COMPOSITION PROFILING OF SOLAR COATINGS AND
MATERIALS WITH AES AND ESCAProgress Report
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Abstract:

The major accomplishments during the first nine months of this grant are the following:

- a) Heat treatment of stainless steel in air at 900°C produces a Cr_2O_3 coating which is an excellent diffusion barrier for preventing SS components at elevated temperatures to enter into a thermal absorber coating stack like Honeywell's AMA on Mo coating. We could demonstrate that this simple-to-apply oxide coating permits us to raise the operating temperature [in vacuum] from < 500°C to > 800°C without noticeable diffusion of constituents from SS into the coating.
- b) The experiments with a torus magnetically enhanced ring-gap discharge convinced us that it should be possible to coat by sputtering rather economically SS tubing with the AMA-Mo stack.
- c) A rather unexpected turn of events occurred when we discovered that one can enrich metal isotopes by sputtering. A paper on this subject is scheduled for the February 15 issue of Applied Physics Letters.
- d) In support of other ERDA's grantees, we provided various Auger and ESCA services.

The numbering and lettering of the following sections concurs with that of our updated work statement of the proposal.

As a result of an unforeseen discovery, as described below under item A,f which may have important implications in the energy field we have deviated to a certain degree from our suggested work statement.

Items A,a and A,b, concerning the study, characterization and improvement of electrolytically deposited solar thermal absorber coatings such as black Cr and black Ni, were de-emphasized. We could afford to do this because these coatings have been and are thoroughly investigated at Sandia and at Honeywell under other ERDA and NASA contracts. The only major effort was concerned with a thorough Auger and ESCA study of the changes which occur in black Ni coatings when they are exposed to high humidity. The analysis was performed by Physical Electronics Industries from where we received a detailed report, documented with about 40 Auger and ESCA spectra of exposed and of corresponding control samples at various depths, and Auger composition versus depth profiles. The results are to a considerable degree of a chemical nature in which Honeywell, which produced and humidity-exposed these samples and tested the optical properties before and after the humidity exposure has much more expertise. We discussed the results with Honeywell and decided that Honeywell would be in a much better position to evaluate and report these results intelligently to ERDA.

Item A,c, concerning the studies of the diffusion barrier properties of a Cr_2O_3 coating on stainless steel turned out to be very successful. We learned, mostly from the Int. J. of Hydrogen Energy,

of the exciting work which is going on in the area of catalytically-enhanced thermo-chemical reduction of water. If one wants to use this process for large-scale generation of hydrogen by solar energy, a need arises for a cheap solar absorber coating which will survive in vacuum at temperatures of the order of 800°C. Diffusion processes in Honeywell's AMA on Mo on stainless steel coating, which were the subject of extensive studies under our previous NSF/RANN/SE/GI-34871 "Research Applied to Solar Thermal Power Systems" Grant, make this coating useless at temperatures > 500°C. If this coating is, however, deposited not on SS but on a Mo substrate, it survives temperatures in excess of 800°C. We had previously shown with Auger composition profiling that the reason for failure on SS is that the SS components diffuse at > 500°C into the Mo and AMA stack. Therefore, a need exists for a diffusion barrier between the SS and the Mo. Under the same NSF-RANN Grant we had studied the air oxidization of SS and found, as described in the enclosed reprint, that with air oxidation at 900°C, one can build up on the surface a dense Cr_2O_3 layer. It became obvious that it would be very worthwhile to study if this cheaply-to-produce oxide layer might provide the desired diffusion barrier. The enclosed composition vs. depth profiles obtained with our Auger Thin-Film Analyzer shows clearly that this is indeed the case. Figure 1 shows the depth profiles of two samples which consisted of SS304 coated side by side by sputtering with a Mo film. The only difference between 1a and 1b is that the SS sample in 1b had been heat-treated in air for fifteen minutes at 900°C before the Mo deposition and became covered, as is clearly visible, with the Cr_2O_3 layer. Figure 2 shows the same two samples after a 700°C one-hour vacuum heat treatment. Figure 2a shows that the C which is readily movable in SS304 has

outdiffused from the SS and begun to convert near the interface the Mo to Mo-carbide. The carbide formation, of course, destroys the low infrared emissivity of the Mo. Figure 3, which is analogous to Figure 2, with the only difference that the samples were exposed to one hour at 900°C in vacuum instead of the 700°C, shows the diffusion barrier properties of the Cr_2O_3 layer much more dramatically. Without this barrier, Fig. 2a, all the SS304 components have penetrated the Mo film [with an interesting accumulation at the surface of the sample]. Figure 3b shows how well the diffusion of the SS components was stopped by the Cr_2O_3 layer.

Item A,d, which concerns the study of the suitability of a cone-covered SS surface subsequently coated with black Cr or black Ni for producing unusually high solar absorbance, has been postponed. The reason is that our third-year NASA-Lewis Grant, which starts on Jan. 1, 1977, has as the main subject the study of the cone formation phenomenon and its possible useful applications. It will make more sense when we run these studies concurrently and this we attempt to do in the remaining three months of the present grant.

Item A,e. Finding a cheap tubular substrate material like SS304 and a cheap method for covering it with an effective diffusion barrier solves only part of the problem, because for the AMA on Mo coating one still has to coat the tubing with a rather pure, oxygen-free, Mo film and the Al_2O_3 - MoO_x - Al_2O_3 stack on top. Our main expertise in knowledge and equipment has been "sputtering" and it was only natural for us to investigate if one could not find an economical scheme for coating tubing with this stack by sputtering. High-rate sputter deposition of films has in recent years made some remarkable progress with the so-called planar magnetron approach [R/D, Vacuum Technology,

January 1974]. With magnetic and electrostatic focusing of the electrons in a ring-gap plasmatron discharge one can achieve in cathode vicinity on a given closed directrix (such as a ring or racetrack) a very high plasma density and thereby achieve sputter deposition rates of the order of microns-per-minute. The same principle as used in this planar ring-gap discharge can be applied to a torus configuration. One can sputter towards the major axis and coat tubing uniformly from all sides without the necessity for rotating the tubing. We set out to explore the performance of such a torus ring-gap discharge. Figure 4 shows the [very tentative] setup and Figure 5 shows the bright plasma ring which forms in the ring-gap region where a magnetic field of the order of 500 Gauss is maintained with the attached horseshoe magnet.

To pull a polished cylindrical tubing through rubber O-rings into various vacuum and sputtering chambers and out to air again is a simple engineering task which has already been solved, because it is used for moving samples from air or a processing chamber into UHV apparatus for Auger-ESCA analysis.

During our studies we became aware of another group in East Germany [Schiller, Heisig and Goedicke, Forschungsinstitut Manfred von Ardenne, Dresden DDR, to be published in Thin Solid Films] who is experimenting with such torus ring discharges.

Our experimental results showed that a ~ 1 cm Diam substrate tubing was coated with 600 Å of Mo over 3 cm length in about 1 Min (750 volt DC discharge voltage, 12 ma/cm² Hg ion current density on a Mo target cylinder of ~ 6 cm Diam, 1 m Torr Hg gas pressure, 0.5 cm gap between magnetic poles). The setup is still far from being optimized.

We estimate from such very preliminary and conservative results that it should be a rather straightforward engineering task to build a coater in which 4 kilometers of SS304 tubing are coated per month with a stack which consists of about 1000 Å of Mo, 600 Å of Al_2O_3 , 300 Å of MoO_x , and 600 Å of Al_2O_3 . In cross section such a coater would look like shown in the attached sketch (Fig. 6.).

Item A,f was erroneously called A,g in the proposal. Under this item we had included the possibility that we might pursue promising unforeseen ideas and new results as they may possibly arise during the course of our study. Such a situation arose when we could demonstrate experimentally that different isotopes sputtered at low bombarding ion energy as neutral metal atoms from a flat target have a different angular ejection distribution. The idea and its verification emerged from a lucky combination of experiments in which our ERDA's acquired Auger equipment played as important a role as certain alloy sputtering studies, which we performed for NASA-Lewis in their ion thruster. The enclosed paper, which is scheduled to appear in the Feb. 15, 1977 issue of Applied Physics Letters, explains the subject matter in detail. This paper has been made the basis of an isotope enrichment proposal which is presently being evaluated at the ERDA Nuclear and Application Research Division.

Item B. We had fewer requests for Auger or ESCA thin-film analysis service in support of other ERDA solar projects than we expected, although we tried to make this [to ERDA's grantees charge-free] service as widely known as possible. Our steady customers were: Dr. Venkatesetty, Honeywell Corporate Research Center, in support of ERDA Grant E[04-3]-1109 [corrosion in molten eutectic salts]. Dr. Henry Mar, Honeywell Systems and Research, in support of ERDA

Grant EY-76-C-02-2930 [electrolytically-deposited black Cr, Ni and Fe's solar absorber coatings] and Dr. Dave Zook, Honeywell Corporate Research Center, in support of JPL-ERDA Grant 954356 [photovoltaic polycrystalline Si films on carbonized ceramic substrates].

The results obtained from this service have been or will be reported in detail in the technical progress reports of the grants for which the service was provided.

The principal investigator, G. K. Wehner, has devoted 1 month summer time and 30% of his academic time (5 1/2 months so far) to this contract.

Fig 4

Fig 5.

Fig 6.