

#### **TALAT Lecture 5205**

## **Plating on Aluminium**

19 pages, 23 figures

Level: Advanced I

prepared by P. Møller, Dansk Technisca Hoogschol, Lyngby

#### **Objectives:**

 to describe the processes of electroless, electrolytic, as well as physical and chemical vapour deposition of metals on the aluminium surface in order to achieve variations in its surface properties for functional and decorative purposes

#### **Prerequisites:**

- knowledge of the surface properties of metals, metallurgy and electrochemistry of aluminium
- TALAT lectures 5101, 5102, 5105

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# 5205 Plating on Aluminium

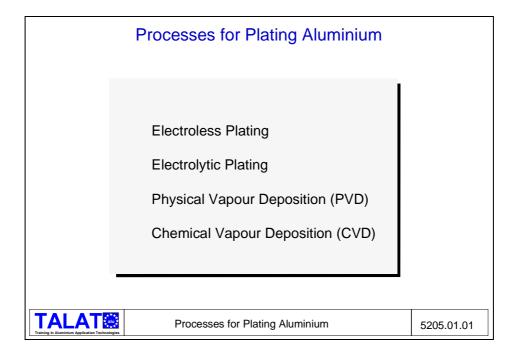
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#### **5205.01 Plating Characteristics of Aluminium**

The processes for plating on aluminium can be divided into the following groups (**Figure 5205.01.01**):

- Electroless Plating
- Electrolytic Plating
- Physical Vapour Deposition (PVD)
- Chemical Vapour Deposition (CVD)



The group of electroless methods can be defined as: Reactions taking place as a result of chemical action, i.e. no external source of electric power is present.

The group of electrolytic methods can be defined as: Reactions taking place as a result of electrochemical action, i.e. an external power supply is used.

PVD processes can be defined as: Reactions taking place between a gas and a solid due to high physical action to the solid. The mixed gas plates on the surface at low pressure and high temperature.

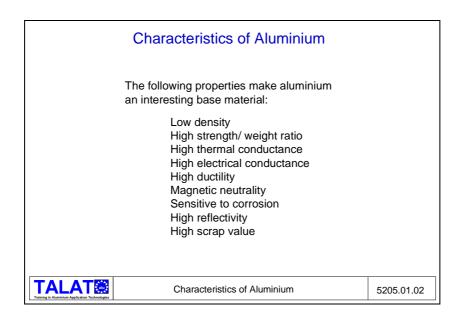
CVD processes can be defined as: Reactions taking place due to chemical reactions taking place in vaporised gas under high temperature and low pressure.

These definitions may overlap, but can be used for a preliminary division into groups.

#### Aluminium Characteristics:

Some basic characteristics of aluminium are (**Figure 5205.01.02**):

- Low density
- High strength/weight ratio
- High thermal conductance
- High electrical conductance
- High ductility
- Magnetic neutrality
- Sensitive to corrosion
- High reflectivity
- High scrap value



#### Problems of Plating on Aluminium:

There are a number of difficulties to be considered when electroplating on aluminium (**Figure 5205.01.03**):

- 1. Aluminium is amphoteric, i.e. it is dissolved in both alkali and acid.
- 2. The difference in potential, between the aluminium matrix and second phase constituents can affect the deposition reaction.
- 3. The position of aluminium in the electrochemical series can lead to formation of immersion deposits in the plating solution.
- 4. The coefficient of thermal expansion of aluminium and its alloys differs from most of the metals commonly deposited on it.

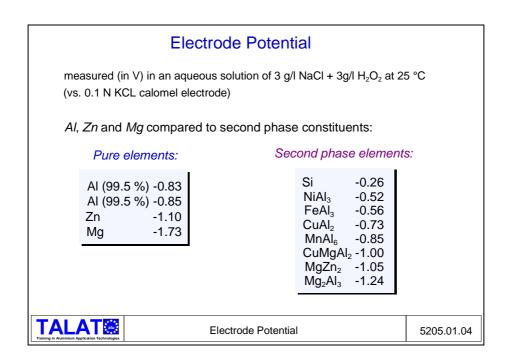
5. The difference in atomic diameter and crystal lattice structure between the aluminium substrate and the metal deposited on it.

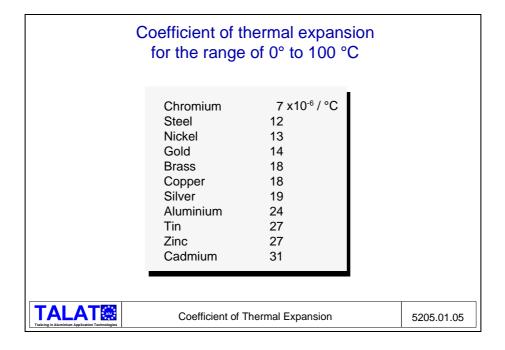
#### Difficulties in Plating Aluminium are: Aluminium is amphoteric aluminum is dissolved in alkaline and acidic solutions Aluminium is very reactive due to the position of aluminium in the electrochemical series ion-exchange reactions can occur in the processing solutions **Alloying constituents** phases containing alloying elements can have a potential different from the matrix High coefficient of thermal expansion coating and aluminium do not expand equally Difference in atomic diameter and in crystal lattice structure TALAT Difficulties in Plating on Aluminium 5205 01 03

One of the major things to be considered when plating on aluminium is the readiness by which aluminium reacts with the air to form oxide. Direct plating processes (see later) can eliminate this, but are not so commonly used. It is also important to notice that aluminium is amphoteric, i.e. aluminium is dissolved in both acidic and alkaline plating baths. Due to the reactivity of aluminium unwanted ion-exchange processes are also likely to occur in the plating solution. All of these characteristics can be eliminated by using an intermediate pretreatment layer deposited by ion-exchange plating (zincate or stannate process as described later).

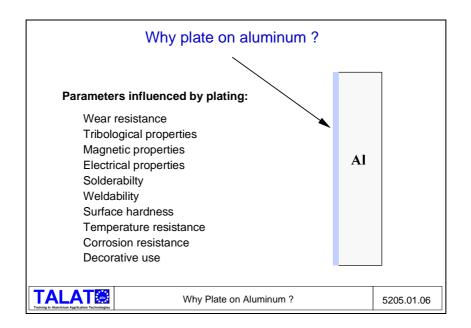
The *electrode potential* of aluminium compared to some other metals shows that differences between aluminium and pure elements as well as second phase elements can be considerable (**Figure 5205.01.04**). This shows that proper care should be taken when plating on aluminium to avoid alloying elements giving big electrode potential difference leading to unwanted electrochemical actions during the plating process.

The *coefficient of thermal expansion* of aluminium is high compared to other metals. The consequence is that if the plated specimen is subjected to a temperature chock or temperature elevation the coating is mechanically stressed different than the substrate. This can course decohesion of the coating or form cracks through the coating. Especially if the coating adhesion to the substrate or the pretreatment layer is poor decohesion of the coating can occur, see **Figure 5205.01.05.** 

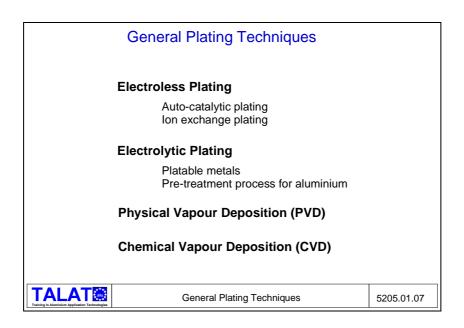




Though plating on aluminium is a relatively expensive technique, it is increasingly important because of the possibility of combining the low density of aluminium with the functional properties of the deposit (**Figure 5205.01.06**). Good results can be obtained with a suitable combination of metal and process. The platable metals are listed later. The achievable properties that can be added to aluminium are mechanical, magnetic, electrical, thermal, corrosive and decorative. As an example it could be interesting to add wear resistance (abrasive or adhesive wear), hardness and corrosion protection to aluminium. This would be possible with f.ex. an electroless nickel coating or a chromium coating.



Plating techniques can be divided in Electroless plating and electrolytic plating (**Figure 5205.01.07**).



Electroless plating is deposition of metal, usually nickel or copper from an aqueous solution by use of a reducing agent RA in the solution or by dissolution of the substrate whereby electrons are freed. The plated metal is dissolved in the plating solution as metal ions which plate on the surface.

Electrolytic plating is plating where the electrons are supplied by an external power supply. The plated metal is either dissolved in the plating solution and/or supplied by the anode material used (this is further explained under electrolytic plating).

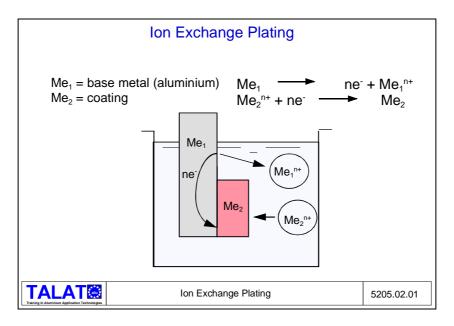
#### **5205.02 Electroless Plating**

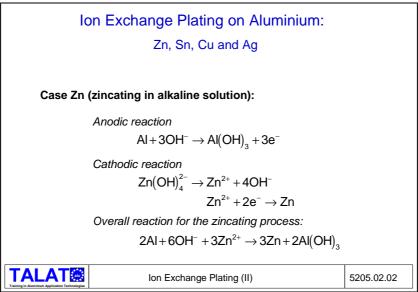
Electroless plating is used for engineering and electronic parts to give increased wear-resistance and in some cases corrosion resistance (special pretreatment) or the technique can be used as the primary step in a conventional electroplating sequence. The process has an excellent throwing power independent of the specimen geometry. The layer can be kept constant within a tolerance of only +/- a few percent also at the inside of tubes and holes. Only when the specimen contains gaps or hollow spheres where air or evolved gas can be captured, these areas will not be plated. As an example electroless nickel is used for computer hard-discs in combination with a magnetic material such as cobalt. Many mechanical precision parts are plated with electroless nickel to maintain strict dimensional tolerances. Composites of electroless nickel containing silicon carbide (SiC) or Teflon (PTFE) particles can increase wear resistance and decrease the coefficient of friction respectively.

Electroless plating can be subdivided in *ion-exchange plating* and *autocatalytic plating*.

The *ion-exchange plating* process is based on oxidation (dissolution) of the aluminium substrate whereby electrons are freed so that a reduction (deposition) of another metal coming from the aqueous solution is possible. (**Figures 5205.02.01** and **5205.02.0212**). The metals deposited by this technique are usually zinc or tin. The layers deposited are thin, because the deposition stops, when the aluminium is all covered and can no more supply electrons by oxidation. The processes are used as a pretreatment to plating (electrolytic- and electroless). These ion-exchange processes are known under the names: zincate-, stannate- or modified zincate/stannate-process. The electrolytic plating processes often require this pretreatment to improve the adhesion and to avoid the aluminium from getting dissolved in the plating bath, because aluminium is amphoteric (dissolves in both alkaline and acid solution).

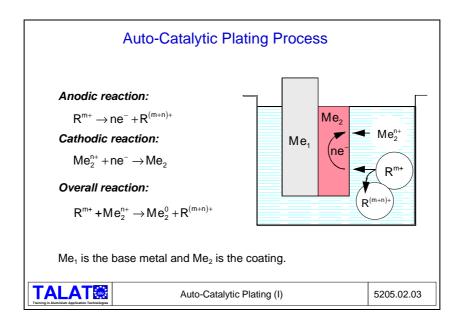
The *autocatalytic plating* process is driven by electrons freed by reduction of the reducing agent RA. These freed electrons join the metal ions in the solution and form solid metal on the surface (**Figure 5205.02.03**). Because the electrons are coming from the reducing agent the process can keep on running also after the substrate is covered, i.e. high coating thicknesses are possible. Electroless nickel is an example of autocatalytic plating (**Figure 5205.02.04**).

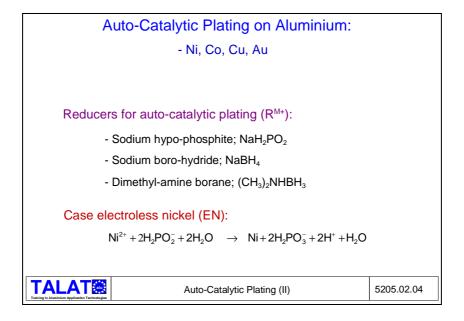




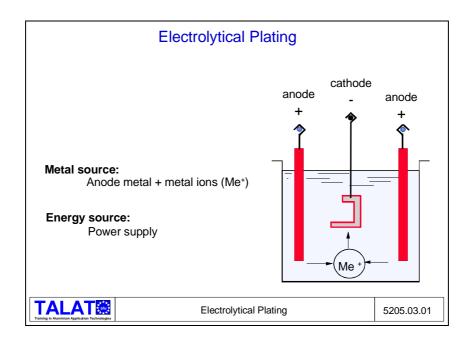
## 5205.03 Electrolytic plating

When plating by electrolytic plating the process is supplied with electrons from an external power (current) supply. The power supply can be regulated by a current or a potential limit. The negative pole (cathode) is connected to the sample to be plated. The plus (anode) is connected to one or more metal bars or sheets in the solution (**Figure 5205.03.01**). The anodes consist either of the plating metal or of a metal insoluble (in some cases titanium) in the bath solution. In both cases the bath solution contain the metal ions to be plated. They are added as metal salt. During the process the anodes will dissolve or if the anodes are insoluble more metal salt is added to maintain a certain concentration of metal ions.





The coating metal distribution on electro plated specimens is not homogeneous as it is for electroless plating. The coating will build up on corners and edges where the current density (A/dm²) is higher rather than in grooves and inner corners with low current density. Plating properly inside a narrow tube and similar shapes is normally not possible except if inner anodes are used in the tube. Coatings like chromium have a very bad distribution ability (throwing power). Chromium needles easily form on the edges of the specimen. To improve the coating distribution, if desired, the current distribution over the surface should be changed by using anodes that surround the surface to be plated. The anode to cathode distance should also be kept as constant as possible. If for example a metal sheet should not form needles at the edges, a current thief in the form of a wire around near the edges of the sheet can be used. The thickness distribution of for example zinc, silver and gold is normally not a problem except inside tubes etc.

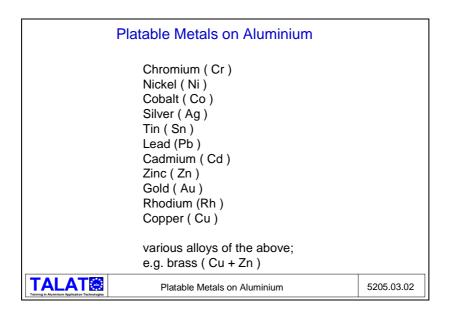


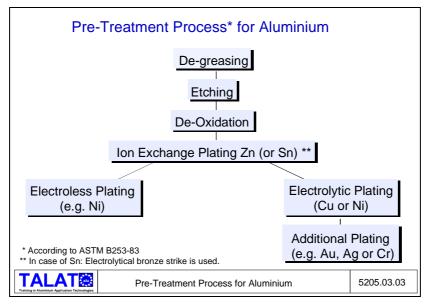
Plating on aluminium does as mentioned earlier often involve a pretreatment coating (zincate or stannate). This is the most commonly used method to plate on aluminium.

When the oxide is removed in the same bath as the electrodeposition takes place, i.e. no pretreatment in form of zincating or other, the process is called a direct plating process. It is possible to electrodeposit copper, nickel, silver, brass and chromium by using the direct plating method. This technique has only limited use in the industry. The most frequent technique used is to plate an intermediate pre-treatment layer, deposited by the ion-exchange technique as described earlier.

Some *common applications* of plated aluminium coatings are machine elements and many light weight components. The metals that are platable on aluminium either directly or by use of an intermediate zincate or stannate layer are many. The most common ones are chromium, nickel, silver, gold tin, zinc and copper (**Figure 5205.03.02**). Also many alloys of these are platable.

When the ion-exchange plating process is used as pre-treatment to electrolytic plating, correct process parameters are of great importance to the adhesion and corrosion resistance of the plated coating. The standard ASTM B253-83 specifies the correct pre-treatment process routines for aluminium (zincating etc.) (**Figure 5205.03.03**). It is especially important that the procedure of several succeeding coating and stripping procedures is followed when zincating. The zincating process should be repeated two to three times with the specified stripping of the zincated coating in sodium hydroxide in between. If this procedure is not followed the result could easily be a poor adhesion of the zincated layer to the aluminium. If the final top coating, f.ex. nickel, is plated on the poorly adhering zincate the result will be decohesion and flaking off of the top coating.





## **5205.04 PVD plating**

The vapour deposition methods are divided in two types:

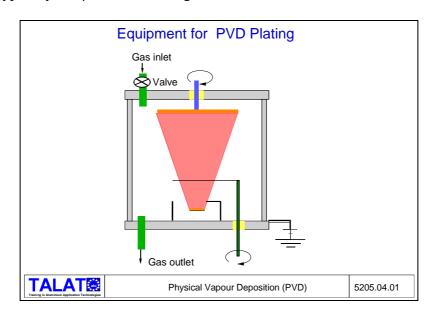
- Physical Vapour Deposition (PVD)
- Chemical Vapour Deposition (CVD)

PVD processes were defined as reactions taking place between a gas and a solid due to a high physical action to the solid. The mixed gas plates on the surface at low pressure and high temperature.

CVD processes were defined as reactions taking place due to chemical reactions in vaporised gas under high temperature and low pressure.

Plating on aluminium by the PVD process means heating the sample to 300-550°C. The

metal (f.ex. Titanium) is evaporated f.ex. by applying a high potential. The vaporised metal gas will react with the gas in the chamber (e.g. Nitrogen) and plate on the specimen surface (**Figure 5205.04.01**). It is not possible to plate into deeper grooves etc. Typically only the surfaces that are visible from the evaporator(s) of the solid metal will be plated. Typical coatings to be plated by PVD are Titanium Carbide (TiN) and Titanium Nitride (TiN) (**Figure 5205.04.02**). They have high hardness and low coefficient of friction. The coating thickness is typically 3-5 µm and has a high wear resistance on tools etc.

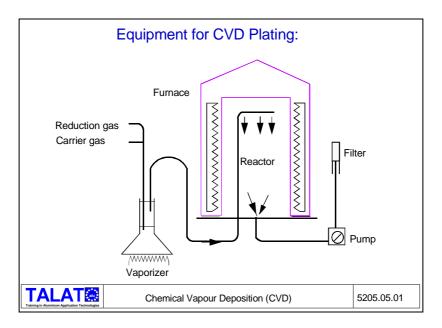


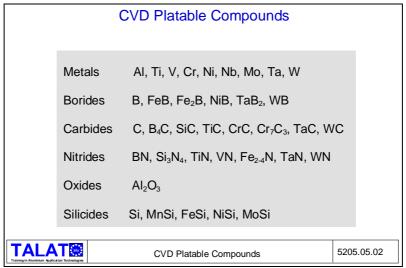
	PVD Platable Compounds	
Metals	AI, Si, Ti, Cr, Co, Cu, Zn, Ge, Se, Mo, Rh, Po Ag, Cd, In, Sn, Ta, W, Ir, Pt, Au, Pb	d,
Alloys	FeCr, NiCr, NiCrFe, Brass	
Carbides	B <sub>4</sub> C, SiC, TiC, CrC, MoC, RuC, TaC, WC	
Nitrides	$Si_3N_4$ , TiN, CrN, MoN, TaN, WN	
Oxides	Al <sub>2</sub> O <sub>3</sub> , SiO, SiO <sub>2</sub> , Fe-oxide, PbO	
Others	Graphite, Polyamide, PTFE, CaF <sub>2</sub> , Fe <sub>2</sub> B, MoS <sub>2</sub> , MoSe <sub>2</sub> , WS <sub>2</sub> , WSe <sub>2</sub>	
Training in Aluminium Application Technologies	PVD Platable Compounds	5205.04.02

Because of the high temperature involved, the process is not commonly used for plating on aluminium. Only a limited number of aluminium types will be able to manage these temperatures without being damaged or loosing their original shape. The process is under a constant development to reduce the process temperature and may therefore within years become generally usable for aluminium.

#### **5205.05 CVD Plating**

CVD plating involves heating to temperatures of 850-1200°C. At this temperature a chemical reaction between an evaporated metal and a gas takes place (**Figure 5205.05.01**). The coating will plate all over the surface of the specimen. Typical coatings are TiC and TiN. Also diamond coatings are possible (**Figure 5205.05.02**). The CVD coatings have high wear resistance and a low coefficient of friction. Typical coating thicknesses are 3-10µm.



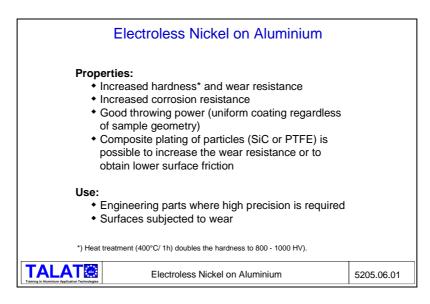


Because of the high temperatures involved, the thermal CVD methods are not usable for aluminium. But the chemical reactions can also be activated by a discharge method instead of the high temperature. By this method the temperature can be lowered to 100-800°C which will be acceptable for some aluminium types. These so called plasma CVD processes are not yet fully developed for tribological purposes, but a lot of effort is given by research institutions in this area. So in some years it may be possible to use CVD processes for aluminium also.

#### 5205.06 Cases on Plating Aluminium

There are many different reasons for wanting to plate on aluminium. Some of them were listed earlier in this text. To give an impression of applications some examples are given on solder ability, wear resistance and decorative uses.

Electroless nickel phosphorus (approx. 10% P) on aluminium (**Figure 5205.06.01**) is used to achieve some of these properties. The process can be used to increase the hardness of the surface and thereby increase the wear resistance of the coating. The Vickers Hardness of electroless nickel phosphorus is about 400-500 HV and can be doubled to 800-1000 HV by a heat treatment at 400°C for one hour. The adhesive wear resistance of electroless nickel phosphorus is comparable to that of hard chromium, which makes the coating very effective to avoid adhesion at high contact forces against for example steel surfaces. The high wear resistance of the coating is due to the content of phosphor, which therefore should be plated as high as possible.



Electroless nickel boron is another similar coating with an even higher hardness.

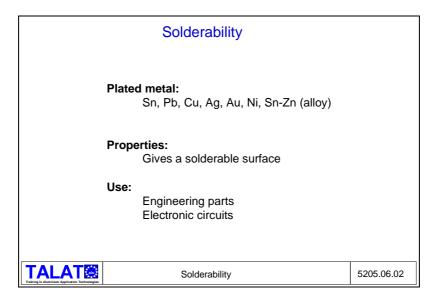
The corrosion resistance of electroless nickel phosphorus is very good. Used with a standard 25-30 µm thick coating the corrosion resistance is good.

Electroless nickel can be plated as a *composite* by including particles suspended in the plating solution. Particles of Silicon Carbide (SiC) are used to increase the abrasive wear resistance. But it should be noted that the coating it self will then act as an abrader to other surfaces. If Teflon (PTFE) is plated in the coating the coefficient of friction in dry contact is very low, i.e. comparable to that of lubricated contact.

The throwing power of electroless nickel is very good and a totally homogeneous coating distribution is possible also within *holes* and *tubes*. Therefore the coating can be used for engineering parts where *tolerances* should be strictly maintained.

When aluminium parts are to be joined, *soldering* is a good method. The aluminium surface can be made solder able by plating tin, silver, gold or other metals on the surface (**Figure** 

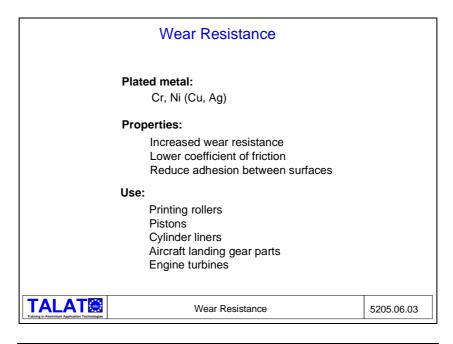
**5205.06.02**). A newer solder able coating type, only available from a few suppliers is tin-zinc alloy coatings. These coatings are very corrosion resistant and at the same time solder able.

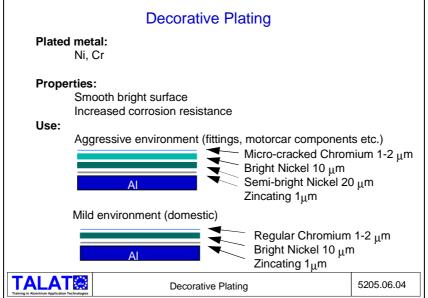


Aluminium parts can be used for engineering parts subjected to *wear*. Aluminium it self has a low wear resistance and severe adhesion on to most other surfaces will occur. Plating wear resistant coatings on the aluminium makes it possible to use aluminium for wear parts also. Examples of wear resistant coatings are chromium, electroless nickel, silver and copper (**Figure 5205.06.03**). Each of these are used for different wear situations (abrasive, adhesive, corrosive or erosive wear). Chromium coatings reduce abrasive, adhesive and corrosive wear. Electroless nickel was mentioned earlier (**Figure 5205.06.01**). Silver, copper, gold etc. normally are used against adhesive wear and to avoid galling.

Decorative plating is one of the most common types of plating. Many different coatings are possible. One of the most common decorative coating types is electrolytic nickel under chromium. These coatings are used when a smooth and bright surface is desired (**Figure 5205.06.04**). Many decorative coating types will need to have a post treatment like a lacquer layer or passivation coating to avoid instant corrosion of the surface.

When chromium is plated for decorative use and should also be resistant to corrosion an underlying nickel layer is used. This is for example the case on fittings and motor car components. The aluminium is zincated, coated with a thick layer of semi-bright nickel, a thinner layer of bright nickel and finally a micro cracked chromium layer (**Figure 5205.06.04**).





For decorative uses in mild environments the 20µm semi-bright nickel layer is neglected.

As an example of *combining some plating techniques*, gold is deposited on aluminium for an aerospace application. The process is:

- Zincate / stannate
- electrolytic copper deposit, 5µm
- electrolytic nickel deposit, 10µm
- electrolytic gold deposit, 5μm

By using the above process sequence it is possible to eliminate the difficulties when plating aluminium that were listed earlier. The copper deposit has an excellent ability to absorb stress resulting from differences in the coefficient of thermal expansion. The nickel deposit

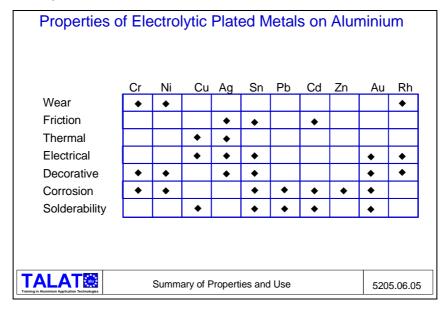
eliminates the risk of galvanic corrosion by forming a dense and pit-free layer. The nickel layer is also necessary to prevent diffusion of copper into the gold. The gold is the desired top coating and by depositing  $5\mu m$  a pit-free layer is obtained, i.e. no corrosion of the underlying layers is possible. The gold layer is 100% resistant to corrosion and has the desired electrical and thermal characteristics.

The above described gold-plating is tested by the following test sequence:

- 10 temperature-shocks (quick) from -55°C to +125°C.
- 200 temperature cycles (slow) from -55°C to +125°C.
- 240 hours at 95% relative humidity at 40°C.
- High temperature storage at 125°C for 1000 hours.

After this test cycle no visible or electrical changes can be allowed.

The obtainable mechanical properties by plating aluminium are changed wear resistance and coefficient of friction as well as changed strength and ductility. Thermal conductivity, solder ability and electrical resistance are main properties in many electronics. The commercially most common reason for surface treatment are decorative or corrosion resistance related. (**Figure 5205.06.05**).



#### **5205.07** Literature

Wernick, S., Pinner, R. and Sheasby, P.G.: "The Surface Treatment and Finishing of Alumnium and its Alloys", 5th Edition

Metals Handbook, 9th Edition, ASM, Metals Park, Ohio

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