The behavior of gases and vapors in materials is often an important factor in vacuum coating. The simplest form of gases or vapors in solids is that of solubility. Many metals will “take up” hydrogen, and most polymers will take up water vapor. Metals with hydrogen in them may be embrittled. For example, high-strength steel can become brittle with the inclusion of hydrogen during electroplating, and the hydrogen must be carefully baked out to regain its toughness. This is a problem with electrolytically deposited chromium in that the metal is “charged” with hydrogen.

Some polymers have residual water in them from their formation process (e.g. Kapton® about 2%). Processes such as hot injection molding, form polymers with very low concentrations of moisture. This can be maintained if the environment is controlled before coating. Water vapor in a polymer can present problems with outgassing during processing.

The solubility limit is the maximum amount of gas or vapor that the material can take up and be in equilibrium with its surroundings. For example, if you soak nylon in water for a long period of time it will absorb over 10 weight percent (10 wt%) water. To reach equilibrium and maximum solubility often requires long periods of time; therefore, the process, handling, and storage history of the material is important in determining how much water vapor may be in a polymer. If it is stored on a loading dock in the rain for a long period of time, it will have more water vapor in it than if it was stored in a room with low humidity.

How does the gas or vapor get into a solid? “Diffusion” is the term used for the movement of a gas or vapor into, through, or out of a solid. Diffusion is driven by a concentration gradient, and the gas or vapor moves from a high concentration to a lower concentration. The rate of diffusion is called the “diffusivity” and depends on a number of factors and mechanisms. For example, water vapor will diffuse into a low-density polymer faster than it will into a higher density form of the same polymer. There may be several different mechanisms for diffusion. In metals, diffusion may occur along grain boundaries, through the bulk grain, or if there are free surfaces (such as in a porous material) by surface diffusion. The diffusion rate is also dependent on the temperature. Higher temperatures give higher diffusion rates.

Gases and vapor get out of a solid in the same manner as they get into the solid – by diffusion under a concentration gradient and as a function of time and temperature. Figure 1 shows the typical outgassing of various polymer materials in vacuum as a function of time as measured by weight loss. Note the long times involved. If the outgassing doesn’t stop as a function of time, it is an indication the polymer may be decomposing at that temperature.

Outgassing prior to deposition is important in preparing a material for vacuum coating. Outgassing during deposition can give a porous, nonadherent coating. It is generally much easier to keep moisture out of a material through proper handling and storage than it is to eliminate it. In some cases, mobile species, such as water vapor, are sealed into a polymer material by a surface coating (called a “basecoat”) of a low-permeation rate material such as a UV curing epoxy.
Permeation is the movement of a gas or vapor through a material from one side to the other. An important packaging problem is the permeation of water vapor through a coated or uncoated polymer film or container. This is called the "water vapor transmission rate" (WVTR). One unit that is used to measure the WVTR is g/m²/day, where g is grams of water. Another permeation problem is the oxygen transmission rate (OTR). One unit for the OTR is cc/m²/day, where cc is a standard cubic centimeter of oxygen. Permeation through a vacuum coated polymer can produce problems. For example, a polymer film may be aluminum metallized on the front side to prevent water vapor from entering, but water vapor can permeate from the backside and cause loss of film adhesion.

In sputter cleaning of substrates, inert gases can be physically incorporated into the surface region by implantation of the bombarding gaseous species into the near-surface region of the material ("subplantation"). Generally it takes ions having several hundreds of electron volt (eV) energy to physically penetrate into a metal surface. In crystalline materials, these implanted atoms may be trapped by lattice defects and reach several atomic percent (at%). Inert gases trapped in the near-surface region beneath a film may cause long-term adhesion problems if they migrate to the coating-surface interface during subsequent processing or service.

Gas incorporation can be a concern in various types of vacuum coating processes. Energetic inert gas ion bombardment during deposition is used to densify the depositing coating and tailor some of the coating properties. High-energy particles that enter the surface are easily trapped by subsequently deposited material. In some cases, over 20 at% of the inert bombarding gas has been incorporated in the vacuum deposited material [1, 2]. This physically incorporated gas can be released to the detriment of adhesion and other coating properties. Heating during deposition minimizes gas incorporation. By using ion energies below about 200 eV and high ion bombardment currents, densification can generally be obtained at low temperatures without gas incorporation.

The presence or impact of gases or vapors in materials is often overlooked but can be a significant problem.

References