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**ELECTROFORMED NICKEL-GRAPHITE COMPOSITE**

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## Introduction

Future x-ray astronomy will demand larger optics than Chandra, currently in orbit. Ways must be devised to produce cheaper and lighter x-ray mirrors to save the cost of manufacturing and launching this future telescope. One technique, being developed at Marshall Space Flight Center and elsewhere, is electroformed nickel replication technique, wherein mirror shells are electroformed (using pure nickel or a nickel alloy) onto super-polished and figured aluminum mandrels and are subsequently released by cooling. This technique can produce relatively inexpensive mirrors, but is hampered by the high density of nickel (8.9 g / cm<sup>3</sup>). An alternative is to develop a composite, with lower mass density and compatible mechanical properties to the nickel cobalt alloy, as the mirror shell material.

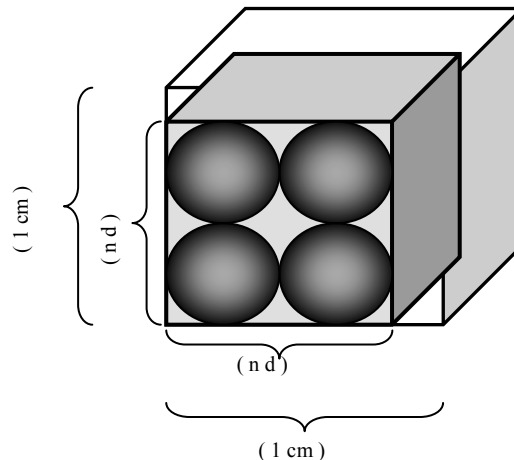
Electrocomposite films can be formed using traditional electroplating techniques in a plating bath mixed with various inert particles.[8,5,7,6] These composites typically have a considerably higher yield strength, hardness, and lower mass density than the pure metals. Assuming a composite is packed with identical spherical particles next to each other and the space between the spheres is filled with metal as shown in Figure 1, the density of this composite can be calculated using equation:

$$\rho_{com} = \frac{\pi}{6} \rho_{particle} + (1 - \frac{\pi}{6}) \rho_{metal} \quad (1)$$

Where  $\rho_{com}$ ,  $\rho_{particle}$ , and  $\rho_{metal}$  are the mass densities of the composite, the particle and the metal matrix, respectively. Figure 2 is a plot of  $\rho_{particle}$  versus  $\rho_{com}$  of the above equation at  $\rho_{met} = 8.90$  (nickel). As shown in figure 2, the mass density of the particle must be less than 3.3 g/cm<sup>3</sup> for its composite to have mass density below 6.0 g/cm<sup>3</sup> in this ideal case. In practice, the mass density of a composite would be higher than the value depicted by the graph due to particle size distribution and “poor particle packing”.

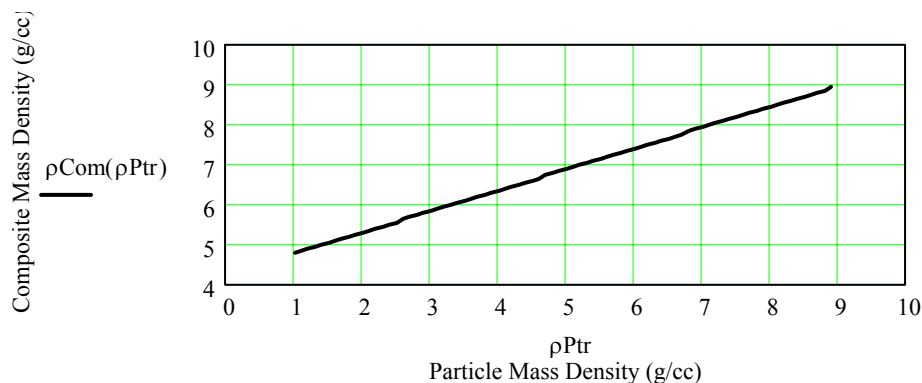
In a previous study [12] involving nickel and  $\gamma$ -phase alumina powder (mass density 3.3 g/cm<sup>3</sup>), we reported 23% alumina particle inclusion (by weight) using a special reverse pulse plating waveform. Applying this waveform, the deposit thickness per cycle is

Figure 1: Model for minimum theoretical density at maximum particle inclusion.



approximately the diameter of the particles at low duty cycle, the lowest mass density of the nickel-alumina composite achieved is  $6.4 \text{ g/cm}^3$ . Further reduction in mass density is desirable. Our goal for this study is to explore other composite systems to produce a composite with mass density less than  $6.0 \text{ g/cm}^3$ . Graphite is chosen in this study because of its low mass density,  $1.9 - 2.3 \text{ g/cm}^3$ , and availability (small sized powders, one micrometer or less, are commercially available.) The minimum theoretical mass density of this composite at maximum particle inclusion is  $5.2 \text{ g/cm}^3$ .

Figure 2: The theoretical minimum mass densities of composites as a function of mass densities of incorporated inert particles at maximum particle inclusions.



## Experimental

Nickel composite shells were formed in a 3.5-liter glass beaker. The electrolyte was nickel sulfamate bath as shown in Table 1. Synthetic graphite powder,  $1-2 \mu\text{m}$ , from Aldrich Chemical Company was used. All of the bath components were mixed with de-ionized water and blended in a blender for 2 minutes. The bath was stirred mechanically with a magnetic stirrer to keep the powder in suspension. The plating temperature was controlled automatically at  $47 \pm 1^\circ\text{C}$ . The pH of the bath was adjusted to  $4.0 \pm 0.2$  using sulfamic acid before plating each sample. The anode is a titanium coil in contact with nickel chips in a cylindrical basket. The cathode is a rotating nickel plated aluminum cone. After each shell was plated, the nickel composite shell (about  $220 \mu\text{m}$  thick) was removed from the cone using a mechanical pusher. The cone was then washed with Micro-90 concentrated cleaning solution and cotton wipes, rinsed with warm water and de-ionized water, dried with compressed air, dipped in  $5 \text{ g/L K}_2\text{Cr}_2\text{O}_7$  solution for 90 seconds to passivate the cone's metal surface, and further rinsed with de-ionized water. The cone was ready to be used again. KEPCO's BOP 20-20M bipolar power supply is used in this experiment to enable reverse pulse plating. This power supply was controlled by Labview software via a PC. The densities of the nickel-graphite composites were determined using Archimedes' principle.

## Results and Discussions

Many models have been developed throughout the years in attempting to understand the mechanisms of metal and inert particle co-deposition process.[4,1,3,9,11] It is understood the amount of particle incorporated is affected by the competition between the charge-transfer controlled metal deposition reaction and the mass-transfer limitation of the inert particle

deposition process. Generally speaking, the amount of particle incorporated increases as the particle loading in the plating bath increases. However, the gain is insignificant at particles loading above 20 g/L.[12,4] Thus, 20 g/L graphite powder loading was used for this study.

Table 1: Chemical composition of the electrolytes.

Nickel Metal as Sulfamate	100 g/L
Boric acid	35 g/L
Sodium Dodecal Sulfate (SDS) (wetting agent)	0.2 g/L
Graphite Powder (1~2 μm)	20 g/L

Unlike composites formed by metal matrix and inert particles, the conducting graphite powder makes it possible for this composite to plate in areas initially nonconductive during long time (more than 10 hours) plating. It is found that at 20 mA/cm<sup>2</sup> plating current density, about 50% of the composite was plated on the sample holder. Lowering the plating current density to 5 mA/cm<sup>2</sup> prevents this to happen completely. The current density threshold inhibiting this to happen lays between 5 mA/cm<sup>2</sup> to 10 mA/cm<sup>2</sup>.

Shell 4 was plated in direct current mode with 20 mA/cm<sup>2</sup> current density. Shell 6 and 10 were plated with reverse pulse plating waveforms. In the cases shell 6 and 10, the anodic current density was chosen twice that of the cathodic current density, as suggested by Tang, et al.[10] Shell 6 was initially plated by direct current at 10 mA/cm<sup>2</sup> current density for two hours followed by reverse pulse plating. Approximately two diameter (2D) of the graphite powder particles is plated and one diameter (1D) of the graphite powder particles is removed in each cycle. Shell 10 was initially plated by direct current at 5 mA/cm<sup>2</sup> current density for ten hours, then followed by reverse pulse plating (plating 3D and removing 2D.) As shown in table 2, mass densities of the composites continuously decrease as the duty cycle decreases.

Table 2 shows the mass densities of the composites plated under various conditions.

Shell #	Plating Mode	J <sub>C</sub> (mA/cm <sup>2</sup> )	T <sub>C</sub> (sec)	J <sub>A</sub> (mA/cm <sup>2</sup> )	T <sub>A</sub> (se <sup>c</sup> )	ρ(g/cm <sup>3</sup> )
4	DC	20	—	—	—	8.3
6	2D/1D	10	560	20	100	7.5
10	3D/2D	8	1050	16	250	5.62

The inner surface of this composite is rough, not suitable for mirrors. Most likely, an x ray mirror shell will require plating a thin layer of metal, such as nickel-cobalt alloy, followed by a thick nickel-graphite composite coating. This will increase the mass density of the mirror shell. The ratio of the composite mass (m<sub>com</sub>) to metal mass (m<sub>met</sub>) can be calculated for a targeted shell mass density using equation:

$$\frac{m_{com}}{m_{met}} = \frac{(\rho_{met} - \rho_{shell}) \cdot \rho_{com}}{(\rho_{shell} - \rho_{com}) \cdot \rho_{met}} \quad (2)$$

where ρ<sub>met</sub>, ρ<sub>com</sub>, and ρ<sub>shell</sub> are the mass densities of the metal, the composite, and the shell, respectively. Using our data, ρ<sub>met</sub> = 8.90 g/cm<sup>3</sup>, ρ<sub>com</sub> = 5.62 g/cm<sup>3</sup>, and ρ<sub>shell</sub> = 6.00 g/cm<sup>3</sup>, the mass ratio (m<sub>com</sub>/m<sub>met</sub>) should be larger than 5.

## **Conclusion**

Reverse pulse plating waveform, plating ND and removing (N-1)D each cycle, can be used in electroplating nickel-graphite composite to obtain low mass density. The lowest mass density of the composite achieved in this study is 5.62 g/cm<sup>3</sup>. This composite appears having sound mechanical properties, compared with brittle copper-graphite composite.[2] To inhibit nickel-graphite composite plating around sample holder, the cathodic current density should be kept below 10 mA/cm<sup>2</sup>, ideally at 5 mA/cm<sup>2</sup>. The roughness of the surface of the composite is not suitable for a mirror surface. Most likely, an x-ray mirror shell will require plating a thin layer of metal covered by a thick layer of nickel-graphite composite.

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## **References**

1. J. P. Celis, J. R. Roos, C. Buelens, J. Fransaer, *Trans. Inst. Metal Finish.*, **69** (4), 133, (1991).
2. C.G. Fink and J.D. Prince, *Trans. Am. Electrochem. Soc.* **54**, 315 (1928).
3. J. Fransaer, J. P. Celis and J. R. Roos, *Metal Finishing*, **91** (June), 97 (1993).
4. N. Guglielmi, *J. Electrochem. Soc.*, **119** (8), 1009 (1972).
5. A. Hovestad, L. J. J. Janssen, *J. Appl. Electrochem*, **25**, 519 (1995).
6. D. Landolt, *Journal of the Electrochem. Soc.*, **149** (3), S9 (2002).
7. M. Musiani, *Electrochimica Acta*, **45**, 3397 (2000).
8. R. Narayan and B. H. Narayana, *Reviews on Coating and Corrosion*, **4** (2), 113 (1981).
9. I. Shao, P. M. Vereecken, R. C. Cammarata, and P.C. Searson, *Journal of the Electrochem. Soc.*, **149** (11), C610 (2002).
10. P. T. Tang, H. Dylmer, and P. M. Oslender, *United State Patent* 6,036,833, (March, 2000)
11. Patrick R. Webb and Neil L. Robertson, *J. Electrochem. Soc.*, **141** (3), 669 (1994).
12. P. Xiong-Skiba, D. Engelhaupt, R. Hulguin, R. and B. Ramsey, to be submitted to *J. of the Electrochem. Soc.*