper coatings (as a seed layer of the thickness from tenths to one micron and more) are necessary for flexible p-c boards manufacture and in some other industries. It requires certain adaptation of existent processes. Thus, the “thick” layer one-run depositing could be solved only by decrease of winding speed: from 100...600 m/min in traditional roll coaters down to 1...10 m/min. The deposition process productivity issue induces the attention to the substrate thermal relaxation under vacuum conditions. Earlier experiments on heat transfer from roll substrates in vacuum demonstrated the efficiency of a gas gap between the substrate and cooling surface when heat flows of 80 ... 100 kW / m^2 density are removed [2]. As example, we cite some results, which refer to the gap heat conductance between PET film and chilled surface (smooth curved surface with $R=0.3$ m) at air supply into groove [2]. The groove was made on the surface along PET film centerline. Film width was 80 mm, pressure to the surface (film tension) – 2000 Pa. Other experimental conditions: measured gap size – 6...10 microns, air pressure within the gap – 500 Pa. Air distribution was such, that it pressure on the film edges was 90 Pa. Crosswise heat conductance distribution is shown in Figure 1.

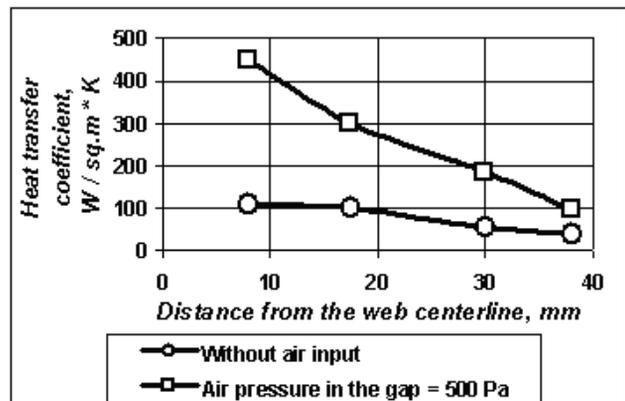


Figure 1: Gas pressure effect on heat transfer.

Without air input heat transfer coefficient was made 50...100 $W/m^2 \cdot K$. Air input into gap increases heat transfer near the

groove up to 5 times. At the same time, heat transfer coefficient near the film edges increased up two times. That results totally corresponds to the general regularities of heat transfer by the gas: the higher gas pressure in the gap – the higher gap heat conductance. Heat transfer coefficient reduction to the film edges shows insufficient gas distribution across the web and gas leakage from the gap. Other mechanisms of heat transfer in real processes (heat transmission by contact conductance and radiation) provide only 5 ... 10% of dissipated heat. For maximum efficiency of heat transfer through the gas gap it is necessary, on the one hand, to provide maximum pressure in the gap, on the other hand, do not allow significant deterioration of vacuum in the chamber. Thus, for example, for classical thermal deposition method pressure in the deposition zone should not exceed 0.067 Pa. Otherwise the coating may be formed as a fine powder but not as a film. These requirements are contradictory. Therefore, success of one or another technical solution is determined by the capability to achieve the compromise between the mentioned requirements. By now various technical solutions of the heat removal intensification and optimization of deposition temperature conditions are known.

Polymer substrates contain atmospheric moisture on their surfaces (physical adsorption) and in bulk (diffusion and dissolving). It allows running the process at a relatively high heat load of the substrate. In this case, the film heating leads to water vapors emission into the gap between the film and drum, thus increasing heat transfer to the drum [3]. Yet, such method has some drawbacks. Firstly, moisture content in the film is determined by the film history (for example, by the film storage conditions) and the polymer nature. Thus, for example, PET film moisture content is usually 0.8%, while PP film moisture content is some 0.03%. It brings some uncertainty of the expected heat transfer level. Secondly, if it is necessary to deposit a double-side coating, one may come across the situation when heat transfer conditions on opposite sides of the substrate are quite different. After coating the first side of the film, it loses essential content of moisture, which might be a heat transfer agent. As a result, depositing the layers of equal thickness on both sides of the film is becoming a difficult task. And finally, it is extremely difficult to provide necessary water vapors pressure in the gap when metal foils should be coated, not to mention the problem of metal coating oxidation by water vapors, especially in case of depositing very active metal, such as lithium. In our opinion, inert gas application for heat exchange between the substrate and processor drum may be a universal method, available for any substrate types, including polymer films and metal foils.

“VENTING” DRUM DESIGN

Over a long period, we have been used so called “venting” drum for depositing “thick” layers onto metal and non-metal web materials. An inert gas gap is provided between the substrate and cooled surface of such drum.

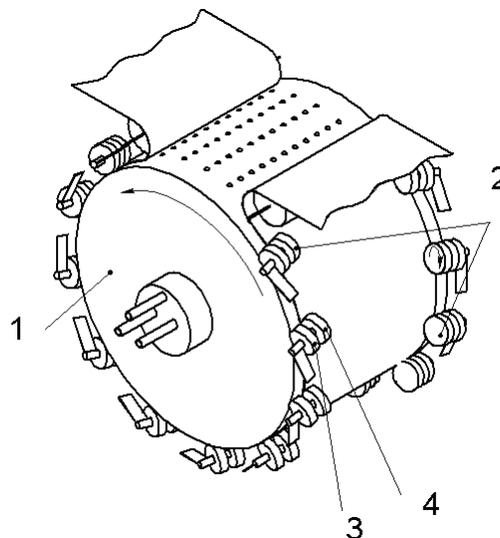


Figure 2: Sketch of the processing drum [4].

The drum shell 1 is provided with channels for cooling agent circulation. It also has mesh size holes for Argon supply outward. Amount of the supplied gas is controlled with standard means. When depositing “thick” coatings with a previous design of a similar drum we observed separation of the substrate edges from the drum and its thermal degradation due to difference of the film and drum contact conditions on the middle and edges of the substrate. It increased leakage of the gas, supplied into the gap. Therefore, in the new drum a system of hold-down twin rollers 2 is provided. The rollers axes are oriented a bit angularly relative the substrate longitudinal axis. Roller 3 of each pair is in touch directly with the drum surface, while roller 4 contacts with it through the substrate edge. The mentioned rollers perform double function. On the one hand, they hold-down the substrate edges to the drum, thus decreasing gas leakage into the evaporation zone, on the other hand due to their orientation they generate friction force component, directed across the substrate. In some cases, this force is sufficient for the substrate spreading, for example when coating PET film 6 ... 12 microns thick. It allows facilitating the film drift due to its thermal expansion during deposition process.

EXPERIMENTAL DETAILS

Cooling capabilities of the “venting” drum of 300 mm diameter were investigated in depositing double-side lithium coating 20 ... 25 microns thick onto PET film 12 microns thick and copper foil 10 microns thick. Figure 3 shows general view of the laboratory machine for depositing double-side coatings in one run. The machine is equipped with two “venting” drums.

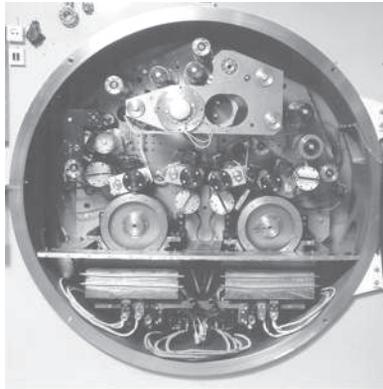


Figure 3: Pilot Li coater.

Optimal deposition conditions were determined during preliminary experiments based on the substrate mechanical properties and admissible level of gas pressure in the chamber at lithium thermal evaporation. Lithium evaporation temperature was 595 °C and deposition rate was up to 25 microns per minute. The heat-transfer coefficient was determined indirectly by examination of the substrate experimental temperature profile in the lithium deposition zone and calculated profile. The latter was derived under conditions that the deposition rate is uniform within the deposition zone. Heat flow to the substrate was calculated by the deposition rate and lithium heat transfer, corresponding to evaporation temperature set point 595 °C. Heat transfer value for lithium evaporation temperature 595°C was 38 kJ/g. Finally heat flow density to the substrate was 8.5 kW/m² at deposition rate 25 microns per minute. By heat-transfer coefficients variation some calculated temperature profiles were obtained. Temperature of the 150 mm wide substrate was registered with flat gauging thermocouple “K,” stuck to the PET film backside with high-temperature scotch on the basis of PI film or soldered to the foil backside. The thermocouple thermal junction was additionally insulated from the drum with aluminized PET film. More detailed experiment conditions and results are described below.

HEAT TRANSFER COEFFICIENT AT LITHIUM DEPOSITION ONTO PET FILM

Lithium was deposited onto 12 microns thick and 150 mm wide PET film at the substrate tension on the drum 50 N, argon pressure in the drum 500 Pa, the drum temperature minus 20 °C and total pressure of residual gases in the vacuum chamber 0.033 Pa. A barrier layer of nickel was deposited beforehand to prevent lithium interaction with residual moisture of the substrate. The film winding speed at evaporation temperature 595 °C was 0.35 m/min. Final coating thickness made 20 microns at the deposition zone length 0.3 m. Figure 4 shows changes of the film temperature in its travel through the deposition zone. The rated temperature profiles for different heat-transfer coefficients are also presented in the figure.

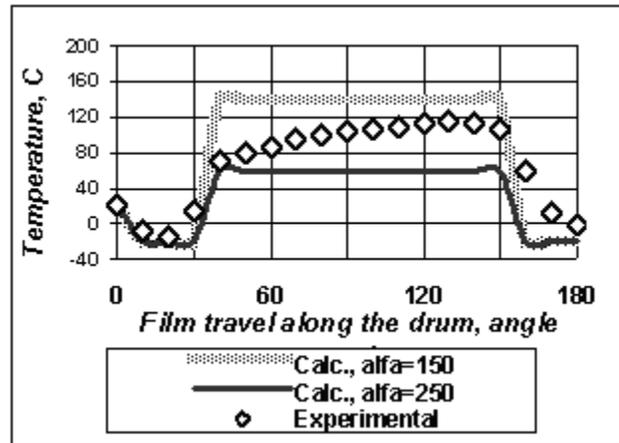


Figure 4: PET film temperature variation along the deposition zone.

As it follows from the graphs comparison, the heat-transfer coefficient was within 150...250 W/m²•K under the experiment conditions. It is quite agreeable with the data of work [3]. The lithium double-side coating of total thickness of 42 microns was deposited onto 12 microns thick PET film without temperature monitoring (simultaneously on two drums in one pass). The coating appearance shows that there was no overheating or buckling of the film during deposition process. Attempts to intensify heat removal by further increase of argon pressure in the drum and the film tension failed: large burnout areas of the film appeared at tension 60 N and gas pressure 660 Pa. It shows that upper limit of heat removal intensity of this drum design for PET film has been achieved.

HEAT TRANSFER COEFFICIENT AT LITHIUM DEPOSITION ONTO COPPER FOIL

The same laboratory machine was used for single- and double-side lithium deposition onto copper foil 10 microns thick and 150 mm wide. The foil tension on the drum was 60N, gas pressure in the drum was 240 Pa, and the drum temperature was minus 20 °C, pressure of residual gases in the vacuum chamber was 0.04 Pa. Argon pressure was lower in comparison with coating the PET film due to the foils mechanical properties (insufficiently tight adherence of the foil to the drum at admissible level of tension) and reached upper level of total pressure in the chamber. The film winding speed at lithium evaporation temperature 595 °C was 0.30 m/min., while final thickness of the coating reached 25 microns. Figure 5 shows changes of the film temperature in its travel through the deposition zone. The rated temperature profiles for different heat-transfer coefficients are also presented in the figure.

As it follows from the graphs comparison, the foil heat-transfer coefficient was within 100...150 W/m²•K under the experiment conditions. It is lower of the PET film coating results.

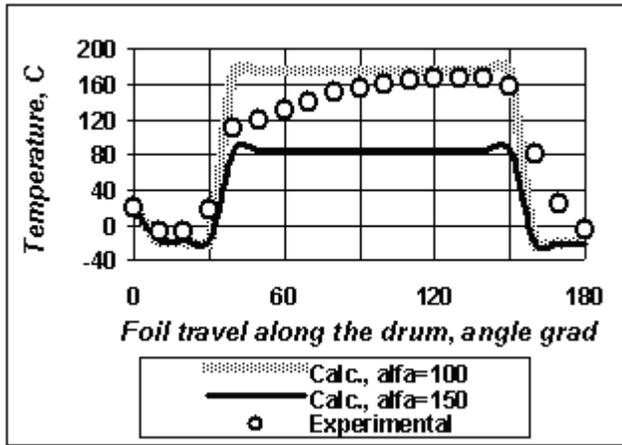


Figure 5: Copper foil temperature variation along the deposition zone.

DISCUSSION

Maximum gas pressure in the gap between the substrate and drum is determined by the balance of available pumping speed and gas leakage flow through the space between the drum uncovered areas and substrate edges. Total gas pressure in the vacuum chamber is the criterion and the flow of gas, supplied in the drum, or gas pressure at the drum input, is the adjustable parameter. The gas pressure value in the gap depends on resistance to gas flows through the drum structural elements (the gas distribution system) and through the gap. It means that actual pressure in the gap is always lower of that at the gas input. Yet for further estimations we assume that pressure in the gap is equal to gas admittance pressure, i.e. it is 240 ... 500 Pa. According to known Knudsen criteria, the molecular flow in the rarefied gas starts under the following conditions:

$$Kn = \frac{L}{d} < 0.33 \quad (1)$$

Where: L – mean free pass of gas atoms, d – gap size.

Applying Argon atoms mean free pass dependence up pressure at constant temperature 300 K equation (1) may be converted to the following format:

$$P(Pa) < \frac{2000}{d(\text{microns})} \quad (2)$$

For the admitted values of argon pressure in the gap, from equation (2) follows, that molecular flow at maximum gas pressure 500 Pa is prevailed at gaps sizes below 40 microns.

The gap heat transfer conductance at the molecular flow is obtained according to [2]:

$$\alpha = A \cdot \frac{(\gamma + 1)}{(\gamma - 1)} \cdot \sqrt{\frac{R \cdot P}{8 \cdot \pi \cdot \mu \cdot T}}, W/m^2 \cdot K \quad (3)$$

Where:

- A – argon accommodation factor (estimated as 0.74)
- γ – adiabatic index (for argon it is equal 1.67)
- R – absolute gas constant, kJ/ k-mol K
- P – argon pressure in the gap, Pa
- μ – argon molecular weight, kg
- T – gas temperature (assumed as 300 K).

After substitution of all values for argon the following equation is derived:

$$\alpha (W/m^2 \cdot K) = 0.5 P (Pa) \quad (4)$$

The gap heat transfer conductance estimation may be derived by equation (4). Heat transfer conductance value is 120 $W/m^2 \cdot K$ at pressure 240 Pa (lithium deposition onto the foil) and 250 $W/m^2 \cdot K$ at pressure 500 Pa (lithium deposition onto the PET film). These values may be compared with the experiment data not as absolute ones, but as relative estimations, because we do not know actual pressure in the gap. For example, when lithium is deposited onto PET film actual pressure in the gap may be even higher than Argon admittance pressure due the water vapors desorption from the film into the gap. In case of the foil coating, this pressure may significantly be lower of admittance pressure, because of less tight adherence of the foil to the drum and gas leakage into the vacuum chamber. With regard to the above, the conformance of the experimental and rated estimations may be assumed as satisfactory.

In conclusion one more advantage of inert gas instead of water vapor as heat transfer agent should be noted. As it is known, water vapor pressure and consequently heat conduction of the vapor filled gap depends very much on temperature. The lower temperature, the lower vapor pressure. The authors of work [3] explain films heat removal decrease at deep cool down of the drum by the above-mentioned dependence. According to equation (3), heat conduction of the gap, filled with inert gas, is a function of temperature at the power “ $-1/2$ ”. Therefore, heat removal from polymer film and metal foil substrates remains constant at a wide range of deposition temperatures.

SUMMARY AND CONCLUSIONS

The results of experiments demonstrate successful implementation of the idea of intensifying heat removal from the web by forming the gap with inert gas. This solution is quite promising for thick layers depositing (above 1 micron). Two vacuum deposition machines were built. Each of them was

designed for simultaneous double-side coating. Two “venting” processor drums were installed in each coater. One of them is the laboratory machine, shown in Figure 3, another is the industrial-experimental machine, shown in Figure 6. This machine is designed for coating metal foils 25-40 microns thick with metals and alloys up to 10 microns thick, as well as with compounds.

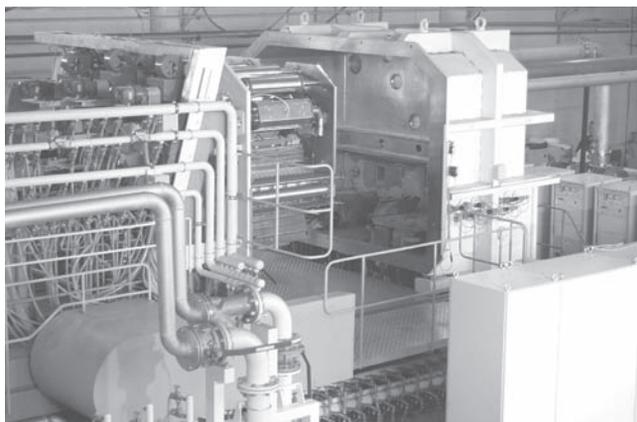


Figure 6: Industrial scale vacuum machine.

In conclusion, it should be emphasized that the achieved heat exchange level ($150 \dots 250 \text{ W/m}^2 \cdot \text{K}$) does not exhaust the possibilities of the described method of web cooling. There are plans to continue updating of the design in order to increase heat conductance of the gap. Positive effect of the planned works will inspire new more productive coaters developing in order to produce materials for batteries and solar cells.

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