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Summary

Purified air is being considered as a cost-effective alternative to evaporated liquid nitrogen for cooling laser amplifiers in the National Ignition Facility (NIF). Atmospheric corrosion of the associated flashlamp reflectors could cause significant degradation of overall laser performance. Therefore, a comprehensive study has been undertaken to address this important problem. Specific contributions include:

- A detailed literature search, with a critical analysis of published data;
- Predictive calculations based on the published data, as well as new measurements made at Lawrence Livermore National Laboratory (LLNL);
- Analyses of proposed coolant gases to determine the actual concentrations of H_2S , SO_2 , COS , CS_2 , H_2O , NO_2 , Cl_2 , and organic forms of sulfur; and
- Investigations of both ultra-filtration of air and protective optical coatings as possible means of preventing mirror tarnish.

Background Information

Ag Flashlamp Reflectors. Ag has been chosen for fabrication of the NIF flashlamp reflectors because it is well matched to the Xe lamp emission and Nd:glass absorption. Light from the flashlamps is absorbed at wavelengths below about 380 nm, since the quartz flashlamp tubes are doped with cerium. In comparison to other known materials, Ag has the highest reflectivity in this region. The surface plasmon resonance in Ag occurs below 320 nm and defines the optical "cut off" for this metal. Furthermore, Ag has small polarization splitting at non-zero angles of incidence when compared with other metals. The useful region of the spectrum is assumed to be 400–1000 nm for the purpose of this study.

Tarnish Formation. Numerous studies have been published on the atmospheric corrosion of Ag by H_2O , H_2S , SO_2 , COS , CS_2 , NO_2 , Cl_2 , and other corrodants such as dimethyldisulfide (organic

sulfur compounds). A variety of techniques including electrical resistivity, ellipsometry, electrochemical reduction, SEM, XRD, XPS, and SIMS have been employed. Synergistic effects between these corrodants cause accelerated rates of corrosion, greater than the rates that can be achieved with individual corrodants. Tarnish formed in the presence of sulfur usually consists of Ag_2S , with typical rates of formation in the range 0.1 to 10 nm/hr. Initially, the tarnish growth obeys a linear growth law, since the film nucleates and propagates across the Ag surface as a number of individual islands. However, growth begins to obey a parabolic law after these islands merge and cover the entire surface. When attempting to mitigate this type of atmospheric corrosion, a higher priority is placed on eliminating moisture than on removing H_2S , SO_2 , or other impurities. Tarnish formation appears to be no worse on Ag than on comparable Ag-based alloys. Brightening and leveling agents incorporated into electroplated Ag mirrors may have a minor effect on atmospheric corrosion. Tarnishing due to gas-phase impurities can be prevented by: keeping the Ag surface under dry nitrogen; protective inorganic PVD films (MgF_2 , MgO , BeO , SiO_2 , TiO_2 and Al_2O_3); protective organic films (1-phenyl-5-mercaptopotetrazole or PMTA, benzotriazole, other mercaptans, mixture of morpholine and 2-mercaptopbenzothiazole); various chemical treatments used for passivation (chromating and adherent oxide formation); and ion beam implantation (with boron). Unfortunately, organic films are readily destroyed in the NIF environment by free radicals generated during ultraviolet (UV) radiolysis. In some cases, tarnish films have demonstrated photochemical activity. Such behavior complicates understanding of the corrosion phenomena at high fluence. Once formed, detrimental tarnish can be removed from mirrors by reaction in a reducing hydrogen plasma.

Impact on Reflectivity. Optical properties for the Ag and Ag_2S have been found and used to

calculate the effect of Ag₂S islands and continuous films on the reflectivity of Ag mirrors. Time-dependent predictions of reflectivity loss due to such sulfidation have been made available to those involved in the design and construction of such "mega lasers." Experiments are being used to verify and enhance computational models that have been developed to assess the long-term performance of the NIF flashlamp reflectors in relevant environments.

NIF Environment. Methods of controlling the atmospheric corrosion of silver surfaces at constant ambient temperature and normal exposure to light are well studied, as the literature study indicates. However, the details of what occurs depend very strongly on the specific gas-phase composition, solid-phase impurities, temperature excursions, as well as photon flux and wavelength, and are not well understood or quantified. This unique investigation focuses on the unusual environment encountered in large high-energy lasers. The specific conditions expected in the NIF laser amplifiers are:

1. Short bursts (~500 μs) of broadband (400–1000 nm), high-intensity photons capable of generating a high concentration of free radicals that may exacerbate tarnish formation.
2. A high thermal load that may instantaneously elevate the surface temperature by several hundred degrees, depending on substrate material. During this short-duration thermal pulse, associated stresses in the surface layer may crack protective ceramic layers.
3. A high instantaneous surface temperature that could eventually cause segregation of solid-state impurities from the bulk material to the surface. Such impurities may be introduced intentionally or accidentally during deposition of the reflective coating, and may exist at higher levels in electroplated Ag.
4. Acoustic shockwaves from the discharge in the flashlamps.

Predictive Calculations

Using published rates of tarnish growth in various environments, as well as published optical properties for the substrate, tarnish and protective coatings, predictive calculations have been performed to determine: (1) the effects of

gas-phase impurities on the tarnishing and reflectivity of flashlamp reflectors over long periods of time; (2) acceptable concentrations of various impurities in the gas phase; and (3) the loss of reflectance due to proposed protective coatings.

The modeling has involved taking dispersion data from the literature for the most probable corrosion products and calculating the reflectance as a function of time for these tarnish films grown on Ag. Reflectances were predicted over the entire spectral range of interest. This important work directly establishes long-term performance of a crucial NIF component.

The first model used by the authors to predict the thickness of tarnish films assumed that bare silver was subjected to time-dependent H₂S in the presence of various levels of moisture, specifically:

$$d = 0.5565 X_1^{0.44} X_2^{0.11} X_3^{0.42}, \quad \text{Eq. (1)}$$

where d is the thickness of the tarnish, in Å; X_1 is the relative humidity in percent; X_2 is the concentration of H₂S in v/ppm; and X_3 is the time of exposure in hr. Data used as a basis of this correlation were obtained from Pope et al. and Bennett et al.[1,2] Using this growth law, the reflectance of the unprotected flashlamp mirror at a wavelength of 500 nm and normal incidence was calculated as a function of time ($R_t = R_p$ at normal incidence). These initial calculations show that at ~5% RH and 0.1 ppb H₂S, the reflectance will drop from 99 to 95% over 10 years, which is believed to be acceptable. However, at a H₂S concentration of 1000 ppb (1 ppm), the reflectance drops to about 70% after 10 years, which is clearly unacceptable. Representative predictions are shown in Figure 1(a) and (b). The effects of AgCl and Ag₂O films on Ag reflectance have also been studied.

Figure 1. Representative predictions.
(a) Film thickness predictions ranging from 0.1 to 1000 ppb; (b) Reflectance calculations ranging from 0.1 to 1000 ppb.

Experiments

Measured reflectivities of electrodeposited silver, before and after exposure to 10^4 flashlamp pulses in Livermore air, were compared to model predictions. If one assumes that the increase in tarnishing rate observed in the flashlamp test facility is solely due to the effect of light, then the 1-month exposure to 10^4 flashlamp pulses should simulate 100 months of actual NIF operation. As Figure 2 shows, the predicted reflectance of bare silver agrees very well with experimental measurements from 400 to 800 nm. The solid curve (top) is the theoretical reflectance of a bare surface calculated with published values of the complex refractive index for silver. The dashed curve (bottom) is the theoretical reflectance predicted for a tarnished surface, assuming that the silver is covered by an Ag_2S film with a thickness of 8.67 nm. A Cary spectrophotometer was used to measure reflectance. Data from samples that were not exposed to flashlamp radiation are represented

by the open squares, which coincide with the curve for bare silver, as expected. Data from samples exposed to 10^4 flashlamp pulses are represented by the circular points and coincide with the curve for silver covered by Ag_2S . Experiments at LLNL show the following: (1) The tarnishing rate of a bare silver surface exposed to 10^4 flashlamp pulses and LLNL laboratory air flowing at a velocity of 10 m/s for 1 month is approximately 20 nm/month. If one assumes that the density of the tarnishing layer is 50% that of Ag_2S , this is equivalent to $80 \times 10^{-4} \mu\text{g}/\text{cm}^2 \text{hr}$. (2) The tarnishing rate of silver exposed to air is approximately 5 nm/month or that of $\sim 20 \times 10^{-4} \mu\text{g}/\text{cm}^2 \text{hr}$, if one assumes a density of the tarnishing layer is approximately half of Ag_2S . (3) One month exposure under simulated NIF conditions leads to a reduction in reflected power of about 16%.

Figure 2. Predicted reflectance of bare silver agrees very well with experimental measurements from 400 to 800 nm.

A new experimental test facility has been designed and constructed that will enable more precise quantitative predictions. Additional accelerated tests are being conducted in this facility at contaminant levels between 30x and 1000x the ambient (average) levels for: NH_3 , 51; SO_2 , 22; NO_2 , 13; H_2S , 1.6; COS , 0.6; and HCl , 0.4. To generate this mild tarnishing gas mixture for a 3-month-long experiment, cylinders of pure NH_3 , SO_2 , and NO_2 , and dilute mixtures of H_2S , COS , and HCl are being used. The gas handling system has been designed and the documentation required for its use is almost completed. Analysis techniques are also being developed to determine the level of these species in ambient air.

Industrial partnerships have been established with several commercial sources. The physical structures, surface and bulk compositions, and reflectivities of commercially available silver mirrors are being studied. Various substrates, including aluminum, stainless steel, and plastic, as well as prototypical protective optical coatings of MgF_2 , MgO , BeO , SiO_2 , TiO_2 , and Al_2O_3 are also being evaluated. The extent of protection prided by the best, commercially available protective coating during exposure to contaminated air and high photon fluxes will be established. Clearly, more investigation is warranted.

Summary

Work performed thus far provides a sound basis for specification of the gas purification process that will be needed by the NIF. Experiments that are in progress will provide valuable insight into the use of protective coatings as a viable alternative.

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