ELECTRODEPOSITED NANOSCALE MULTILAYERS OF INVAR WITH COPPER

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ABSTRACT
Low coefficient of thermal expansion (CTE) alloys have applications ranging from thermomechanical actuation to mold insert fabrication. An alloy of NiFe in the Invar range and copper are electroplated in nano-multilayers on a ceramic substrate with a copper plating base. A pulse plating scheme was implemented to deposit the layers of NiFe and copper into the recess with the correct composition. The required electroplating solution was configured using Hull Cell experiments. The plating range for the individual layers was determined by polarization and impedance analysis on the Invar-Cu plating solution. The multilayer microposts were tested for the mechanical properties such as the CTE and micro hardness. As deposited, the multilayer alloy exhibited a negative CTE, but after annealing had a small positive CTE comparable to that of bulk Invar. Characterization of the layers was done using SEM, TEM and Auger analysis. Magnetostatic interactions of the multilayer are being tested using Magnetic Force Microscopy (MFM).

INTRODUCTION
Materials with very low coefficients of thermal expansion (CTE) that would survive the large temperature cycling in injection molding are of interest. Mold inserts patterned with microstructures are used in injection molding to produce different molded parts. The temperature of the mold insert is increased from room temperature to a desired level say, 300°C and maintained at that higher temperature during injection. The temperature is decreased during demolding. As a result of this thermal cycling, dimensional variation in the microstructures occurs. The molded parts obtained after injection molding will not have the precise dimensions as the original mold insert, so the insert must be designed to accommodate thermal expansion effects.

Using a low thermal expansion material such as Invar (64% Fe, 36% Ni), may reduce the relative dimensional change. Previous work on electropositing Invar in micronatterns, confirmed that the low CTE of the Invar was limited by the Curie temperature [1, 2]. Since the low CTE in Invar is result of a balance between magnetic and thermal expansion forces, the potential of a multilayer microspost, having Invar (ferromagnetic) and copper (nonferromagnetic) as the alternating layers was considered. Nanolayers of copper interspersed between Invar layers would both minimize or restrict grain growth, and possibly modify the magnetostatic behavior, permitting control of the thermal expansion behavior of the structures.

EXPERIMENTAL METHODS
The electroplating bath was designed with optimum concentrations of individual chemicals for obtaining Invar composition in microposts. Earlier work [Palaparti, et.al 2003] used a NiFeCu bath in electroplating multilayers of NiFe and Cu, which proved to have a low CTE of 0.847µm/°C. The plating bath was modified using rotating Hull Cell experiments [Fig.1]. A brass rod was electroplated with cobalt along its length before the experiment. This was done in order to avoid the interference in the reading of the %Cu in solution with that in brass. The sample was plated for varying current densities along its length and analyzed using X-ray fluorescence (EDXRF) to the relative composition of the individual elements. Sodium saccharin was added to relieve stress in the deposit. The temperature of the plating bath was maintained at 40°C and pH at 2.0. The experimental apparatus is shown in Figure 1.

Fig.1. The rotating Hull Cell apparatus with cobalt plated brass rod as cathode and platinized titanium mesh as anode in the Electrochemical Engineering Laboratory.

The Invar plating range was determined by compositional analysis, and calibrating the plated sample with a Hull Cell model. Polarization and Impedance Spectroscopy was carried out on the solution. Polarization curves for Nickel, Iron and Copper were obtained (Fig 2.).
MICROFABRICATION

X-ray LIGA was used to fabricate multilayer micro posts on a copper sputtered ceramic substrate. PMMA was used as the resist being bonded to the substrate. The X-ray mask [3] consisted of 130 X 130 grid circles with a uniform diameter of 100µm and with uniform spacing of 300µm. PMMA was fly cut to around 100µm, and the sample was exposed to X-rays using a synchrotron facility at CAMD. Electrodeposition was carried out by pulsing the current between two levels for Invar and copper. Invar, with small amounts of copper, was deposited at high current and copper alone at the low current. The plating setup consisted of an electroplating tank maintained at 40°C in a water bath with the ceramic substrate as the cathode and platinized titanium mesh as the anode. The solution was constantly stirred and filtered.

RESULTS

The deposition parameters were determined by referring to the polarization curves [Fig 2] obtained for the solution. The current density used in the Invar range was 55mA/cm² and that of copper is 0.5mA/cm². Initially, around 1µm thick multilayers of Invar-Cu and Cu were plated. The layers were visualized using the SEM. The SEM sample was gold coated before the analysis, in order to obtain a back scattered image of the layers as shown in Fig 3.

Fig. 2. Comparison of polarization curves for Ni, Fe and Cu at 150, 400 and 650 rpm.

Fig.3. Micro multilayers of NiFeCu and Copper as seen under SEM.

Microposts having nanolayers of copper and Invar-Cu were tested for their CTE behavior on a TA Instruments 2940 Thermo Mechanical Analyzer (TMA), using a 0.05Newton loaded expansion probe from ambient to 300°C with a 5°C/min at Stork Technimet Inc. (New Berlin, WI). Preliminary results showed a negative thermal expansion behavior in the microposts having a 5nm thick layer of copper [Fig 4]. After slow cycling between room temperature and 300 C, the CTE becomes positive. The negative CTE for Invar is predicted by theory [4, 5], but is a less stable form of the alloy. These experiments appear to confirm that, although the data are preliminary.

In ongoing work the effect of the copper layer thickness on the behavior of the alloy is being studied by electroplating multilayer samples with copper layer thicknesses of 1nm, 3nm, 5nm, 7nm and 9nm, alternating with the Invar-Cu layer, which is maintained at a constant thickness of 25nm. In addition, TEM, magnetic force microscopy (MFM), and Auger measurements are being made on as-deposited and annealed samples.

Fig.4. Subtraction curve showing negative CTE for an increase in temperature from ambient to 300°C.

FUTURE WORK

Characterization of the nanolayers has to be done on TEM. We are looking for MFM analysis to be done on samples, which detects the magnetostatic interactions in the layers. We are also looking into the hardness of the nanolayer posts that would give us an idea on its strength.

REFERENCES