The Synergism of Hydrogen Sulfide and Nitrogen Dioxide in the Tarnish Process of Silver

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The objective was to determine the roles of hydrogen sulfide, nitrogen dioxide, water and oxygen during the process of tarnish film formation on silver. Silver was exposed to atmospheres with additions of hydrogen sulfide and nitrogen dioxide alone and to a combination of both corrosive gases. For each gas condition, the exposures were in moist air, dry air and moist nitrogen.

In order to get a better understanding of the atmospheric tarnish process, silver was exposed in mixed flowing gases containing 75% relative humidity (R.H.) at 25 C, and the resulting tarnish films were analyzed with a combination of techniques. The growth kinetics of tarnish films during the exposure was monitored by a quartz crystal micro-balance (QCM). X-ray Photoelectron Spectroscopy (XPS) was used for chemical analysis, and Field Emission Electron Microscopy (FESEM) was used to examine the surface morphology of the tarnish film.

The exposure of silver to 100 ppb hydrogen sulfide at 25 C and air containing 75% relative humidity produced a bulk film consisting of silver sulfide. For this exposure, the tarnish rate was initially linear and then exhibited parabolic behavior after the initial period. Exposure to 100 ppb hydrogen sulfide at 25 C in nitrogen containing 75% relative humidity produced a film less than a few nm thick consisting of silver sulfide or adsorbed hydrogen sulfide.

The exposure of silver to 1.2 ppm nitrogen dioxide at 25 C and air containing 75%(or 15%) relative humidity produced a thin film of silver nitrate and silver oxide (Ag_2O). The tarnish film profile was complete coverage of the surface with many nodules or hillocks protruding from the continuous film. The size and density of nodules increased with time for the humid exposures. Film growth did not conform to either parabolic or logarithmic behavior.

A major synergism of hydrogen sulfide and nitrogen dioxide on increasing the tarnish rate of silver is shown in Figure 1. The exposure of silver to all conditions containing 100 ppb hydrogen sulfide and 1.2 ppm nitrogen dioxide at 25 C and air produced a thick film consisting of silver sulfide. The kinetics of tarnish film growth conformed to linear behavior throughout the exposure. The tarnish rate was independent of the amount of relative humidity or the presence of oxygen; however, tarnish rate was sensitive to the flow rate.

The tarnishing process comprises a gas-liquid-solid system. Important parameters include: reactivity of pollutant gas, humidity affecting surface mobility and reaction mechanism, stability of a the substrate in ambient environment, stability of the substrate exposed to a pollutant gas, saturated aqueous solution condensed upon the tarnish film, electrical and ionic transport properties of tarnish film.

The combination of environment, substrate and tarnish film affects the behavior. The chemical stability and transport properties of the tarnish film are particularly important. A process model is presented in Figure 2 to delineate contributing chemical and electrochemical processes.

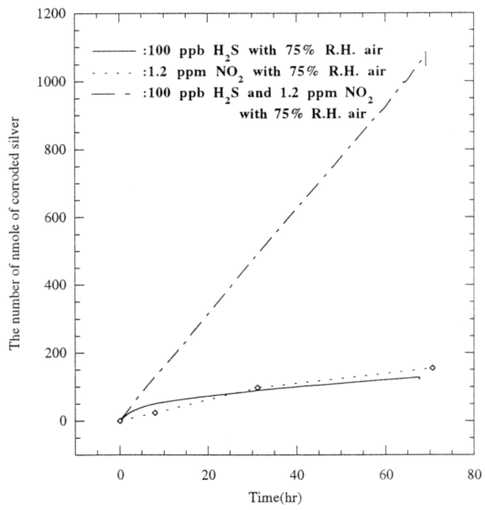

Figure 1-Synergism of H2S and NO2 on tarnish rate

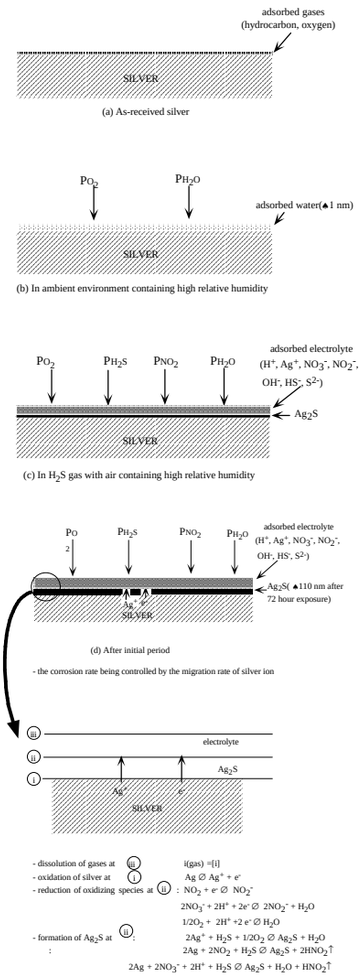

Figure 2-Chemical and electrochemical processes of film growth in humid air containing H_2S and NO_2