

Figure 1. Arc evaporation technology.

Closed-field Unbalanced Magnetron Sputtering

In cases where coating roughness should be extremely small (e.g. jewelry), magnetron sputtering is used as the deposition technology. Another advantage of this technology is a wider choice of target materials, metals and non-metals. In case of bad or non-conductivity of the target material, pulsed DC or RF sputtering can be used. Therefore, this technology offers more freedom in coating design. As the ionization level of the sputtered material is limited to a few percent, these ions cannot be used for the energetic bombardment of the growing film, which is necessary to produce densely structured coatings. To increase the plasma density and the Ar^+ ion concentration close to the products, strong magnets are used on the outside of the cathodes to push the magnetic field lines into the chamber and create an unbalancing effect. The effect is enhanced by strong electromagnetic coils that surround the cathodes. This leads to an increased Ar^+ ion bombardment of the film that is necessary to produce hard and dense coatings. The polarity of the unbalanced magnetron cathodes is altered from one position to the other, leading to the so-called closed-field configuration and almost no loss of electrons to the anode area, giving maximum plasma density near the products.

A typical disadvantage of the sputtering technology is the need for higher bias potentials on the products to generate sufficient ion bombardment. This leads to elevated process temperatures, which makes the technology less suitable for the deposition on low temperature substrate materials like ABS plastic. Depending on coating requirements, the process can also be more sensitive to small changes in reactive gas flow due to target poisoning.

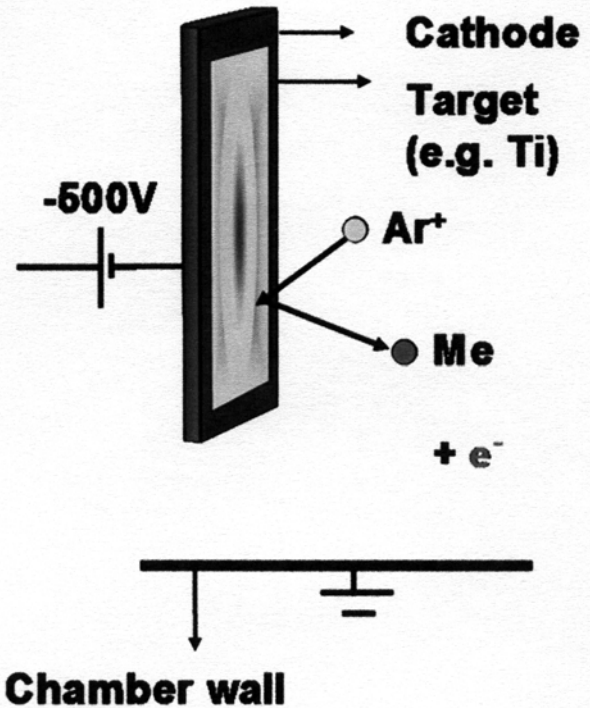


Figure 2. Magnetron sputtering technology.

Arc Bond Sputtering

The arc bond sputter technology [1, 2] combines both cathodic arc evaporation and magnetron sputtering in one cathode. A movable magnet plate is brought in the back position for arc evaporation and is moved forward to sputter the target material. This technology is mainly used to etch the substrate material with metal ions leading to an excellent adhesion, after which a smooth PVD coating can be applied by magnetron sputtering. The disadvantages of the technology are the lack of steering by electromagnetic coils in the arc evaporation mode and the compromise in magnetic field configuration.

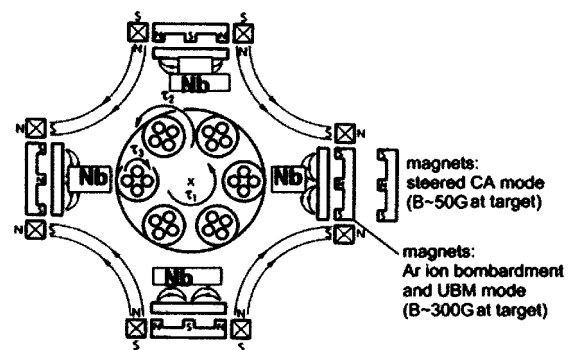


Figure 3. Arc bond sputter technology.

PVD DEPOSITION SYSTEMS

Large Scale Industrial Deposition Systems

The success of decorative PVD coatings followed the successful scale-up from laboratory size and small production installations to large scale industrial deposition systems including related infrastructure [3]. Besides the PVD installation, pre-heat and cool down stations, fast loading and cleaning equipment have been added to meet the demands of mass production of decorative coatings on consumer goods like faucets and door hardware. The chamber volumes of the installations for mass production range from 1 to 7 m³, effective deposition areas from 3 to 25 m². With an increase of the effective deposition area from 3 to 9 m² only leading to 20% higher batch coating costs, the coating cost price per product could be reduced by a factor of roughly 2.5, which opened up the market for decorative coatings in the sanitary and door hardware business. Reactive arc evaporation has been the most used technology in this application field, as it offers the best color uniformity on large products with difficult three-dimensional geometries. Loading densities can therefore be higher than for magnetron sputtering, further reducing the coating cost price per product.

Multiple Cathode Systems

The most ideal set-up for a PVD installation is the multiple cathode system. PVD chambers can be equipped with a combination of advanced controlled arc, closed-field unbalanced magnetron and arc bond sputtering cathodes [4]. Moreover, the different cathode positions can be equipped with various target materials like zirconium, titanium, chromium, niobium, alloys, and non-metals to have a very large flexibility in coating design (e.g. multilayers) without the need to change targets between batches. Examples of these benefits are:

- Addition of a stabilizing metal component to improve the oxidation resistance of grey, black coatings [5].
- The use of Nb metal ions to etch substrates prior to deposition in order to improve the corrosion resistance.
- Increasing the color window of decorative PVD coatings with combinations like ZrCrCN (antique gold color) and TiAlZrN by combined reactive arc evaporation/unbalanced magnetron sputtering (dark bronze color) [6].

Adaptation for Deposition on Various Substrate Materials

Many substrate materials are used in the decorative coating field. Typical examples are electroplated brass, die cast zinc, ABS plastic and materials like stainless steel and titanium. These materials have different degassing characteristics and temperature limitations. Modern PVD installations have the flexibility to coat on all of these substrates. Over the last decade, the use of ABS plastic has grown rapidly. This material has a very open sponge-like structure that adsorbs a lot of water vapor. When a large volume PVD chamber is

filled with ABS plastic, degassing becomes a very important issue. The products cannot be dried at elevated temperatures, the product temperature is limited to roughly 65°C, limiting the ion bombardment possibilities during the etching and deposition phases. Excessive degassing can lead to cracking of the water vapor molecules in the plasma and subsequent incorporation of oxygen in the coating. This can lead to adhesion problems when the oxygen partial pressure is too high during etching and non-uniform, non-reproducible colors of the ceramic hard coating. One approach to solving this problem is a very long pump down cycle to achieve a low base pressure. However, this will lead to higher coating costs. A more favorable method is the use of cryo panels in the PVD chamber to increase the pumping speed for water vapor and offer a cooling method for the products. This technology enables rapid cycle times for ABS plastics in the same range as electroplated brass.

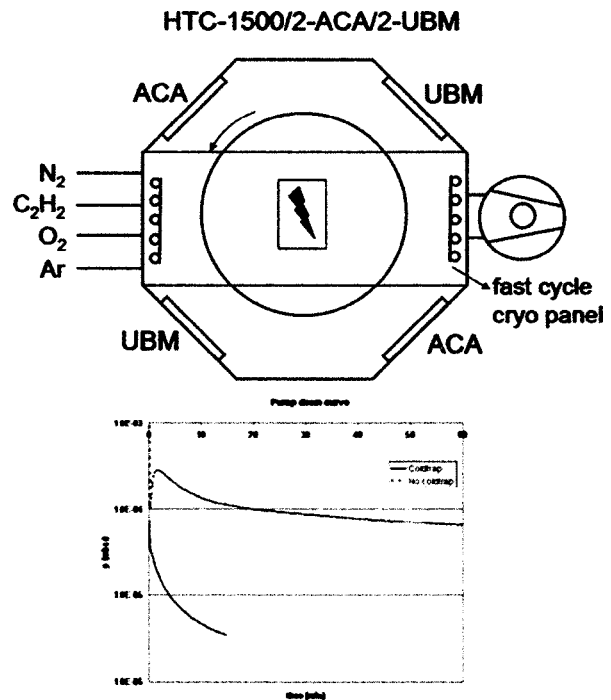


Figure 4. HTC-1500 system including fast cycle cryo panels and typical pump down curve.

PVD COATING COLOR POSSIBILITIES

Metal Nitrides and Carbonitrides

Nitrides and carbonitrides of metals like titanium, zirconium and chromium offer metal-look color possibilities like brass, gold, bronze, stainless steel, nickel, and dark chrome. Figure 5 shows these colors in CIE L*a*b* values [7].

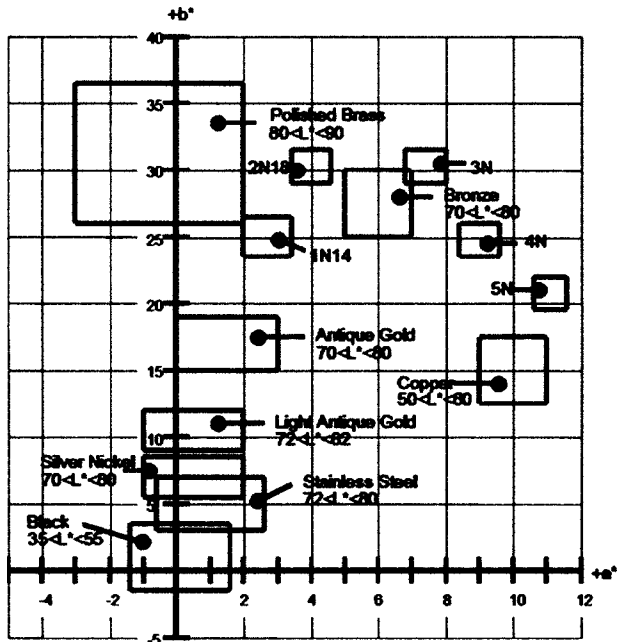


Figure 5. Color possibilities for decorative PVD coatings.

The dependence of the metal (carbo) nitride colors on reactive gas flows have been studied in detail for reactive arc evaporated coatings. These studies have shown that the color is mainly determined by the stoichiometry of the layer and to a much smaller extent on the structure of the film. An example of the color dependence of reactive arc deposited ZrCN coatings on stoichiometry is shown in Figure 6 [8]. All of these colors can be produced at different process temperatures and on different substrate materials. As is obvious from the above figures, the colors are limited to metal-look finishes, mainly in the yellow-red quadrant of the CIE L*a*b* spectrum.

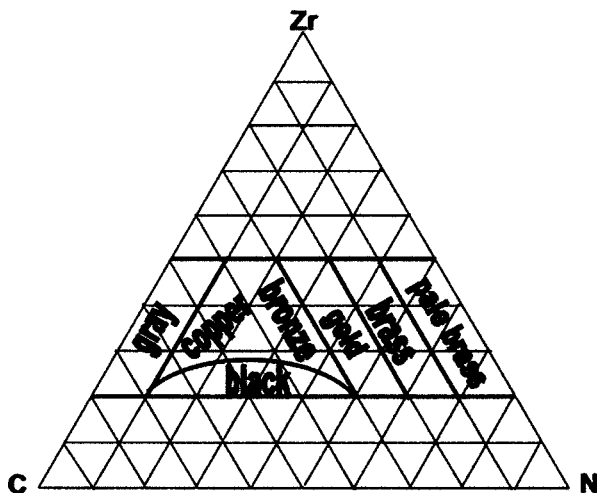


Figure 6. Colors in Zr-C-N ternary diagram.

Metal Oxides

The color window of decorative PVD coatings can be widened by the use of oxygen as a reactive gas [9]. Metal oxides can be produced by evaporating or sputtering the target material in an (argon)/oxygen atmosphere. In this way, (partly) transparent PVD coatings are produced which have colors based on interference effects. Figure 7 shows the principle of the quarter wavelength effect of a transparent layer: extinguishing light with a wavelength of 4 times the coating thickness. When coating thicknesses are chosen in the range of 100 to 200 nm, light with wavelengths in the visible range are extinguished. In this way, primary colors like blue and green can be produced. As the color of the coating is determined by the coating thickness, it is very difficult to achieve color uniformity on three-dimensional products. Only purple and blue colors can be produced with an acceptable uniformity, as these colors are obtained at the lowest coating thicknesses, where color deviations are small. The uniformity problems can be overcome by a combination of PVD technology and wet chemistry.

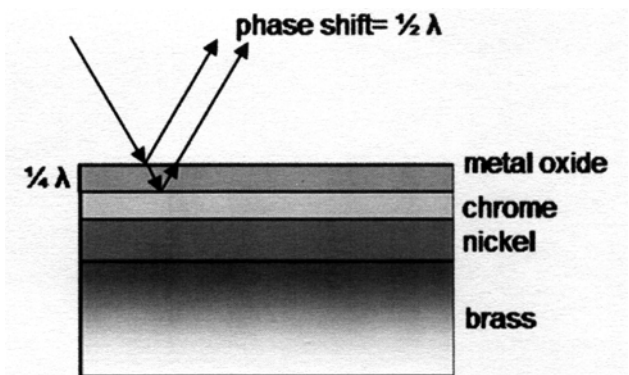


Figure 7. Optical interference, $1/4 \lambda$ effect

Metal Oxides by Anodization

High quality Nb_2O_5 layers have been produced by anodic oxidation of unbalanced magnetron sputtered niobium films. The coatings have been produced using arc bond sputter technology, the arc mode has been used to etch the products with Nb ions, leading to a certain amount of Nb implantation into the substrate material and excellent coating adhesion. Due to the high melting point of Nb, droplet formation during the ion etching step is limited, leading to very smooth coatings. After the deposition of the Nb coating, the film has been anodized in a weak (1%) aqueous electrolyte of citric acid, producing a very dense oxide layer with a low surface defect density. The thickness of the oxide layer D_{ox} is determined by the applied voltage U_a during the anodization step according to the following expression:

$$D_{ox} = \alpha U_a \text{ (with } \alpha \text{ the voltage rate of the oxide growth)}$$

With the right selection of anodization voltage, Nb₂O₅ can exhibit all colors in the visible spectrum, based on the optical interference effect. Table 1 shows the colors of the Nb₂O₅ layers depending on the anodization voltage.

Table 1. Colors of anodized Nb coatings.

Voltage (V)	L*	a*	b*	Color
10	65	0	36	Champaign
20	70	32	-46	Dark blue
30	75	-9	-22	Light blue
40	87	-5	3	Colorless
50	71	-10	45	Antique gold
60	63	6	59	Pink
70	70	67	-58	Purple
80	70	-33	-16	Turquoise
90	78	-36	40	Green
100	75	-17	58	Light green

A variety of mechanical and electrochemical tests have proven the excellent wear and corrosion resistance as well as the high biocompatibility of the anodic oxide of Nb [10].

CONCLUSION

The use of decorative PVD coatings in industry has grown rapidly in the last decade following the introduction of large scale industrial deposition systems. These systems are equipped with multiple cathodes and offer different deposition technologies like advanced controlled arc evaporation, closed-field magnetron sputtering and arc bond sputtering, offering a very large flexibility in coating design. The systems have also been modified for the deposition on different kinds of substrate materials: fast cycle cryo panels have been added to enable fast deposition on ABS plastic. The available color range of decorative PVD coatings has widened considerably, from metal nitrides and carbonitrides with metal look colors like brass, gold, bronze, nickel stainless steel, and grey-black to metal oxides with elementary optical interference colors like blue, green and red. Niobium oxide films have also been produced by a combination of PVD technology and anodization, resulting in smooth, dense, high quality layers with excellent adhesion, wear and corrosion properties.

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