Electrodeposition of Super Invar alloy: effect of glycine

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Introduction

Electrodeposited alloys of Super Invar like composition, 64 wt % Fe, 31 wt % Ni, and 5 wt % Co, are of theoretical research interest because of the anomalous behavior during codeposition. Thermodynamically, nickel, the more noble metal, would deposit preferentially to both iron and cobalt during single metal deposition, however, the opposite is found by suppressing the deposition rate of nickel during iron-group alloy codeposition.[1] Thus, the understanding of anomalous codeposition could allow controlling deposition rates of individual Fe, Ni, and Co metal during codeposition and hence the composition. In addition, electrodeposited Super Invar alloys are of practical interests due to their potential applications in industry, particularly in micro-electro-mechanical systems (MEMS) and further in nanofabrication due to the material's near zero CTE at room temperature in bulk materials. In practice, however, it is difficult to predict the alloy composition and control the composition gradient along the direction of growth, due to the anomalous codeposition behavior. Super Invar has not been widely studied; most studies of the ternary FeNiCo have been focused on Co-rich alloys due to their magnetic property over the last twenty years. In addition, there is an absence of understanding the CTE in electrodeposited structures and how it is influenced by the electrodeposition parameters. In this study, conditions for developing microposts of Super Invar with uniform concentration and the CTE are presented and the effect of the addition of glycine examined.

Experiment

The Super Invar electrolyte contained 0.72 M nickel sulfamate, 0.155 M ferrous sulfate, 0.005 M cobalt sulfate, 0.5 M boric acid, 0.001 M sodium lauryl sulfate, and 0.011 M ascorbic acid. Sodium saccharine and glycine concentration was varied to investigate the additive effect. The bath pH was adjusted to 2.0 using sulfamic acid at 40 ^{o}C. A fundamental study of electrodeposited alloys was determined using a rotating cylinder Hull cell with a shielded geometry in order to determine the applied current density most appropriate for deposition into desired micron recessed features. The substrate preparation for the recessed electrodes was prepared by X-ray lithography at the Center for Advanced Micro Devices (CAMD). Super Invar micropost arrays were electrodeposited using different pulsing waveforms. The composition distribution and CTE along the length of the microposts were examined by SEM, WDS and TMA.

Results and Discussion

RCHC deposits were fabricated under primary current distribution control at a constant applied average current density. The alloy composition was measured along the cathode and correlated with the total current density. Results of the Hull cell experiments showed that Super Invar-like composition was found over a range of current densities between -20 and -60 mA/cm^2 for 100 μm recessed structures. However, the surface of the electrode without glycine was too rough to totally analyze each Fe, Ni, and Co beyond the current density of -60 mA/cm^2, in Figure 1 (a). Therefore, 0.023M glycine was added into the FeNiCo system in order to make a surface smoother. Super Invar composition was also found over a similar range and could analyze Fe, Ni, and Co composition beyond the current density of -60 mA/cm^2, shown in Figure 1 (b). By adding glycine into electrolyte, the surface morphology is improved, although cracks are still are found, in Figure 1 (c) and (d). Therefore, the electrolyte without glycine and with glycine was used to carry out deposition into the deep recesses in order to representing the effect of glycine for microstructures.

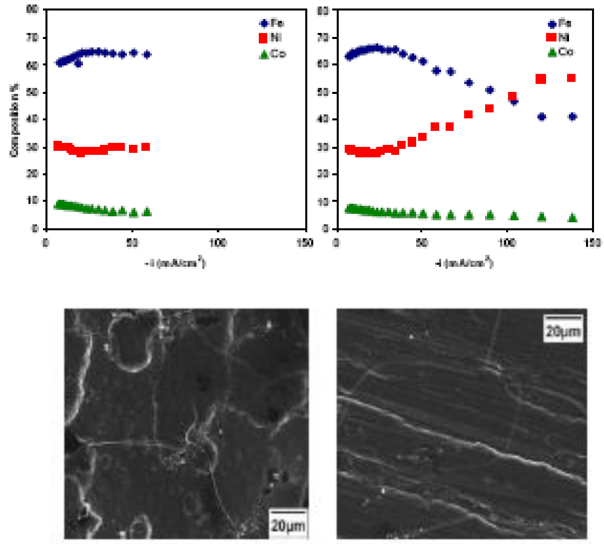

Figure 1: Electrodeposition of FeNiCo alloy from RCHC: composition distribution (a) with no glycine and (b) 0.023M glycine and SEM micrograph of the electrode surface (c) with no glycine and (d) with 0.023M glycine

A pulse current density of -60 mA/cm^2 with no glycine was applied and a uniform composition distribution of microposts was achieved unlike deposits made without pulsing at the same current density. Compared with microstructure of FeNiCo with glycine, a large composition variation along the height of micropost was observed because glycine could affect kinetics of the FeNiCo system, and hence the current distribution. The coefficient of thermal expansion (CTE) was analyzed using a thermomechanical analyzer (TMA) from room temperature to 300 ^{o}C during 1st and 2nd heat cycles. Here, a peculiar characteristic was observed: a negative CTE, *i.e.* the microposts shrink with increased temperature. The CTE value for bulk Super Invar[2] has a positive value, 0.6 μm/m•^{o}C at and near RT and 1.55 μm/m•^{o}C from 50 ^{o}C to 150 ^{o}C.[3] The lowest CTE value over the broadest temperature range occurred by applying a pulse current density of -60 mA/cm^2 when microstructures were nearly crack free with uniform composition distribution.

References

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