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THERMAL AND ELECTRICAL CONDUCTIVITIES OF ELECTROPLATED GOLD

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THERMAL AND ELECTRICAL CONDUCTIVITIES OF ELECTROPLATED GOLD

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Thermal conductivity of electroplated gold at cryogenic temperatures is an important parameter for predicting the thermal behavior of ignition hohlraums that will eventually be fielded on the National Ignition Facility. We have measured the ratios between the electrical conductivities at 4.2 K and room temperature for electroplated gold as a function of bath brightener concentration and plating current density. By using the Weidemann-Franz law we predict thermal conductivities of these samples. We find that even small amounts of bath brightener drastically reduce the conductivities, and that the conductivities have a strong dependence on plating current density.

I. INTRODUCTION

For indirect drive ignition targets fielded at the National Ignition Facility the ignition capsule is centered in a cryogenically cooled gold hohlraum,[a] and the deuterium-tritium fusion fuel is solidified into a layer on the interior of the capsule. The thickness uniformity and smoothness of the fuel layer depend on the thermal environment provided by the cryogenic hohlraum. A thermal shroud to prevent condensation of residual target chamber gasses on the target is removed a few seconds before the laser shot, and the resulting thermal transients due to the sudden ambient radiation heat load must be controlled so the fuel layer is not perturbed. This control is achieved by active feed-back to the heating elements on the hohlraum exterior, and the thermal conductivity of the gold wall is an important parameter.

Gold hohlraum walls are fabricated by electroplating onto a machined copper mandrel, which is removed by dissolving in an acid solution. Details of the entire process are given in an earlier paper by Elsner.[1] To study the thermal conductivity of the electroplated gold and the effects of varying plating conditions, we made measurements of electrical resistance of prepared samples at room temperature and at 4.2 K, and related these to the thermal conductivity through the Weidemann-Franz law:

$$\frac{\kappa}{\sigma} = L * T \quad , \tag{1}$$

where L is the Lorentz number. Then

$$\frac{\kappa_{4.2}}{\kappa_{300}} = \frac{RRR}{71} \quad . \tag{2}$$

In Eq. (2), *RRR* is the “residual resistivity ratio”, which is the ratio of room temperature and 4.2 K resistivities.

II. EXPERIMENTAL

Our aqueous gold electroplating baths are prepared with proprietary components from *Enthone*.[b] The main bath component is sodium aurosulfate [$Na_3Au(SO_3)_2$]. A brightener which contains arsenic in the form of dioxoarsenate ($NaAsO_2$) has traditionally been added to refine the grains and improve surface finish.[1] The sodium arsenate concentration in the brightener solution is “a maximum 5%” according to the product information sheets, but is diluted to a few mg of As per liter of plating solution. In this study, we varied the bath brightener concentration (0, 2.65, 5.3, and 7.95 cc/l) and the plating current (1, 4, and 10 mA/cm^2). For comparison, nominal values of these parameters used in our lab for typical gold platings are 5.3 cc/l and 4 mA/cm^2. Samples were prepared by plating onto 0.5 cm diameter copper cylinders 2 cm long. All samples were 40 μm thick as measured by laser micrometer with 0.1 μm measurement precision. The standard deviation of all samples measured was 1.2 μm. The cylinder diameters and thicknesses were chosen to be close to those of ignition hohlraums, and the length was chosen for measurement convenience. In all cases, at least two samples were made at each coating

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[a] The presence of a thin “cocktail” layer comprising a mixture of gold and uranium on the inside surface of the hohlraum may change the exact details of the thermal field problem, but not its general nature.

[b] BDT 510 from Enthone-OMI.

condition to check for reproducibility. Four-lead electrical resistance of the sample cylinders was measured using a current source settable to 0.01 A and a nano-volt meter (Fig. 1). Solderless electrical contact to the cylinders was made by means of commercially available gold spring-fingers mounted on a sample holder capable of lowering the samples into a 150 l liquid helium storage Dewar. Resistance was measured for each sample at room temperature (21°±1°C in our laboratory) and 4.2 K without de-mounting the sample or moving the placement of the spring fingers on the sample surface. Current leads were reversed at the source for measurements at both room temperature and 4.2 K to allow cancellation of any thermal or material-contact EMFs.

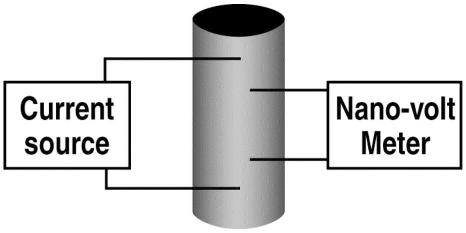

Figure 1. Resistances of hollow electroplated gold cylinders were determined from four-point measurements. All specimens had the same dimensions.

III. RESULTS

Our main experimental results are given in Fig. 2. Each symbol in the figure represents measurement of a different sample. We find that the measured electrical RRRs are maximized at about 30 for 4 mA/cm^2 with no brightener in the bath. Since nearly all gold has a room temperature thermal conductivity of about 3.3 W/cm-K,[2] then by Eq. (2), the thermal conductivity at 4.2 K will be about 140 W/m-K. Even our smallest additions of brightener drastically lower the RRR, and thus κ at 4.2 K.

As a check of our technique with this apparatus, we measured the RRR of a 99.99% pure gold foil to be 72. While this does not constitute a standard, the result is within the range to be expected.[c]

IV. DISCUSSION

Electrical resistivity of most metals at room temperature is generally dominated by conduction electron-phonon collisions, with a smaller contribution from impurity scattering and scattering from lattice defects such as vacancies. However at 4.2 K, the phonon distribution is depopulated to the point that impurity and defect scattering dominate. For low levels of impurities, the resistivity ρ is usually interpreted according to Matthiesen's rule, which states that $\rho = \rho_L + \rho_\iota$, ρ_L being the resistivity from the lattice phonons, and ρ_ι that from impurities including defects. With this interpretation, the residual resistivity at 4.2 K is just the second term, and the *RRR* is thus a measure of the degree to which a specimen approaches a pure perfect crystal. However, for metals with grain sizes that are of the same order as the intrinsic mean-free-path (mfp) of the conduction electrons, grain boundary scattering becomes a third source of resistance.

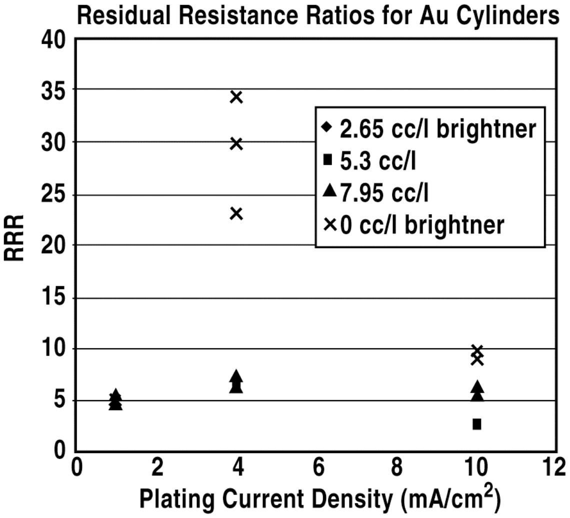

Figure 2. Residual resistance ratios peak at 4 mA/cm^2 with no brightener.

The electroplating literature reports that the grain size of deposited metals decreases when brightener is added to the plating solution, and also decreases with increasing plating current density.[3] A model of the effects of small grain size on electrical conductivity was developed by Mayadas and Shatzkes.[4] Their model shows that the total resistivity including grain boundary scattering, ρ_g, relative to the "intrinsic" resistivity ρ_0, which includes impurities and defects but not grain boundaries, increases with the ratio of the intrinsic mean-free-path l_0 to the average grain size d. Explicitly, their result is that

$$\frac{\sigma_g}{\sigma_0} = \frac{\rho_0}{\rho_g} = 3\left[\frac{1}{3} - \frac{1}{2}\alpha + \alpha^2 - \alpha^3 \ln(1 + 1/\alpha)\right] \quad , \qquad (3)$$

where $\alpha \equiv (l_0/d)(R/1 - R)$. The electron reflection coefficient at the grain boundaries, R, is left as a free parameter. Using a simple Drude-type model and the

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[c] Measured resistance ratios for 5-9s gold ranges from ~50 to ~280 (Ref. 2). Measurements of 4-9s gold below 1 K suggest a *RRR* about half of that for 5-9s (Ref. 2, Fig. 71).

electrical conductivity of gold, the mfp for conduction electrons at the Fermi surface is estimated at about 40 nm at room temperature. For gold with reasonable purity, the conductivity increases on the order of a factor of 100 (similar to our 4-9s standard above), giving an intrinsic mfp of about 4 μm at 4.2 K. Mayadas and Shatzkes find that the electron reflection coefficient for Cu and Al are around 0.2. Assuming the same reflection coefficient for Au, and also our result that with no brightener and 4 mA/cm^2 the resistivity at 4.2 K is about 3 times higher than for pure gold, (i.e., that the RRR is about 1/3 of that for pure gold), we estimate the average grain size for those plating conditions is about 670 nm. At 10 mA/cm^2 and no brightener, the RRR is about 0.1 that for pure gold, leading to an average grain size of 150 nm.

Based upon the Mayadas and Shatzkes model, some of the decrease in RRR upon addition of brightener results from decrease in grain size. However, brightener also adds impurities to the gold, decreasing the intrinsic mfp and increasing the resistivity. We examined several of our samples for impurities by inductively coupled plasma mass spectroscopy. The results for copper and arsenic are shown in Fig. 3. Sodium, if present, was less than the detection limit of 50 ppm. The As source is the brightener, while the Cu most likely is from the coating mandrels.

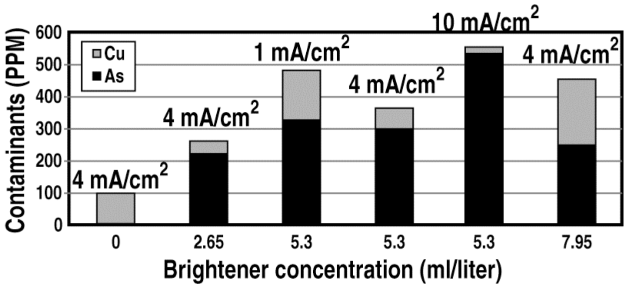

Figure 3. Arsenic and copper contamination concentrations as a function of brightener concentration and plating current density.

It has been reported that impurity concentrations decrease with increasing plating current densities.[c] Our results do not show such clear trends, but it is obvious that impurities result from the brightener. In Fig. 2, at 4 and 10 mA/cm^2 the brightener significantly reduces the RRR. However, most of the reduction at 4 mA/cm^2 can be ascribed to a reduction of grain size to about 100 nm. The room temperature resistance increases only about 10% for these samples, indicating about the same decrease in intrinsic mfp, so this is a reasonable conclusion. A large increase in impurities would have led to a larger increase in resistance from impurity scattering. The RRR reduction at 10 mA/cm^2 can be explained by a further grain size reduction to between 30 and 80 nm. However, the room temperature resistivity in this case increases by about 40%, which must be due to impurity scattering because in Mayadas and Shatzkes' model, for an electron reflectance of 0.2, no effect of grain size on resistivity is seen if the mfp is less than the average grain size. So at 10 mA/cm^2, the decrease in RRR is more sensibly accounted for by a 40% decrease in intrinsic mfp and average grain size decreased to between 20 and 60 nm

The data at 1 mA/cm^2 is puzzling. All of the RRRs collapse to 5.1±0.3, almost independent of brightener concentration. To explain this, the no-brightener point would require 70 nm grains. Why this might occur is not clear, since while adding brightener reduces grain size, grain sizes are reported to increase with decreasing plating current density. Be that as it may, a grain size small enough that it, rather than the impurities, limits the conductivity at 4.2 K would explain the data. While we can interpret our results in terms of the Mayadas and Shatzkes model, corroboration requires measurement of actual grain sizes in our samples.

V. CONCLUSIONS

The addition of brightener lowers the electrical, and therefore thermal, conductivity of electroplated gold at 4.2 K. With no brightener, our measured electrical conductivity is highest at 4 mA/cm^2 plating current density, although we did not scan current density finely enough to ascertain a true maximum. The brightener adds arsenic to the gold as an impurity, and copper is also present from the coating mandrel. The impurity levels are somewhat dependent upon the bath brightener concentration and plating current density, but in our data clear trends are masked by measurement variations. Based upon the model of Mayadas and Shatzkes, we can interpret our data in terms of changes in grain size and impurity concentration, but additional data would be required to corroborate this interpretation.

ACKNOWLEDGMENTS

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[c] Measured resistance ratios for 5-9s gold ranges from ~50 to ~280 (Ref. 2). Measurements of 4-9s gold below 1 K suggest a *RRR* about half of that for 5-9s (Ref. 2, Fig. 71).

REFERENCES

1. F. ELSNER, “Thickness Distribution for Gold and Copper Electroformed Hohlraums,” *Fusion Technol.* **35**, 81 (1999).

2 G. E. CHILDS, L. J. ERICKS, AND R. L. POWELL, *Thermal Conductivity of Solids at Room Temperature and Below*, NBS Monograph 31, September 1973, p. 108.

3. M. PAUNOVICH and M. SCHLESINGER, *Fundamentals of Electroplating Deposition,* 2nd ed., Wiley Interscience (2006), p. 273ff.

4. A. F. MAYADAS AND M. SHATZKES, “Electrical-Resistivity Model for Polycrystalline Films: The Case of Arbitrary Reflection at External Surfaces,” *Phys. Rev.* **B1**, 1382 (1970).