Phase growth in alpha brass with thin layer of electroplated zinc during homogenization annealing

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Abstract

Diffusion mechanism in between thin electroplated Zn coating and Cu – 37wt%Zn substrate during homogenization annealing substantially depends on electroplating parameters. Experiments carried out to determine phase growth and solute profile at various current densities reveal that the increase of current density tends to reduce phase growth. The coefficient of phase growth has been determined and is found to be dependent on the relative density of plating layer.

Keywords Electrodeposition · Diffusion · Current density · Phase growth

1 Introduction

The demand for using a thin coating on metal substrate has arisen because of the need to increase the efficiency of metals in processing industries such as electro-discharge machining wire, aero engines, electronic devices, etc. Diffusion process at interfaces and solute distribution in the interdiffusion zone of such diffusion couple determines the mechanical and physical properties. Several investigations [1–4] have been carried out to understand and provide a better insight into micro-segregation characteristics in diffusion couples with semi-infinite slab. It is known that diffusion characteristics of semi-infinite slab are not readily applicable to homogenization treatment in between thin film coating and a metal substrate. It is apparent that movement of solute atoms and vacancies in the solute rich thin film is dependent on migration of interface which is mostly controlled by characteristics of interdiffusion zones on both sides of the interface.

Electroplating of zinc on α – brass wire and subsequent homogenization annealing treatment at an elevated temperature are adopted to enhance the performance of electro-discharge machining wire. Current density controls the speed of the electroplating process as well as

characteristics of the plating layer. In this study, an attempt has been made to investigate the morphological evolution in between base metal and thin zinc coating during diffusion annealing treatment with various electroplating parameters. In homogenization treatment of solids involving a thin layer of solute on the surface, characteristic lengths in diffusion zone in zinc rich thin layer are restricted by interface and migration of vacancies. Experiments and models to predict characteristics of diffusion in such cases are not yet well documented as deeper understandings of the mechanism of diffusion in presence of thin film are currently unavailable. This paper reports the solute profile and microstructure evolution during diffusion annealing treatment of thin electroplated layer of Zn on α – brass where the current density of electroplating process is expected to influence interdiffusion zone.

2 Experimental

The Cu-37wt %Zn alloy wire was prepared from Cu and Zn metal ingots (purity of 99.9 wt %) and drawn into a round wire form of 0.618 mm diameter. Slices of 50 mm lengths were cut from the wire and electroplated with Zn from zinc

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sulphate electrolytic solution. The metallic zinc content of the solution was maintained between 120 and 140 g/l. The plated wire specimens were taken out from the solution after 120 ± 10 s of plating. The current density was varied. Table 1 displays details of electroplating parameters of the specimens and resulting Zn plating thickness (δ). Several specimens were made under the same condition in order to ensure repeatability of results. The Zn plating thicknesses were measured by optical microscopy of the cross-section of plated wire specimens and the weight of Zn plating was measured by stripping the Zn plating from plated wire specimens by dipping in a solution of 32gms of SbCl_3 dissolved 1000 cc of HCl [5]. For measurement of Zn deposition, the following formula is used;

$$w = (W_1 - W_2)/A \quad (1)$$

where, w = average weight of Zn per unit area (g/m^2), W_1 = weight of specimen after Zn plating (g), W_2 = weight of specimen after stripping in solution (g) and A = the surface area of wire specimen (m^2).

The relative density of the plated layer is calculated as follows:

$$f = \frac{W_1 - W_2}{W_{th}} \quad (2)$$

where W_{th} is the theoretical weight of plated zinc with thickness δ and can be expressed as;

$$W_{th} = \frac{\pi(d_1^2 - d_2^2)L\rho}{4} \quad (3)$$

where, d_1 = diameter of plated wire, d_2 = diameter of base wire, L = length of wire and ρ = density of Zn.

The Zn plated specimens with three different current densities were subjected to diffusion annealing at 160°C for 10 to 90 min in a closed oven. The specimens were kept in small closed vessels submerged in refined mineral oil in order to prevent oxidation and evaporation of Zn from the plated layer. The cross-sections of the diffused wire specimens were polished for the purpose of microstructure analysis in a scanning electron microscope (ZEISS)

and concentration profiles were measured using the spot Energy Dispersive X – Ray Spectroscopy (EDS) analysis.

2.1 Results and Discussion

SEM images of specimens show that diffusion of atoms has been taken place as illustrated in Fig. 1. At an elevated temperature, Zn atoms start to cross the electroplated interface from Zn plated layer towards the base. It is evident from Fig. 1a, b and c that the diffusion zone increases with time from 18 to 54 min for an initial plating thickness of $1.75\ \mu\text{m}$. As Zn atoms cross the electroplating interface into $\alpha\text{-CuZn}_{37}$ of the base wire, α —brass converts to β phase. This has evolved a new interface and can be termed as phase boundary as marked in Fig. 1. The Zn profiles of these diffusion couples have shown that the Zn concentration decreases from phase boundary sharply to bulk composition towards centre of wire specimens. This phase boundary moves towards the centre of wire with the increase of time as β phase grows with time. Clearly, zinc-rich diffused layer grows from the plating boundary and extends to the phase boundary. The Zn content varies from 44 to 65 wt% in this diffusion zone as observed from the composition profiles displayed in Fig. 1. Based on the binary phase diagram of Cu–Zn, it is apparent that the composition range of Zn rich diffused layer should be a mixture of β and γ phase with varied proportions depending on time and temperature of annealing. It is interesting to note that this growing layer of alloy expands in the direction of faster moving species, Zn and it is termed as phase growth (ω) which is calculated as the difference between the distance of phase boundary from the surface of the wire and that from the initial plating interface. Zn concentration profiles from Fig. 1 suggest that this Zn rich layer constitutes of mainly γ and β phases and does not decay smoothly which is in contrary to typical 'S' curve of concentration profile observed by several models and experiments in semi – infinite slabs [1–4, 6].

The calculation of phase growth (ω) and its dependence on CD displayed in Fig. 2 indicates that the more is the current density of plating, the less is the rate of phase growth. From Fig. 2, it is observed that for annealing time of 54 min and CD at 0.0965Amp/cm^2 , phase growth is $8.3\ \mu\text{m}$, whereas, it becomes $2.85\ \mu\text{m}$ when CD is increased to 0.225Amp/cm^2 . The calculation of relative density (f) and its dependence on CD indicates that f reduces with the increase of CD (cf. Table 1). This means that the rise of CD enhances defect structure of the plated layer. The diffusion process at higher CD becomes sluggish and may be attributed to hindrances in the interdiffusion zone due to the presence of growing defects. It is well known that interdiffusion in substitutional alloys is mediated by vacancy [4, 7]. This indicates that sources and sinks of vacancies

Table 1 Details of electroplating parameters and relative densities of plating layer

Current Density of plating, CD (Amp/cm^2)	Average Zn plating thickness, δ (μm)	Average weight of Zn deposition, w (g/m^2)	Relative density of plating layer, f
0.0965	1.75	12.75	0.97
0.161	2.95	19.74	0.92
0.225	3.45	22.11	0.88

Fig. 1 SEM images of diffused layer after annealing of (a) 18 min, (b) 36 min and (c) 54 min. Zn profiles are shown below each image. Phase boundaries and initial plated thickness (1.75 μm) are marked

Fig. 2 Plot of phase growth against time for different current densities

should be abundant on both sides of the diffusion zone for effective diffusion to take place. The atoms across an interface do not change places directly; rather diffusion occurs where voids open, making room for atoms to move in [7]. At the onset of diffusion, Zn atoms, being faster diffusing element cross the interface and initiate Cu atoms

to cross to thin Zn rich layer. As Zn diffusion is faster, more voids from the α - CuZn37 cross the interface towards thin Zn rich layer and lead to coalesce with the existing defects of the plated layer to form macro-defects which is more prevalent at higher CD. This hinders the path of further Cu atoms to diffuse in Zn rich phase as the creation of vacancies is not abundant. This phenomenon in turn may have slowed the creation of vacancies in α - brass because Cu atoms do not readily leave their lattice site. This appears to be the major reason for the slowing of phase growth at the higher CD as vacancies cannot be created abundantly in Zn rich outer layer. Such diffusion is accompanied by shrinkage of the high Zn brass from which Zn is diffusing out.

It is well known that for constant temperature, phase growth (ω) maintains the parabolic relationship with time (t) as $\omega^2 = 2Kt$, where K is the coefficient of phase growth [8, 9]. The determination of K is carried out by the use of linear regression analysis of ω^2 and t data. Figure 3 elaborates that K increases exponentially if the relative density exceeds 0.92 which onsets very active atomistic diffusion. This indicates that phase growth becomes faster when the current density is less. It is to be noted that higher CD does not provide the effective thickness of Zn rich diffused layer after annealing. Clearly, the increase of CD should be optimized between the speed of electroplating and the relative density. The coefficient of phase growth K

Fig. 3 Dependence of Coefficient of phase growth on relative density

determines the speed of phase growth and therefore it is proportional to the diffusion coefficient. Hence, estimation of diffusion coefficient can be made to predict the microstructure and characteristics of diffusion zone after homogenization annealing. It may be pointed out that K in electroplated diffusion couples shows a higher value than bulk diffusion couples and therefore it would lead to a higher diffusion coefficient than the actual value of bulk diffusion coefficient [10].

It is evident from Fig. 3 that the Zn diffusion in α phase becomes sluggish at lower relative density and results in the reduction of phase growth. Similar studies in sintered powder metallic parts have revealed that effective diffusivity steeply decreases when relative density is less than 0.92 [11–13]. It may be pointed out that pores do not take part in the diffusion process and estimated diffusivity decreases with the increase of pores or reduction of f . In presence of pores, grain boundary diffusion and surface diffusion mechanisms are more prevalent [12, 13].

3 Conclusions

In summary, the results indicate that homogenization diffusion annealing in between the thin Zn layer and α brass induces phase growth into α phase. EDS analyses reveal that the growing phase constitutes γ and β phase. The current density of the plating layer determines the kinetics of the diffusion reaction. The rate of phase growth reduces with the increase of current density. The coefficient of phase growth increases sharply if the relative density of plating layer exceeds 0.92 possibly due to the onset of atomistic diffusion.

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Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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