SVC Topics

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PVD Processes: Reactive Cleaning

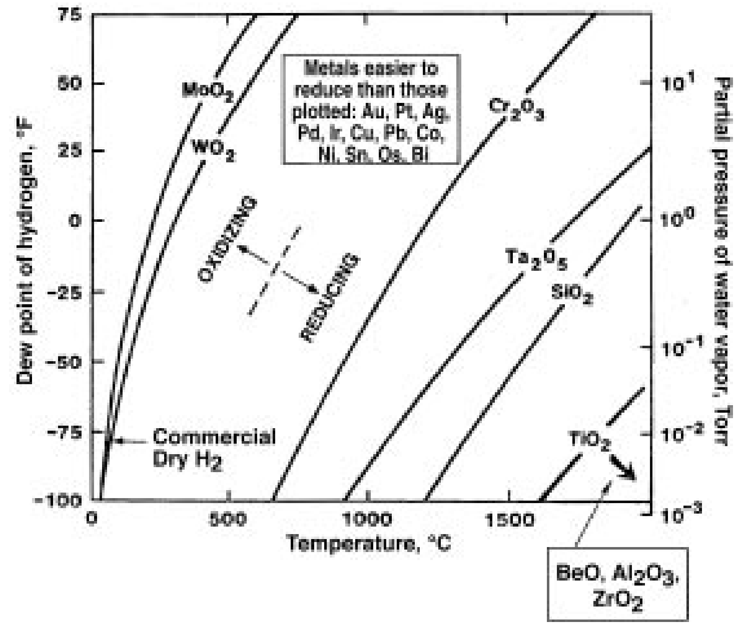
Reactive cleaning uses liquids, gases, vapors or plasmas to react with the contaminant (cleaning) or the substrate surface (etching) to form a volatile or soluble reaction product. If non-volatile products result from the reaction (*e.g.*, silicone oil with oxygen to form silica), a residue is left on the surface. This residue is sometimes easier to remove than the initial contaminant.

Oxidizing solutions are often used for reactive cleaning. Oxidation is the loss of an electron to another atom—typically oxygen (O), chlorine (Cl), fluorine (F) or bromine (Br). Oxidative cleaning can be used to clean hydrocarbon oils from surfaces. Oxidative cleaning using oxygen on hydrocarbons, for example, produces carbon monoxide and water. Oxidative cleaning is applicable to surfaces that can stand the oxidizing environment, such as glass, or those that form stable oxide surfaces, such as silicon. Surfaces that progressively oxidize (corrode) in the oxidizing environment, such as copper, cannot be cleaned by oxidation.

Types of Reactive Cleaning

Reactive gas cleaning uses a reaction with a gas at high temperature to form a volatile material. High-temperature “air fire” is an excellent way to clean surfaces that are not degraded by high temperature. Alumina (Al_2O_3), for example, can be cleaned of hydrocarbons by heating to 1000 °C in air. This technique is used in kitchens with self-cleaning ovens, which are cleaned by air-firing at about 400 °C.

The use of oxidation by ozone (O_3), created by ultraviolet radiation (UV/ozone cleaning) at atmospheric pressure and low temperature, has greatly simplified the production, storage and maintenance of hydrocarbon-free surfaces. The UV is produced by a mercury vapor lamp in a quartz envelope, so that both the 1849 Å and the 2537 Å radiation are transmitted. The short wavelength radiation causes bond scission in the hydrocarbon contaminants and generates ozone, which reacts with the hydrocarbon to form volatile CO and H_2O. Typical exposure times for UV/O_3 cleaning are from a few minutes to remove a few monolayers of hydrocarbon contamination, to hours, days or weeks for storage of cleaned surfaces. In a correctly operating UV/O_3 cleaning chamber, ozone can be detected by smell when the chamber is opened. The smell is similar to that of the air after a lightning storm, and indicates that the ozone concentration is <10 ppmbv (parts per million by volume). Higher concentrations of ozone deaden the olfactory nerves and are harmful. The UV/O_3 cleaning technique has the advantage that it can be used as a dry, in-line cleaning technique and storage environment at atmospheric pressure.



Metal-metal oxide equilibrium diagram for hydrogen plus water, as a function of temperature.

Hydrogen peroxide (H_2O_2) is a good oxidizing solution for cleaning glass. Boiling 30-percent unstabilized H_2O_2 is often used. Commercial hydrogen peroxide is often stabilized, which reduces the release of free oxygen. The hydrogen peroxide that is available at drugstores is two percent and stabilized. Unstabilized 30-percent H_2O_2 is available from chemical supply stores and must be refrigerated to slow decomposition. Hydrogen peroxide is sometimes used with ammonium hydroxide to increase the complexing of surface contaminants, and is used at a ratio of:

$$8\ (30\%\ H_2O_2) : 1\ (NH_4OH) : 1\ (H_2O)$$

The decomposition rate of the H_2O_2, however, is greatly increased by combination with ammonium hydroxide.

In cleaning silicon, the ammoniacal hydrogen peroxide solution may be followed by an acid rinse, known as the RCA cleaning procedure. This solution has been shown to be effective in removing hydrocarbon and particulate contamination from a surface. A recent version of the RCA technique is called the modified RCA cleaning procedure, and is performed using the following steps:

1. H_2SO_4:H_2O_2 at a ratio of 4:1
2. HF:deionized (DI) water 1:100
3. NH_4OH:H_2O_2: DI water 1:1:5
4. HCl:H_2O_2:DI water 1:1:5
5. DI rinse

Many acid-based systems can be used as oxidants. One system commonly used in the semiconductor industry is the piranha solution, which is hot (>50 °C), concentrated (98%) sulfuric acid, plus ammonium persulfate. The addition of the solid ammonium persulfate to the hot sulfuric acid produces peroxydisulfuric acid, which reacts with water to form H_2SO_5 (Caro's acid) and further decomposes to form free atomic oxygen. The ammonium persulfate should be added just prior to the immersion of the substrate into the solution. The effectiveness of this oxidation technique can be shown by first placing a piece of paper in the hot sulfuric acid, where it is carbonized, then adding the ammonium persulfate and watching the carbon disappear.

A hot chromic-sulfuric acid cleaning solution, prepared from potassium dichromate and sulfuric acid, provides free oxygen for cleaning, but has a tendency to leave residues. The surface, therefore, must be rinsed very thoroughly. Disposal of the waste material is also a problem.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

Oxidative cleaning can be performed using chlorine-containing chemicals. A water slurry of sodium dichloroisocyanurate (*i.e.*, swimming pool chlorine), for example, which has 63-percent available chlorine, can be used to scrub an oxide surface to remove hydrocarbon contamination. The combination of mechanical scrubbing with oxidation improves the cleaning action.

Anodic oxidation in an electrolysis cell can be used to clean surfaces. Carbon fibers, for example, which are formed by the pyrolysis of polymer fibers, have a weak surface layer. This layer can be removed by anodically oxidizing the surface in an electrolytic cell, followed by hydrogen firing. This treatment increases the strength of the carbon fiber and improves the bond when the fiber is used as part of a composite material.

Reactive plasma cleaning (etching) uses a reactive species in the plasma to react with the surface to form a volatile species that leaves the surface at much lower temperatures than those used for reactive gas cleaning. Oxygen (pure or from pure "medical" air) and hydrogen (pure or as forming gas) are used for plasma cleaning. Fluorine (from SF_6, CF_4, CHF_3, C_2F_6, or C_3F_8) and chlorine (from HCl, CCl_4 or BCl_3) are used for plasma etching. Most metals are more easily etched using a fluorine plasma, rather than a chlorine plasma, because the metal fluorides are generally more volatile than the metal chlorides. An exception is aluminum, which is commonly etched using BCl_3.

Mixtures of gases are often used for etching and cleaning. Oxygen can be added to the fluorine plasma to promote the formation of atomic fluorine and to oxidize the surface, which is then rapidly attacked by the fluorine, increasing the etch rate. A common gas mixture used to etch silicon is 96-percent CF_4 with 4-percent O_2. When an oxygen plasma is used to clean hydrocarbons from surfaces in a vacuum, the reaction of the oxygen with carbon on the surface can be monitored using a mass spectrometer to determine the CO and CO_2 that are produced.

Hydrogen reduction of oxide layers can be used to clean surfaces in a high-temperature environment. The figure shows the stability of a number of metal oxides at various temperatures and varying dew points (water content) of the hydrogen. For many metals, depending on the dew point and temperature, a hydrogen environment can either be reducing or oxidizing. Dry hydrogen, for example, will reduce the oxide on chromium at 1000 °C, while wet hydrogen will oxidize chromium at the same temperature. The amount of water in the hydrogen is controlled by bubbling dry hydrogen through a water bath.

The use of a hydrogen plasma allows the hydrogen reduction of the oxide to take place at a lower temperature than is necessary using thermal reduction. Reduction of silicon oxide using dry hydrogen, for example, requires a temperature of about 900 °C, while reduction with a hydrogen plasma can be accomplished at 500 °C. Hydrogen plasmas can be used to remove hydrocarbon contamination when oxygen plasmas are unacceptable. High-temperature hydrogen or forming gas (90% N_2 : 10% H_2) removes hydrocarbon contamination by hydrogenating the contaminant and making it more volatile. This technique is used to clean the stainless steel vacuum surfaces in nuclear fusion reactors. Hydrogen cleaning can change the surface chemistry of some materials. Dry hydrogen firing of a lead-containing glass, for example, produces a metallic lead surface by reducing the PbO to lead on the glass surface. ***P&SF***