Plating & Surface Finishing

Zincate Free Plating of Beryllium, Magnesium, Aluminum and Their Alloys

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For over eighty years the plating industry has been dependent upon the use of zincate or related heavy metal compounds such as tin to catalyze the plating of beryllium, magnesium, aluminum and their alloys. It is becoming more and more difficult to use these compounds due to ever more restrictive regulations and they are difficult to work with. This paper presents an environmentally acceptable and easy to use alternative that does not require metallizing the surfaces to be plated.

Keywords: *Zincate-free plating, light metals plating, plating on aluminum, plating on beryllium, plating on magnesium*

Introduction

The lightness, strength and high melting points of beryllium, magnesium, aluminum and their alloys make their use desirable in many applications. Their relative softness and tendency to corrode generates the need to plate them, but transition metals, such as nickel, chromium and copper, form very poor bonds to these light metals and as such they are difficult to plate. For over eighty years now,[1] they have been plated by first depositing a thin layer of zinc metal from an alkaline zinc solution (referred to as "zincate") or a thin layer of another heavy metal such as tin (referred to as "stannate") which will bond to the aluminum and in turn form a bond to the transition metal being plated onto these metals. Simple zincate or stannate is nothing more than the corresponding metal oxide dissolved in sodium or potassium hydroxide, but best results are obtained by adding various cyanide-containing solutions as the cyanide acts to form flat, even and uniform deposits of zinc[2] and/or tin. There are huge numbers of variations to these standard zincate or stannate solution in terms of concentration, pH, etc.,[3] and in some cases, a secondary deposit of copper from a copper cyanide bath is applied to smooth out nicks and scratches or to improve the bonding characteristics of the metal being plated. In many cases, "stannate'' solutions will be used in combination with "zincate" solutions, depending on the metal or metal alloy being plated[4] and, once again, there are quite a few modifications to the standard "stannate" formula.[5]

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The many process variations used in the deposition of a zinc or tin film onto beryllium, magnesium or aluminum and their alloys are the result of the different chemistries presented by the metals and their alloys and the many different surface conditions presented by the metals and alloys in question. A polished surface finish will not react in the same manner as a matte surface finish or a pitted surface, and beryllium will not react the same way as aluminum or magnesium. Then we have the whole issue of how clean the surface is and/or how much metal oxide is present on a given metal surface at any given time during the processing procedure.

The process being presented in this paper negates a large portion of these concerns as the chemistry of the metal in question and/or its surface condition becomes much less an issue. This process generates its own unique and consistent surface characteristics that are no longer dictated by the metal and its surface conditions. This significantly reduces the number of processing steps and the related cost of plating on beryllium, magnesium or aluminum and their alloys. The examples shown in this article involve the use of electroless nickel as this is one of the more commonly plated materials on beryllium, magnesium or aluminum and their alloys. Other elements may be plated if so desired.

Cleaning and deoxidation

In any metal processing procedure, the most important aspect of the process is the proper cleaning and deoxidation of the surface of the metal or alloy in question. Cleaning is the removal of surface oils and/or solid organic matter, while deoxidation is the removal of unwanted inorganic compounds (metal oxides or hydroxides) that would interfere with the metal processing being attempted. The exact cleaner selected will depend on the type of soil being removed and the metal and/or alloy in question. In general, a strong alkaline cleaner will give the best result on beryllium, magnesium or aluminum and their alloys, followed by a rinse in high quality demineralized water, the rinse itself being where the actual cleaning takes place. The deoxidizer most generally used on these metals is a mineral acid (sulfuric, hydrochloric, nitric and/or hydrofluoric) of low or high concentration, depending on the metal and/or alloy in question followed by another rinse in demineralized water. In the past, these metals were quite often deoxidized in a mild chromic acid solution, as the chromic acid would serve to form a passive chromium oxide film on the metals surface and as such prevent the formation of unwanted oxides and assist in the application of the zinc or other metal being plated. Environmental concerns have served to stop this procedure in many plating shops.

Beryllium

Beryllium is a rather expensive, toxic and rare element used primarily in the aerospace industry, due to its very light weight [Density = 1850 kg/m^3 (115 lb/ft^3)], high melting point [1287°C (2350°F)] and a low coefficient of thermal expansion, which makes it useful in making mirrors. In addition, it is rather resistant to oxidation at normal temperatures. Its low coefficient of expansion will in most cases require that the metal be heat treated after being plated.[7] A typical electroless nickel plating cycle would involve the following:

Alkaline soak cleaner	65 - 77°C (150 - 170°F)	8 - 12 min
Rinse		
Etch in 4% nitric acid, 2% HF	Ambient temperature	2 - 3 min
Rinse		
Deoxidize in 70% nitric acid	Ambient temperature	2 - 3 min
Rinse		
Acid zinc treatment[8]	Ambient temperature	5 - 7 min
Rinse		
Strip zinc in 70% nitric acid	Ambient temperature	2 - 3 min
Rinse		
Electroless nickel plating[9]		
Rinse, dry and heat treat		

An alkaline zincate may be used in place of the acid zinc treatment indicated.

The new process being proposed would involve the following:

Strong alkaline soak cleaner	77 - 82°C (170 - 180°F)	8 - 10 min
Rinse		
Deoxidize in 70% nitric acid	Ambient temperature	2 - 3 min
Rinse		

The beryllium or beryllium alloy is then made the cathode in an electrolytic cell containing a conductive emulsion of various polyamines and/or polyamides at about 1.4 A/dm^2 (15 A/ft^2) for a few seconds, followed by a rinse and then immersion in the electroless nickel bath (Fig. 1). Then rinse, dry and heat treat, if necessary.

Figure 1 - Beryllium/aluminum alloy before and after (top) being plated with electroless nickel.

The bonding surface formed on the surface of the beryllium and/or beryllium alloy by this process is at most about 400 nm thick and allowing the part in question to remain the cathode in the treatment solution for more than a few seconds will do nothing to harm the bonding surface, as the reaction that takes place is self-limiting. Any excess polyamide or polyamine compounds that are removed from the emulsion will simply rinse off and go back into the emulsion to be used over again. The adhesion was excellent [heated to 191°C (375°F) for 30 min and quenched in cold water] and plating other metals such as copper on the surface of the electroless nickel was no problem. In addition, it should be noted that after treatment in the emulsion, rinsing and drying the part and storing it for several days at a time did nothing to harm the ability to apply electroless nickel as long as the part is wetted out by letting it soak in demineralized water for about 30 min.

Magnesium

The plating of magnesium has been a difficult problem for some time, due to its extreme reactivity. As a result, it is generally given a copper cyanide strike to fill up and/or cover over any and all pores and scratches on the surface of the metal after treatment in a "zincate" solution.[9] A common procedure for electroless nickel plating of magnesium would involve the following:

Alkaline soak cleaner	82 - 93°C (180 - 200°F)	3 - 5 min
Rinse		
Chromic or phosphoric acid pickle	Ambient temperature	30 - 60 sec
Rinse		
Phosphoric acid - fluoride etch	Ambient temperature	1 - 2 min
Rinse		
Fluoride-containing "zincate"	68 - 71°C (155 - 160°F)	3 - 15 min
Rinse		
Copper cyanide strike	54 - 60°C (130 - 140°F	6 - 8 min
Rinse		
Electroless nickel plating bath[9]		

The new process being proposed would involve the following:

Alkaline soak cleaner	82 - 93°C (180 - 200°F)	8 - 10 min
Rinse		
Deoxidize in mild organic acid solution	Ambient temperature	15 - 30 sec
Rinse		

The magnesium or magnesium alloy is then made the cathode in an electrolytic cell containing a conductive emulsion of various polyamines and/or polyamides at about 1.6 A/dm^2 (15 A/ft^2) for a few seconds, followed by a rinse and then immersion in the electroless nickel bath (Fig. 2). Then rinse and dry.

Figure 2 - Plated magnesium before (top) and after being plated with electroless nickel.

As with beryllium, the bonding surface formed on the magnesium and/or magnesium alloy by the zincate-free process is at most about 400 nm thick, and allowing the part in question to remain the cathode in the treatment solution for more than a few seconds will do nothing to harm the bonding surface, as the reaction that takes place is self-limiting. Any excess polyamide or polyamine compounds that are removed from the emulsion will simply rinse off and go back into the emulsion to be used over again. The adhesion was excellent [191°C (375°F) for 30 min and quenched in water] and plating other metals such as copper on the surface of the electroless nickel was no problem. In addition, it should be noted that after treatment in the emulsion, rinsing and drying the part and storing it for several days at a time did nothing to harm the ability to apply electroless nickel as long as the part is wetted out by letting it soak in demineralized water for about 30 min. It should be noted that this is an excellent surface for the application of organic coatings (*i.e.*, paint) and if that is your objective, just let the part dry and paint it.

Aluminum

Every aluminum alloy will have its own unique cleaning problems and as such it is not possible present one universal cleaning process generally used on all aluminum alloys. It can be stated that plating on aluminum alloys in general will require a zincate treatment of some kind after cleaning. Due to the high silicon content of most aluminum alloy castings, they are generally deoxidized by the use of concentrated nitric acid containing fluorides to remove the silicon with little if any attack on the aluminum itself. Following this type of treatment and a rinse, the polyamides and or polyamines would be applied by making the casting the cathode for a few seconds at about 1.4 A/dm^2 (13 A/ft^2) and then rinsing the casting. Following this procedure generates an excellent surface for painting (Fig. 3) and/or plating.

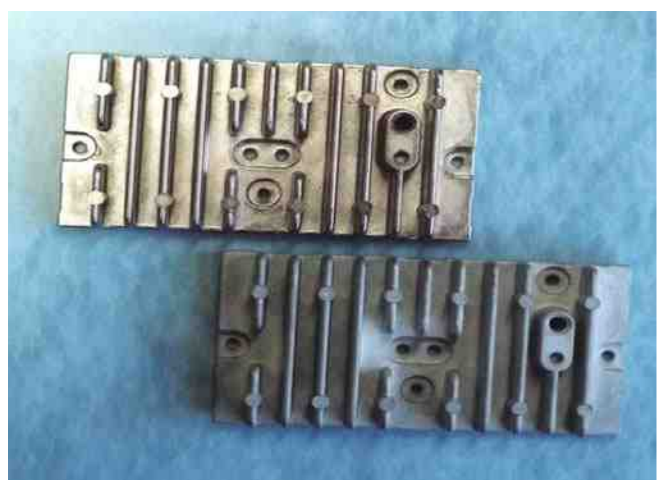

Figure 3 - Plated cast aluminum alloy before (top) and after being plated with electroless nickel.

With the 6000 series of extruded aluminum alloys we get better results if the alloy is cleaned in an alkaline soak cleaner, rinsed, cleaned cathodically in a 1% potassium hydroxide solution at about 2.7 A/dm^2 (25 A/ft^2) for about 30 sec, rinsed and then the polyamides and/or polyamines are applied as indicated below (Fig. 4).

Figure 4 - 6061 extruded aluminum alloy before (top) and after plating with electroless nickel.

It should also be noted that some aluminum alloys give better results if the polyamides and/or polyamines are applied by making the aluminum the anode.

Summary

The electrolytic deposition of a thin film of various polyamides and/or polyamines on the surface of beryllium, magnesium, aluminum and their alloys will allow the metals to be plated with other metals and with far less difficulty than through the conventional application of a thin film of zinc and/or tin by the use of zincates or stannates.

Conclusion

The deposition of a thin, uniform film of zinc and/or tin on beryllium, magnesium, aluminum and their alloys to allow for the further deposition of other metals is far more difficult than the deposition of a thin film of polyamides and/or polyamines to accomplish the same objective.

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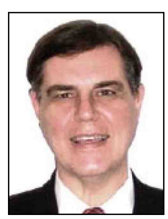

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