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On the Development of Efficient Undercoat for Depositing Copper on Magnesium Alloy AZ80A

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Abstract

In this work, AZ80A, a wrought alloy of Magnesium was chosen for microhardness enhancement as the literatures available in this area are scarce. Electroless coating of magnesium alloys depends on careful pretreatment of surface to obtain a compact coating. Magnesium is a highly reactive metal and easily forms oxides and hydroxides when exposed to the atmospheric air or moisture. In this investigation, various techniques such as application of heat resistant varnish interlayer, Phosphate degreasing process, Pyrophosphate etching treatment and Zincating process were attempted to improve the adhesion of copper on the substrate. It was found that the phosphate ions played an important role in the dissolution of oxide layer. Zincating process yielded compact, dense and adherent copper coating. The microhardness analysis proved that the sample with zinc undercoat yielded the coating with highest hardness. An eco-friendly coating procedure using copper sulphate instead of copper cyanide for coating AZ80A has been established.

Keywords: AZ80A, Pretreatment, Phosphate degreasing, Pyrophosphate etching, Zincating, electroless copper coating

INTRODUCTION

Advances in automobile and aerospace industries demand highly efficient materials in terms of weight and strength. Magnesium has been the most preferred material for structural purposes as it is the lightest of all structural metals with a density of 1.7 g/cc. it has some attractive properties such as good heat dissipation, damping and electromagnetic shielding [1, 2]. However, the surface hardness, wear and corrosion resistance of these alloys have a lot of scope for improvement in order to widen their areas of application. Although various surface modification processes such as conversion coatings, anodizing, plasma electrolytic oxidation (PEO), etc. are available, electroless coating has been proved as one of the simplest and economical method of coating metals [3,4,6]. Therefore this method can be used to improve the surface properties of magnesium alloys by coating hard and corrosion resistant metals. However, Magnesium requires special pretreatment procedures in order to dissolve the oxide layer on its surface which is readily formed on its exposure to atmosphere. If coating process had been done without removing this oxide layer, the coated material will easily delaminate from the surface due to the poor bonding between the substrate and the coat. The general pretreatment procedure of magnesium alloy involves, ultrasonic cleaning of the substrate in deionized water and then isopropyl alcohol. It is followed by mechanical polishing with 600 grit sand paper and alkaline degreasing to break the porous oxide layer [5]. Acid pickling or etching is done to prepare the surface for better adhesion of the coating. Activation of the acid pickled surface is recommended before subjecting the substrate to zinc immersion process. The next step could be electroless or direct electroplating with copper. Electrolytic etching has also been tried by connecting magnesium to the anode to remove the oxide layer and coating copper by electrodeposition process. In this work, magnesium alloy AZ80A was selected for investigation as very few literatures are available on the pretreatment of this alloy. Four pretreatment procedures such as heat resistant varnish interlayer, phosphate degreasing, pyrophosphate etching and zincating were carried out on all samples before coating with copper. The appearance, adhesion strength and microhardness of the copper coated samples were assessed. The sample with zinc undercoat yielded compact layer of copper with the highest microhardness as compared to the substrate.

EXPERIMENTAL WORK

Circular discs of diameter 22mm and thickness 6mm are cut from as rolled AZ80A magnesium alloy rods. A hole of 2 mm diameter was drilled eccentrically in all samples in order to suspend the sample during the pretreatment process. The samples after machining and drilling are presented in Fig 2.1. The chemical composition of the substrate is given in Table 2.1.

Table 2.1. Chemical composition of AZ80A

Element	Mg	Al	Zn	Mn	Si	Cu	Fe	Ni
Weight (%)	91	7.80 - 9.20	0.20 - 0.80	0.12	0.10	0.050	0.0050	0.0050

The machined substrates are mechanically roughened using 1000 grit sand paper and then ultrasonically rinsed in deionized water.

The process is repeated until all the visible oxide layers on the substrate surface are removed. In this work pretreatment

processes with four different variations were attempted for coating copper by electroless technique.

Figure 2.1. AZ80A substrate

The ultrasonically rinsed sample was coated with heat resistant varnish and air dried for one hour. Then it is dried in oven for 1 hour at 200^0C [7]. This is sample was again subjected to alkaline degreasing sensitized with solution containing stannous chloride for 10 minutes and activated with $AgNO_3$ and equal concentration of sodium hydroxide for 10 minutes. The sample was rinsed and transferred to electroless copper coating bath containing copper sulphate, potassium pyrophosphate, sodium carbonate and sodium flouride. The copper coated sample with the heat resistant varnish interlayer is shown in Fig 2.2

Figure 2.2. Copper coated sample with interlayer

The second sample was subjected to ultrasonic rinsing, mechanical polishing, isopropyl alcohol cleaning and degreasing in an alkaline bath containing NaOH, Na_3PO_3 and Na_2SiO_3. The degreased sample was again ultrasonically rinsed and transferred to an acid pickling bath containing Phosphoric acid (85%) and Nitric acid (69%) [8]. Then the sample was ultrasonically rinsed and coated with copper using the bath mentioned earlier. The sample thus coated is displayed in Fig. 2.3

Figure 2.3. Copper coating with phosphate degreasing

The Third sample was mechanically polished, ultrasonically cleaned, degreased and acid pickled as per the aforementioned procedures. The acid pickled substrate was then transferred to an alkaline etching bath containing Tetra Sodium Pyrophosphate, Sodium Carbonate and Sodium Flouride. The sample etched in alkaline bath was then transferred to the same electroless copper bath mentioned earlier. The coated sample is displayed in Fig 2.4.

Figure 2.4. Copper coating with pyrophosphate etching

The fourth sample was subjected to all pretreatment procedures mentioned above. Except for the first sample none of the samples had heat resistant varnish interlayer coating. This sample was ultrasonically rinsed after pyrophosphate etching and transferred to an alkaline zincating bath containing zinc sulphate, tetra sodium pyrophosphate, sodium carbonate and sodium fluoride [9]. The zincated sample was then transferred to the electroless copper coating bath mentioned earlier. The zinc and copper coated samples are shown is Fig 2.5 and Fig 2.6.

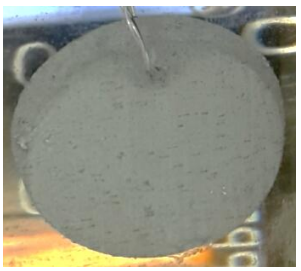

Figure 2.5. Zincated Sample

Figure 2.6. Copper coated Sample

The copper coated sample exhibited a dense flat surface with no peeling as per the quantitative appearance grade standards The microhardness of all copper coated samples were tested using micro Vickers hardness tester (Wilson Wolpert – Germany) with a load of 0.2 Kg and dwell time of 10 seconds.

RESULTS AND DISCUSSION

Effectiveness of undercoats

In this study, the substrates were initially subjected to ultrasonic cleaning in deionized water to remove all impurities. Then they were mechanically polished using a 1000 grit sizes emery paper to remove all visible oxide formation on the surface followed by ultrasonic rinsing in isopropyl alcohol. The first sample was coated with heat resistant varnish in order to create an interlayer between the substrate and copper to avoid rapid oxidation of magnesium. Copper was autocatalytically deposited on the interlayer after sensitizing and activating the interlayer. The copper coated sample displayed in Fig 2.2 exhibited flaky uneven surface and the coating readily peeled off due to the poor adhesion of the interlayer with the substrate. However the adhesion of copper with the interlayer coating appeared acceptable. Therefore the second sample was prepared without interlayer coating and a new step of degreasing with trisodium phosphate was included to study the effect of phosphate. The coating adhesion and the surface appearance was better than the previous sample [10]. The phosphate ions react with the magnesium oxide and hydroxide layer of the substrate and form a soluble ligand which dissolves the oxide layers exposing the substrate as shown below [16].

$Mg(OH)2 + XP_2O_7^{4-} \rightarrow [Mg_2 (P_2O_7) x]^{4-}4x+4OH^-$

$Mg \rightarrow Mg^{2+}+2e^-$

$Zn^{2+} + 2e^- \rightarrow Zn$

It is evident from the above equations that magnesium is oxidized and the zinc ions are reduced on magnesium surface. As soon as the loose complex compound is dissolved zinc deposits on the substrate itself which eliminates the possibility of void formation in the coating. Therefore the adhesion of copper in this case was better than previous. However, the coated surface exhibited discontinuity and roughness. This indicated that the surface appearance had to be improved. Hence in the next sample all steps up to phosphate degreasing were applied, followed by pyrophosphate etching. The sample coated with copper after pyrophosphate activation is shown in Fig 2.4. The flaky and uneven surface appeared in the previous sample had been converted in to a thin coating with a uniform surface due to the inclusion of pyrophosphate. This could be attributed to the prevention of anodic dissolution of α phase of magnesium and cathodic deposition on the β phase by the phosphate ions. At the anodic α phase, magnesium disassociates into magnesium ions and in the cathodic β phase deposition of nickel takes place as shown below.

$Mg \rightarrow Mg^{2+} + 2e^-$

$Ni + 2e^- \rightarrow Ni$

This led to uniform deposition of copper throughout the sample surface. However, the coating texture needed enhancement and localized peeling must be prevented in this sample. Therefore, to obtain a coating of uniform thickness with better adhesion sample 4 was subjected to zincating process in the bath of composition mentioned earlier. Instead of applying a coat of organic interlayer as in the case of sample 1, a zinc interlayer was created in this case due to autocatalytic reaction. The reaction was allowed to continue until the zinc layer or required thickness was grown on the substrate surface. A compact smooth film of zinc with finer grains was produced during this procedure. Then the zincated sample was subjected to copper electroless coating and the coated sample is shown in Fig 2.5. This sample displayed smooth, adherent and pore free coating with no visible peeling on the surface. This was due to the formation of dense zinc coating on the two phases of magnesium alloy preventing preferential deposition of copper. Dissolution of porous oxide layer by the phosphate ions followed by the immediate deposition of zinc ions led to the uniform formation of zinc layer and subsequent copper layer on the substrate. Moreover, the fluoride ion from sodium fluoride in the zinc immersion bath also contributed to the smoothness of zincate coating in addition to offering superior corrosion resistance to the substrate [12, 13-15].

Microhardness

The microhardness of the uncoated substrate was found to be 114.16 HV. The microhardness of all copper coated samples with heat resistant varnish, phosphate, pyrophosphate and zinc undercoats were found. The results are displayed in Fig. 2.6. It is evident from the graph that the hardness gradually increases from sample one through sample 5. The highest microhardness is exhibited by the zincated sample. Sample 2 with heat resistant varnish interlayer shows a little improvement in microhardness due to the loose and flaky coating. The microhardness of sample 3 is better than sample 2 due to the better adhesion of copper by removing the oxides. However the pyrophosphate treated sample 4 yielded better hardness due to enhanced adhesion due to the combined action of phosphate and fluoride ions which yielded a comparatively smoother surface.

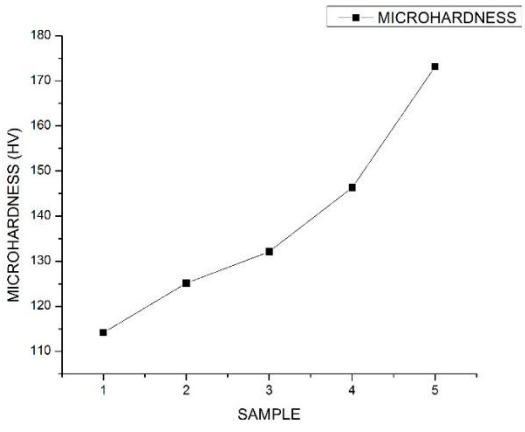

Figure 2.6. Microhardness comparison

Sample 5 yielded the highest microhardness due to the immediate deposition of zinc soon after the removal of oxides by the phosphate ions. This eliminated the formation of voids and defects leading to the formation of a compact and dense copper coating.

CONCLUSIONS

In this work the effectiveness of heat resistant varnish, phosphate, pyrophosphate and zinc undercoats in yielding a compact copper film of higher hardness on AZ80A was assessed.

The results indicate that the combination of phosphate degreasing, pyrophosphate etching and zinc treatment yield a dense, compact adherent copper coating.

The combined action of phosphate and fluoride ions played an important role in determining the adhesion and appearance of copper coating on the substrate.

The rapid action of phosphate ions in removing the metallic oxides on the substrate followed by the immediate deposition of zinc during the zincating process is responsible for the pore-free adherent copper coating which ultimately yielded the best hardness as compared to its counterparts.

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