Technical Article

# Process for Autocatalytic Brass Plating On Zamak Alloys

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**This paper deals with a process for electroless brass plating on Zamak alloys obtained by centrifuge casting for handicraft applications. This process is an alternative method to conventional electrolytic brass plating. Advantages of the electroless process are cost reduction, process simplification, lower sensitivity of plating to the size of the workpieces and better color uniformity.**

Since its discovery by Brenner and Riddell in 1946, electroless metal plating has been widely applied in industry to improve upon traditional plating obtained by electrolytic deposition of pure metals or alloys on metal surfaces.[1] Most developments have concerned copper or nickel plating on metallic substrates.[2] Actually, electroless plating may be carried out depositing not only single metals but also alloys, and substrates can be non-metallic materials, like plastics and ceramics.[3] Generally, alloys are selected to satisfy both functional applications like corrosion and wear resistance, and decorative uses.

Usually, brass plating is applied by an electrolytic process. It has some problems such as inhomogeneous color, variability of thickness with complicated shapes, and a strong dependence on cathode-to-anode distance, as well as problems associated with polarization.[4,5] Generally, polishing of the finished parts is required, and the harmful properties of the chemicals used in the plating solutions, like cyanide, have led to the search for new processes.[5]

Little work has been published on electroless brass plating, probably because the main use of brass plating is for handicraft products, where electroplating is considered as a part of the craftsmanship. This work deals with electroless brass plating of handicrafted pieces made of zinc-based alloys. During this work we found the potential for application to other metallic substrates.

## Experimental

For this study, Zamak alloy samples were used as substrates and experiments were conducted to obtain uniform plating and the typical color characteristic of crafted brass products. As is well known, for this purpose the Cu/Zn ratio must be at least 3:1.[5,6] Zinc oxide was used as the source of zinc ions source and copper cyanide provided the cupric ions. Before electroless plating, the specimens were treated by chemical and cathodic processes to degrease and activate the surface. The samples were then immersed in the electroless brass bath for specified times. Immersion time, the reduction agent, the metal complexing agent

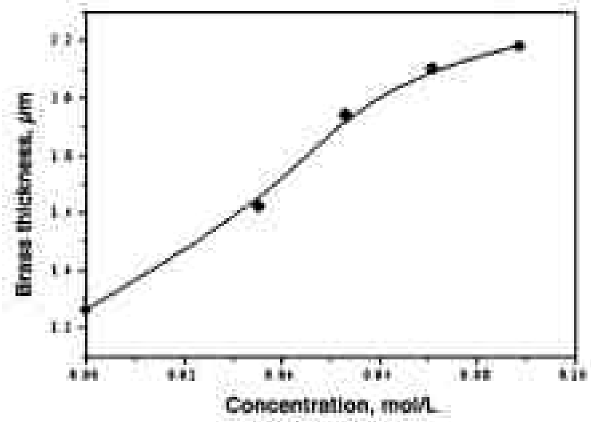


*Fig. 1—Effect of reductive agent concentration on brass layer thickness.*

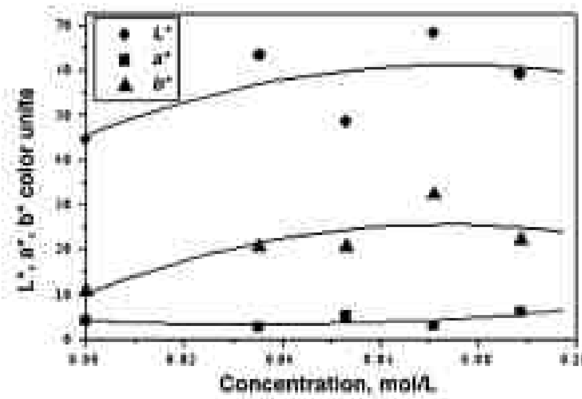


*Fig. 2—Effect of reductive agent concentration on color parameters L*, a*, b*.*

and the bath temperature were optimized to obtain brass plating with homogeneity and good adhesion to substrate. The final operating conditions and bath composition are shown in Table 1. After water rinse, the samples were immersed in a fixation bath in order to seal any microcracks that might be present.

Analysis of the electroless plated samples was made by scanning electronic microscopy equipped with an energy dispersive X-ray analyzer in a JEOL SEM, model JSM-5800 LV. Samples were cut transversely to measure thickness. For SEM studies, the samples were cut and prepared by typical metallographic techniques. Color measurements were made with a tristimulus Color-Eye 7000A spectrophotometer. Readings are reported in the L*, a*, b* system (corresponding to lightness, redness and yellowness, respectively).

## Results & Discussion

After pre-treatment, the substrate surfaces were free of grease. The surface was then activated to obtain

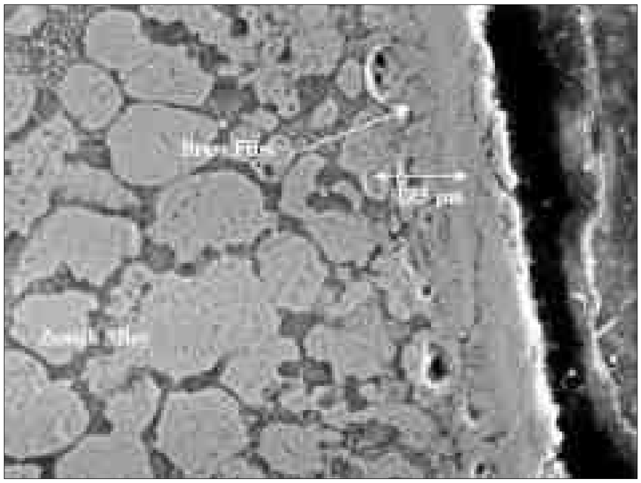

*Fig. 3—Scanning electron microscopy micrograph of obtained electroless film.*

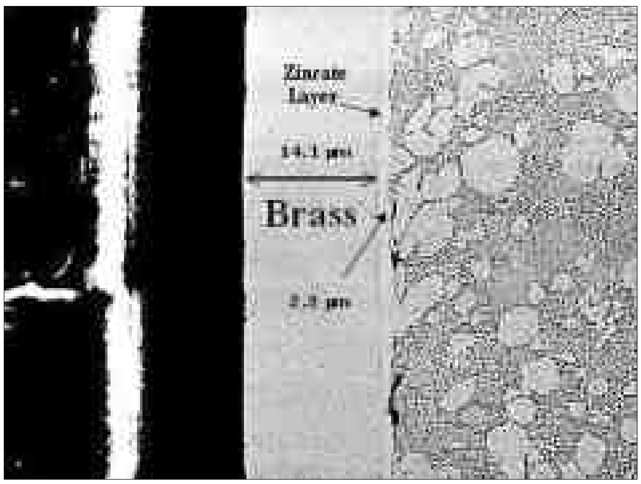


*Fig. 4—Scanning electron microscopy micrograph of commercial electrolytic brass deposition on Zamak substrate.*

hydroxyl groups on the surface. This allowed the metallic surface to promote autocatalytic metal deposition.

While determining the best conditions for brass plating, we observed that one of the main control variables was the metal salt concentration. As the concentration increased, the plating rate increased. Further, there was no observed preferential deposition of either copper or zinc. Instead, the composition was a function of the concentration of each metal in the bath.

As observed in Fig. 1, an increase in the concentration of the metal complexing agent results in an increase in the thickness of the brass layer at a constant immersion time. A maximum deposition rate is obtained near 0.07 mol/L and any further addition of complexing agent does not affect the deposition rate. Temperature shows similar characteristics. As it is increased, the deposition rate also increases up to 60ºC. Higher temperatures inhibit brass plating.

By proper selection of the metal complexing agent concentration it is possible to control the final color, as shown in Fig. 2. For the parameters of this particular study, at the complexing agent concentration of 0.07 mol/L, the lightness (L*), and yellowness (b*) are at a maximum for typical brass colors for handicrafts produced by electrolytic plating. Further increase of the complexant concentration tends to give a more reddish color through the enrichment of copper in the brass layer. This can be seen in Fig. 2 at the maximum complexant concentration where the lightness (L*), and yellowness (b*) are declining and the redness parameter (a*) starts to increase.

**Table 1**
**Electroless Bath Composition**

| | |
|---|---|
| Copper Concentration | 24 g/L |
| Zinc Concentration | 16 g/L |
| Reducing Agent | 20 g/L |
| Metal Complexing Agent | 20 g/L |
| Caustic | 28.5 g/L |
| Stabilizers | 53 g/L |
| Buffers | To maintain pH |
| Temperature (°C) | 55-65 |
| Dipping Time | 10-15 min |
| pH | >11 |

**Table 2**
**Chemical EDAX Analysis of Brass-plated Zamak Obtained by Electroless & Electrolytic Processes**

| Sample | Cu (Wt%) | Zn (Wt%) | Al(Wt%) |
|---|---|---|---|
| Electroless | 55.74 | 44.26 | - |
| Electrolytic | 64.69 | 35.31 | - |
| Zinc layer | 35.06 | 61.20 | 1.16 |

The final operating conditions are shown in Table 1. After electroless treatment, the samples were air dried to avoid stain formation on the surface. Visual inspection indicated that the deposit and color were very homogeneous, and adhesion of the brass film was strong. By modifying the copper/zinc cation ratio, it was possible to modulate the color tone from a greenish to a reddish appearance.

Figure 3 shows an SEM micrograph of the electroless film. As can be seen, the thickness is approximately 10 ∝m, which is enough to obtain a homogeneous color and texture. There were no voids between the brass layer and the Zamak surface, indicating good adhesion.

As a comparison, Fig. 4 shows an electrolytic brass deposit on similar Zamak surface. As can be seen, there is a thin zinc strike layer between the Zamak surface and the brass film. This layer is deposited electrolytically and is necessary to obtain a surface sufficiently active for electrolytic deposition of brass. This step is not necessary for the electroless process. This reduces labor and chemical costs as well as the process time when electrolytic and electroless brass deposition processes are compared.

The chemical composition of the brass layers for both the electrolytic and electroless brass processes are shown in Table 2. There were not observed significant differences among these processes. As was mentioned above, for the electrolytic brass layer, there is a zinc rich layer which is deposited to activate the surface for electrolytic deposition. Zamak substrates of different compositions were plated by the autocatalytic process and the same results were obtained.

## Conclusions

We have studied an electroless process for brass plating on Zamak alloys, which can provide an alternative to the conventional electrolytic process. As with the electrolytic process, it is possible to select the finish color by controlling the electroless process variables.

Labor costs, chemical costs and process time are lower for the electroless process when compared to the electrolytic process.

Finally, the electroless process will produce films as thick as those obtained from an electrolytic process.

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