Where Films meet Foils, Some Perspectives on Thicker Vacuum Coatings

By
R. Swisher
Sheldahl
Northfield, MN
www.sheldahl.com

Keywords
Vacuum Web Coating, Evaporation, Sputtering, Web Heating

Abstract

Billions of square meters per year of plastic films are coated with 400 to 600 Å of Aluminum and provide wonderful service to the food and decorative packaging industry. Many other rolls of oxide coated films in the 600 to 1000 Å range provide some environmental barrier and a peek at the food in the package. Other, much more expensive, oxide coatings look at you from your cell phone or computer monitor and soon will from your home TV screen. Metal coatings from 500 to 5000 Å (0.05 to 0.5 µ) have a variety of uses in electronics: Magnetic Tapes, Durable visible light reflectors, rf antennas, shielding, and etc. This paper addresses some of the physical limits to roll coatings in these thicker regimes. Its purpose is to stimulate your thinking about such films as replacements for foils where they may be cost effective. We attempt to offer some practical rules of thumb that can be useful in your evaluations.

Introduction

This paper will attempt to give you some perspective on the possible process speeds and important cost components that can be achieved with near standard processes. It is a summary of mostly previously presented work but arranged in we hope a more useful way for quick analyses. Some results which have accrued over the years are included.

There may be some interesting niche markets waiting for vacuum coating processes to serve them. These niches will involve sub-foil metal thicknesses. There are some thin foil (thick coating) applications that may have significant growth opportunities. A number that may become important is 30 milliOhms/square in copper coatings. It seems to fit several rfid product plans.

In this paper the Metals of interest are: Al, Cu, Li, & Sn.

We leave out thick oxide protective layers such as:
1. Armstrong World Industries work on 5 µ of Al_2O_3 for spike heel protection on linoleum floors.

2. NREL's current quest for a few microns of Al_2O_3 for protection of Ag reflectors.

This way we only have to worry about modulus, adhesion, and "bendability" without considering stoichiometry.

Fundamental things to remember.
The thinner you manufacture a rolled foil, the higher is the cost per unit area and it is definitely higher per kilogram. Most rolling processes start with a standard thickness billet. To get very thin you must go back and forth through the rolling process many times. This adds cost. Also the material being rolled may work harden and need to be annealed a time or two in the process. Fun stuff like Lithium needs to be processed in an Argon or absolutely dry atmosphere and it also likes to stick to the compressing rollers. Plus when very thin, it has the strength of processed cheese.

A very challenging problem in rolling metal films that are a few µ's in thickness is that the large, stiff calendaring rollers may not have a flat enough profile to make high quality foil. Machinists boast of ten-thousandth inch accuracy in turning rollers. This is 2.5 µ. If you are trying to roll Cu foil at 6 µ the profile of the resulting foil will be awful. One clever way of solving this problem when hot rolling Cu foil is to continuously measure the profile of the Cu foil and where it is too thin, then spray cold water on the hot calendar rollers to shrink their diameter a bit. Simple but effective.

Some recent expressed demands for material combinations:

1. 0.5 to 3 µ of Al on various polymer bases, frequently PET
2. 0.5 to 3 µ of Cu on various polymer bases, frequently PET, and Polyimide, and PEN
3. 0.5 to 15 µ of Li on various polymer and foil bases, frequently Polypropylene.
4. 0.5 to 2 µ of Sn on various polymer bases, frequently PET, and Polypropylene

Item 1 above is requested for thin film battery constructions and several rfid development projects. It must be low resistance enough to service the rfid chip and be easy and fast to pattern, usually by etching. The thicker constructions are mostly for battery electrodes.

Item 2 above is requested for thin film battery constructions and several rfid development projects. It must be low resistance enough to service the rfid chip and be easy and fast to pattern, usually by etching. It is easier to get reliable electrical connections than with Al. The thicker constructions are mostly for battery electrodes.

Item 3 above is requested for thin film battery constructions. It presents wonderful challenges in handling the material during coating and safely thereafter.

Item 5 above is requested by food engineers. It performs tasks during produce shipment that I really don't want to fully know about.

Physical limits of the processes:

How fast can we run?
This depends on how we cool the base web. If you are coating metal foils as the base web, much more latitude is possible. Sometimes you must avoid creating Aluminide compounds with the base foil. Then cooling is necessary.   For coating Copper onto Stainless Steel, the more heat the better is the metallurgy of the Copper. In the author's personal experience 1.5 μ of Copper and Aluminum have been coated onto 12 μ PET webs. This was done with one source in one pass. The speed must remain proprietary, but it was economically useful. This type of web and coating requires advanced heat removal techniques. These techniques have only been demonstrated up to web widths of about 500 mm. They are not expected to work well above that width. This process has allowed 15 to 20 μ of Li to be coated onto Stainless Steel coated 12 μ PET webs in one pass (Swisher, 2001).

Alternatively, you can work with present web cooling methods and wide machines. You must be able to reverse direction of the web coating while remaining in high vacuum. Some consideration of the level of vacuum in the unwind-rewind zones is also important. Using this technique you can coat many passes of metal to build to the necessary thickness. This will result in a metal "foil" that is not very ductile. It can pass over idlers and rollers quite nicely, but frequently it will break when bent sharply at 180°. However its electrical resistivity is about the same as much thinner evaporated coatings which can make it quite useful for electronic uses like rfid antennas and simple flexible circuits. We find the Cu resistivity to be about 200 Ω*Å and Al to be about 300 Ω*Å. Using this process we have coated 3 μ of Cu and 3 μ of Al onto opposite sides of 12 μ PET. To be more specific, we used 30 passes of high speed coating. Less passes would have been possible, but they don't save much time, just a minute at the turn-around, and they are somewhat difficult to program into our computer controlled reversible machine. Some days you long for the old time speed knob. You do need to pay special attention the keeping the source shutter from shedding its load during all the shuttling to and fro. The effective web speed is controlled by the source output plus a few minutes lost at web turn-arounds.

How much heat are we putting into the web?
By evaporation

For comparisons we can look at the maximum possible evaporative coating efficiency setup. This is running a web over a very hot bucket of metal. The capture efficiency is very high. Using the vapor pressure of materials curves (from Dushman, 1962) and a fair assumption of radiant heat energy emission and capture we can derive curves for the limits of the evaporation process for metals of interest.
Figure 1 presents the results for our metals of interest, considering grams/cm^2 of deposit.
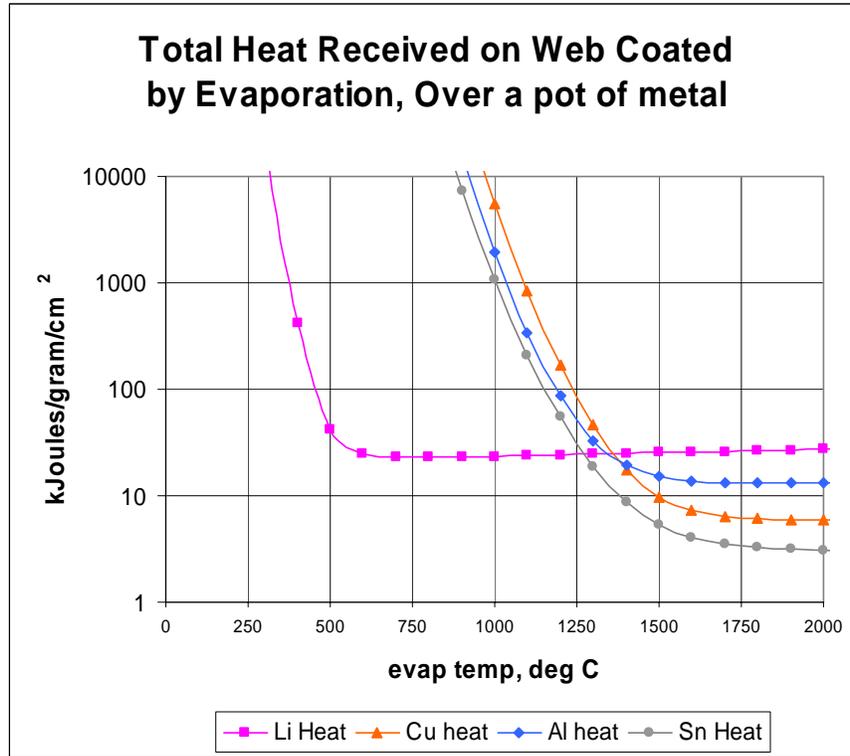
Figure 1. Heat deposited on the web per gram/cm^2 of various metals by evaporation

Looking at the same data but scaling to thickness (Li is 0.53 g/cm^3) we have:
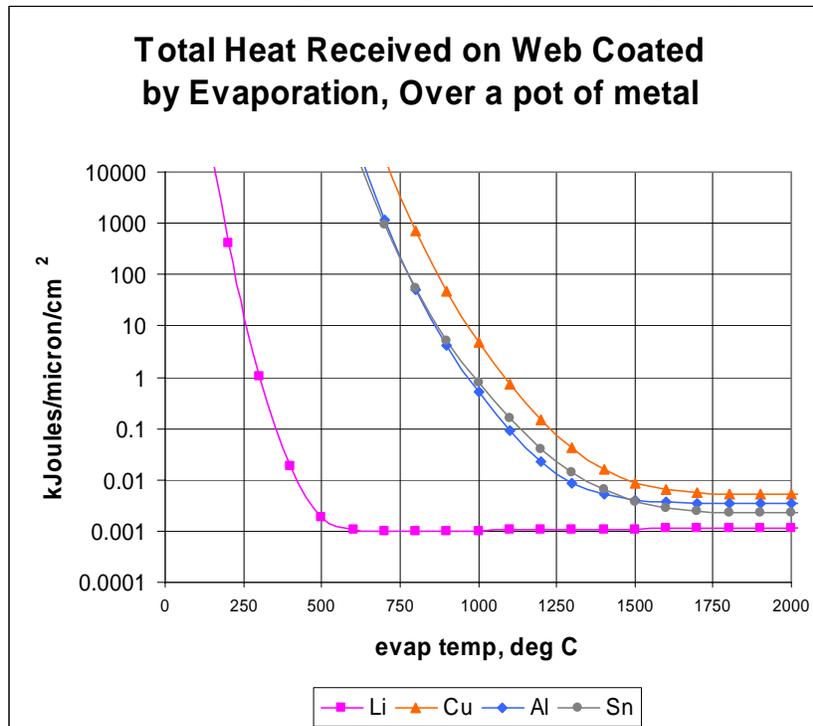

Figure 2. Heat deposited on the web per µ/cm^2 of various metals by evaporation

Here we can see why the boat temperatures we run at are quite important. The faster we can transfer metal the less total heat we will put into the web. This situation is actually approximated rather closely when thick Li is deposited (Swisher 2001, Affinito 2001)

If we look at the heat deposited by evaporation into the polymer web as an impulse of evaporation and no cooling at all we can compute:
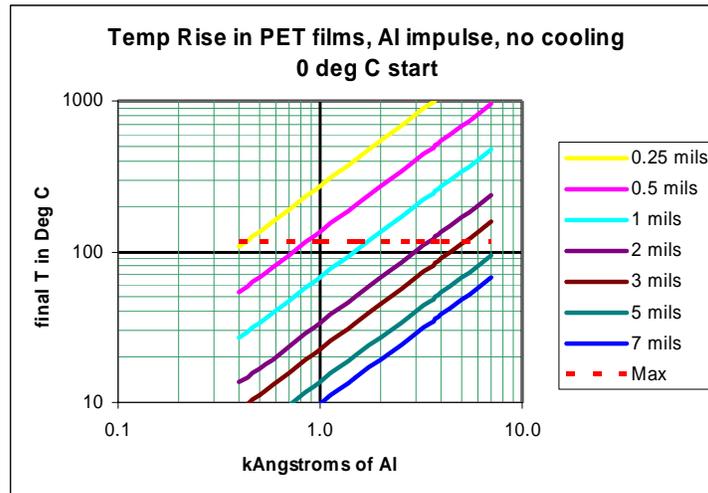

Figure 3. Heat deposited in the various webs per kÅ of Al by evaporation

We have shown 115 °C as a temperature to start worrying about web deformations. We assumed the drum starting temperature was 0 °C.
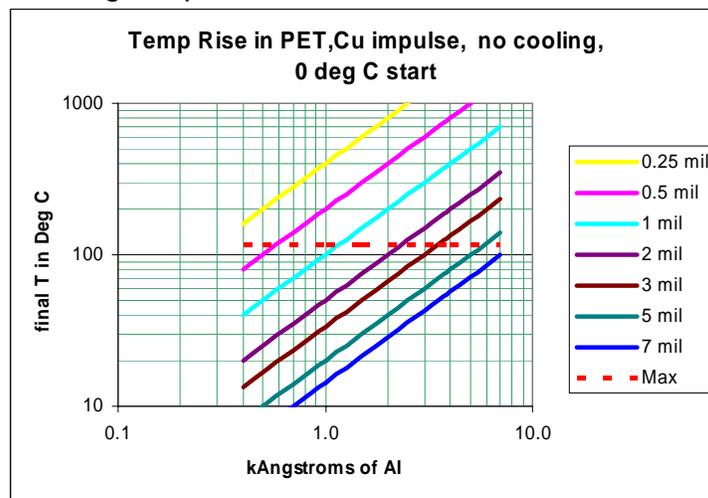

Figure 4. Heat deposited in the various webs per kÅ of Cu by evaporation

As you can see, many sins are possible when using the thicker webs customary for transparent electrode materials for displays. These are essentially the parameters of free span coating.

How fast can we run in a more typical machine (non Lithium)?

To keep out of proprietary problems we used the published rate data of Schiller for a fast Al machine (Schiller 1995) for 12 g/min wire feed into big boats at 10 cm spacing and about 65% collection efficiency on the web. As you can see at 0.04 µ (400 Å) you can fly and at 3 µ you can almost time the process with a sand glass.

**Speed vs. Thickness, Al coating,
1 drum, standard systems, evap.**

12 g/min of Al wire per boat
10 cm boat spacing
65% collection efficiency

Max possible speed, m/min

1000
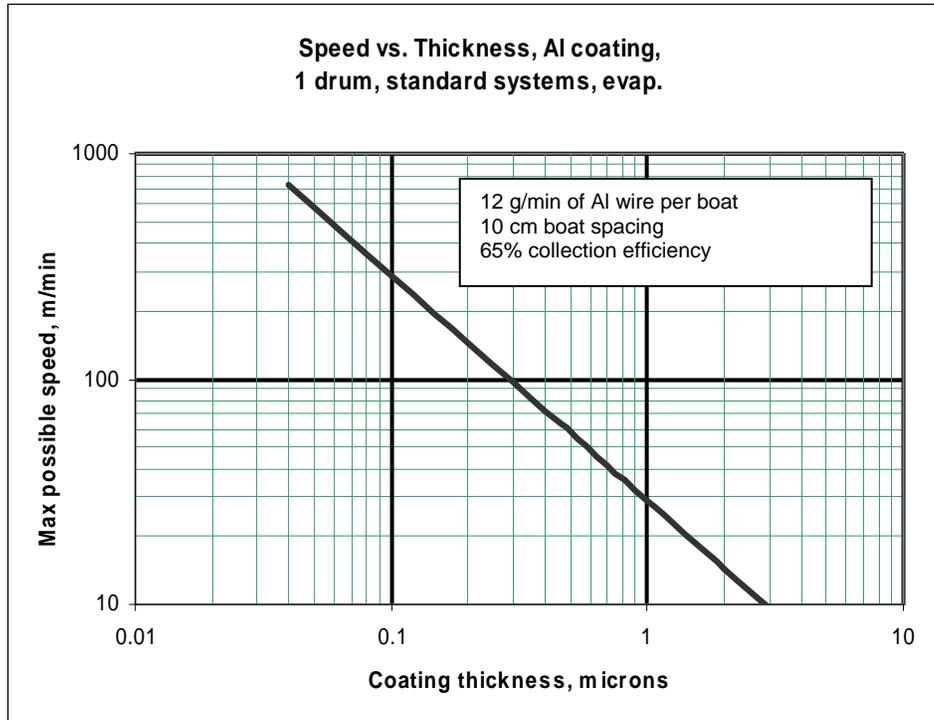
100

10

0.01

0.1

1

10

Coating thickness, microns

Figure 5. Web speeds for a single bank of large Al evaporating boats.

Copper coating is not quite as fast, but still in the ballpark.

Consider sputtering?

If we use the published data of rates at about 11 W/cm^2 (Johnson, 1984) we get figure 6 for a single planar cathode rate.
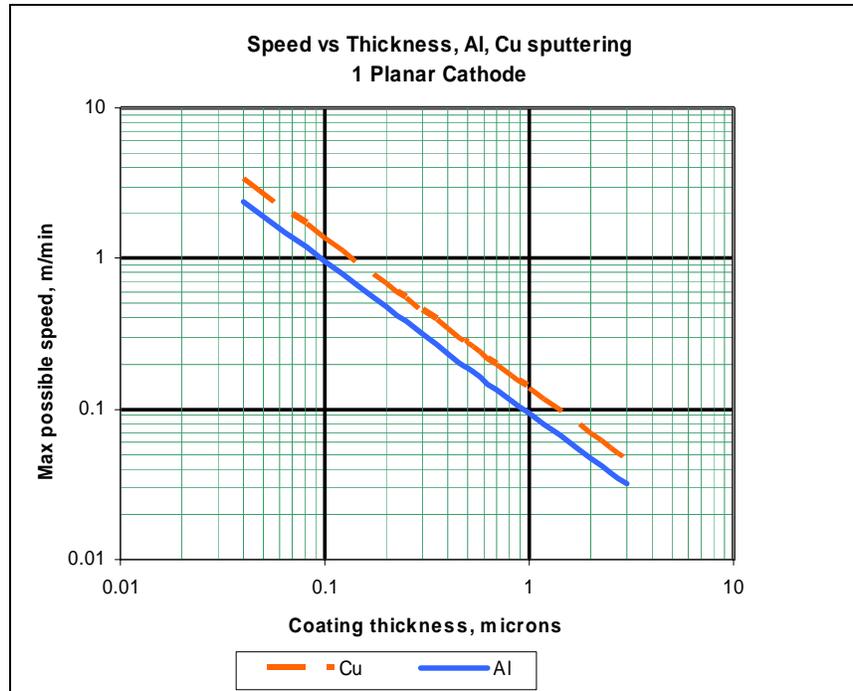
Figure 6. Web speeds for a single planar cathode.

Of course we can go much faster with more cathodes. Just draw new lines parallel to the starting values. This will gladden the hearts of the machine manufacturers. Rotary Cathodes can apply more power to the problem and achieve better rates. But notice that the single source sputter graph tops out where the evaporation chart begins. At these slower speeds, though much cooling can and must occur to prevent web damage.

Table 1 compares the approximate deposited energy for Cu and Al by evaporation and by sputtering.

	Energy deposited in Web	
	Evaporated	Sputtered
	kJ/μ*cm^2	kJ/μ*cm^2
Cu	5.29E-03	1.63E-02
Al	3.51E-03	1.06E-02

Table 1. Comparison of heat in web from Evaporation process (fast) and sputtering.

The delicate issue of cost:
Discuss it with the machine manufacturers! These thick coatings will run very slow compared to packaging rates. The cost of the machine will be a very significant part of the cost per square meter. However there is an asymptotic cost that every body has to pay in energy per gram or cm^3. We have to get it from the solid form into a gas, condense it, and chill the result to near room temperature. We used the generally accepted values for heats of condensation, fusion, and specific heat to cool to room temperature. Since radiant energy is only about 5% of the problem when the sources

are really cooking, we ignored it as a cool down cost. We assumed $0.07 per kW*hr for electricity prices. Assuming some published efficiencies these numbers look like:

Cost per m^2 for power, consumables, but not metals of a 1 μ coating			
	evap energy	evap+boats	sputt energy
Cu	$ 0.00446	proprietary	$ 0.133
Al	$ 0.00296	$ 0.011	$ 0.131

Table 2. Rough power costs of evaporation and sputtering processes.

These numbers were calculated from published values of 11 W/cm^2 sputter power density on planar cathodes. That runs about 80 Watts/linear cm of racetrack power (Johnson 1984).   That is about as much power as we like to see with simple target bonding systems. For Al it is apparent that sputtering is out of consideration. Of course rotating cathodes using pipes of Cu or Al could go faster, but they will consume about the same energy per gram of deposit. The cost of the Cu evaporation boats that we use are considered proprietary and we have left out the data. They are much more expensive than the average Al boat. We get significantly more life per evaporated kilogram of Cu but of course Cu is much denser. This table shows that the cost of the consumables used up in evaporation are very much to be considered in the thick coatings.

Conclusions:

Very thick vacuum coatings of metals are practical in some situations. The heat deposited in the web can be handled in one of two ways: Direct transfer to the drum in one pass or multi-pass coating. You must very carefully cost out the running cost of the machine and the finance costs for these slow processes.

References:

1. Progress in Vacuum Deposited Lithium Metal Anode Structures, R. Swisher, E. Yadin, G. Pipkevich, The 18th International Seminar & Exhibit on Primary & Secondary Batteries, March. 5, 2001

2. Vacuum Heat Transfer Models for Web Substrates: Review of Theory and Experimental Heat Transfer Data M. Roehrig and C. Bright, and D. Evans, SVC 43rd Annual Technical Conference Proceedings, April 2000

3. Reactive Aluminum Oxide Coating of Plastic Films-Possibilities and Limitations for High Deposition Rates, S. Schiller, M. Neumann, H. Morgner and N. Schiller,

Society of Vacuum Coaters 38th Annual Technical Conference Proceedings, 1995

4. Scientific Foundations of Vacuum Technique, Dushman, S., John Wiley & Sons, 1962, pp 691-705

5. Web Substrate Heating and a Thermodynamic Calculation Method for Li Film Thickness in a Thermal Evaporation System, J. Affinito; M.J. McCann, C. Sheehan and S. Bullock, SVC 44th Annual Technical Conference Proceedings— April 2001