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**Proceedings
Second Annual Conference on Absorber
Surfaces for Solar Receivers**

**Sponsored and Organized by:
Department of Energy
Solar Energy Research Institute**

January 24 & 25, 1979

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January 24 & 25, 1979
Hilton Harvest House
Boulder, Colorado

✓ Patrick J. Call
Editor

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INTRODUCTION

The Second Annual Conference on Absorber Surfaces for Solar Receivers was hosted by the Solar Energy Research Institute on 23-24 January 1979. The meeting was attended by representatives of the materials R&D community, the solar coatings industry, and collector manufacturers/distributors.

PURPOSE, GOALS AND OBJECTIVES

The Purpose of the conference was to provide a forum for coating developers to report on recent advances and for receiver developers/manufacturers to discuss evolving needs and field experience with available absorber materials. Interaction between these two groups both from the podium and in unstructured time periods was emphasized. A primary SERI objective for the meeting was to review ongoing R&D projects and opportunities for future externally contracted work.

CONFERENCE HIGHLIGHTS

Three conference topics are highlighted in this summary:

- 1) the development of microstructural models for black chrome selective solar absorbers;
- 2) the stabilization of black chrome for applications to 350° C; and
- 3) the laboratory demonstration of cermets for applications to 600° C.

The work in each of these areas is detailed in papers which appear in this proceedings.

Black Chrome Models (C. Lampert and J. Washburn, LBL; A. Ignatiev, U. of Houston; R. Pettit and R. Sowell, Sandia - Albuquerque)

Two distinct models have been developed for black chrome using both experimental and theoretical techniques. The LBL work based on SEM, TEM, and EDAX studies yields a model indicated in Figure 1a. Small (~ 100Å) chromium metal particles are imbedded in larger amorphous Cr₂O₃ particles (0.05-0.3 µm) that are loosely packed together to form the electrodeposited coating. The University of Houston model (based on XPS and SEM experiments; followed by theoretical calculations) is a film comprised of a layer of chromium metal ellipsoids (0.065 µm) with a thin Cr₂O₃ skin covered by a surface layer of

smaller ($0.035\text{ }\mu\text{m}$) Cr_2O_3 particles (Figure 1b). Accurate representation of the black chrome reflectance curve in the solar and thermal infrared spectral regimes is claimed to be unique to this model, which is also supported by Auger electron spectroscopy studies at Sandia Albuquerque Laboratories. Work in 1979 will continue to resolve this apparent contradiction so that improved black chrome coatings may be engineered based on a detailed understanding of the degradation modes.

Black Chrome Stabilization (R. Pettit and R. Sowell, Sandia - Albuquerque)

Following observations that some black chrome samples degrade (lose solar absorptance) at 300°C when deployed in single-axis tracking solar concentrators, an intensive effort was launched to determine a black chrome electroplating formulation that yields a high temperature stable solar coating. This work has established that the Cr^{+3} concentration in the plating both is a critical parameter and that with proper control ($\sim 8\text{ g/l}$) an absorber coating stable to 400°C for long periods of time ($\sim 3000\text{ h}$) can be produced.

Cermets (A. J. Sievers and H. Craighead, Cornell University)

A $\text{Pt/Al}_2\text{O}_3$ coevaporated cermet on a platinum-coated quartz substrate has been demonstrated to have excellent optical properties ($\chi_s \approx 0.94$, $\epsilon_t(500^\circ\text{C}) \approx 0.30$) and long term thermal stability at 600°C ($\sim 1000\text{ h}$). Work on other cermet systems (Fan, MIT; McKenzie, University of Sydney) suggests that this vacuum processing approach holds considerable promise for producing intermediate and high temperature selective absorbers.

SOLAR MATERIALS AND R&D PLANNING

It is the intention of the SERI Materials Branch, in cooperation with the SERI Solar Energy Information Data Base (SEIDB), to maintain updated information on research, developmental and commercial absorber materials, and a bibliography of publications and patents. The database will include lists of materials and suppliers/developers, laboratory properties, and documented field exposure data. A display of materials on 4 in. by 4 in. substrates with the name of the supplier, material description, and properties is also being developed. The cooperation of the absorber materials development community and commercial industry is essential to the success of these service functions. It is SERI's desire to establish a community spirit in solar materials research, development and manufacturing. Using the Materials Branch/SEIDB as a point of focus for materials and information, we believe that the development of this community will be accelerated. Although to date the response to calls for materials and information has not been enthusiastic, a bibliography is suitably mature to be appended to this years' proceedings. (An abbreviated "new materials" section is also appended.)

Materials R&D program planning documents are being readied by the SERI Materials Branch in cooperation with other national laboratories. These planning documents are being organized by function as outlined in Figure 2 and are (or will be) available through SERI or NTIS by the report numbers listed in Table 1. The R&D Plan for Absorber Surfaces (SERI TR-31-103) was distributed

at the January conference. It is intended that these plans be evolving documents updated on a yearly basis and incorporated into the appropriate DOE multiyear program plans and budget cycles to ensure adequate support. Industry and materials community review and criticism of these plans is part of this process, feedback regarding the Absorber Surfaces R&D program should be addressed to the editor.

There has not been a coordinated Solar Materials Activity, so one goal of the SERI Materials Branch is to create an integrated and vigorous program. Success will be achieved only with the cooperation and support of all interests: research, commercial, and government.

MEETING EVALUATION AND PLANNING

Although the call for papers explicitly requested papers on field exposure studies, durability, and user feedback, no such papers emerged and the sessions were limited to R&D topics that were not entirely appropriate for the general audience present. This mismatch between audience and speaker interest was the most frequently noted criticism of participants in a response to a survey conducted at the conclusion of the meeting. To address this concern, a session entitled Testing, Durability, and Field Evaluation is being organized as part of the American Electroplaters' Society Symposium on Solar Coatings to be held in St. Louis, Missouri, on October 16 and 17, 1979. This session will deal solely with the practical experience using solar coatings to 300°C, the tests that have evolved to screen prospective coatings, and the results of these tests when applied to presently available absorber coatings.

TABLE 1

Functional Area		Planning Committee	SERI Report No.	Status
Optical Materials	Absorbers		TR-31-103	Published; Industry Review
	Transmitting Materials	SERI, Sandia, LASL, JPL, PNL, NBS	MR-31-301	In process (9/1/79)
	Reflectors		MR-31-302	In process (9/1/79)
			(glass - RR-31-145) (status - TR-31-137)	Published Published
Fluids/Containers		Sandia, JPL, SERI	MR-31-247 (Resource document - TP-31-248)	In process (8/1/79)
Structural Materials		To be determined	MR-31-303	To be started (7/1/79)

a. SEM, TEM, EDAX (Lampert and Washburn, LBL and U. C. Berkeley)

b. XPS, SEM, Auger Theory (Ignatiev, U. of Houston; Pettit and Sowell, Sandia-Albuquerque)

Figure 1. Microstructural Models of Electrodeposited Black Chrome on Nickel

Solar Materials—National Planning

Figure 2.

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THE SURFACE MICROSTRUCTURE - OPTICAL PROPERTIES RELATIONSHIP IN SOLAR ABSORBERS

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ABSTRACT

The relationship between the surface microstructure and the optical properties of solar absorbers has been theoretically analyzed and applied to the optimization of the optical response of particulate solar absorbers. The relationship indicates that for pure metallic particulate coatings, α/ϵ of >50 can be expected. The relationship has also been applied to the Black Chrome system where it has been shown that Black Chrome's optical response is in fact due to its particulate nature. In addition optical degradation in Black Chrome has been tentatively linked to the growth of thick oxide skins on the chromium particles constituting the bulk of the coating.

MICROSTRUCTURE -OPTICAL PROPERTIES RELATIONSHIP

Our recent studies of the optical response of particulate systems has resulted in a theoretical model, the Spheroid Model [1,3], for the description of their optical properties dependent on the shape and distribution of the particles in the material.

Selectivity

According to the Spheroid Model, the dielectric function for a low density particulate composed of metallic particles whose shapes are represented by spheroids of various eccentricities imbedded in vacuum can be defined as a function of the distribution of particle eccentricities, i.e. a distribution of particle shapes. Particles of given eccentricities (or semimajor to semiminor axis ratio, m) define the wavelength dependence of the absorption coefficient for the system as shown in Figure 1 for metallic chromium particles.

FIGURE 1.
THE DEPENDENCE OF THE NORMALIZED ABSORPTION COEFFICIENT ON
WAVELENGTH FOR SPHEROIDS OF CHROMIUM IN A FILM OF $1\mu\text{m}$
THICKNESS AND PACKING FRACTION OF 0.06. M IS THE SPHEROID
SEMIMAJOR TO SEMIMINOR AXIS RATIO.

This therefore brings to mind the point that a specific distribution of particles will posses a specific spectral response. The specific response currently sought is that of the selectivity step function. In this work the step in absorptance has been put at $3\mu\text{m}$ and distributions of nickel, gold and chromium spheroid particles have been generated that minimize the difference between the respective metallic systems and the ideal step function, i.e. best approximate the step function. It can be seen from Figure 2 that the optimal distributions are quite different for the different metal systems stemming from both different interband and Drude contributions in the respective metals.

FIGURE 2.
ABSORPTANCE OF GOLD, NICKEL AND CHROMIUM FILMS OPTIMIZED TO
APPROACH THE DEPICTED STEP FUNCTION. OPTIMAL SPHEROID
DISTRIBUTIONS ARE SHOWN IN THE INSERTS.

In the above data, the optimal total distributions were obtained by varying the intensity of any of three Gaussians chosen to represent the particle shapes in the distribution. Three gaussians (each at a different m) were chosen to represent the distribution for ease of computation instead of using all possible eccentricity (m) spheroids. The thickness of the films (all with packing fraction of 0.06) was also varied in the optimization. It should be noted that under realistic coating thicknesses (0.4 to 5 μm) good semblance to the step function has been obtained with α/ϵ at ~ 25 to 30. Increasing the grid of the particle distribution to include five (5) gaussians instead of three has resulted in still better selectivity with α/ϵ of 58 for nickel and an α of 0.91 [4].

It is clear from this work that spectral response of a particulate system can be tailored by varying the particle shapes and distribution, i.e. the microstructure of the coating.

Black Chrome

The Spheroid Model has also been applied to analysis of the optical properties of Black Chrome and degradation of the optical properties upon furnace heating samples in air to 350 C.

Optical Properties

Our previous XPS and SEM work on Black Chrome has defined the exact microstructure of the coating [5,6]. This was used as an input to the Spheroid Model calculations in order to obtain the theoretical optical response for a particulate medium with the structure of Black Chrome. Figure 3 indicates the previously determined particulate structure of the Black Chrome coating along with three calculations and the measurement of the optical response of the coating.

FIGURE 3.
MICROSCOPIC STRUCTURE AND REFLECTANCE FOR BLACK CHROME.
CURVE A: EXPERIMENT; CURVE B: SPHEROID MODEL CALCULATION;
CURVE C: THIN FILM INTERFERENCE STACK CALCULATION.

The quite striking agreement between the Spheroid Model calculation and experiment clearly indicates that the proper optical response cannot be obtained for a particulate system unless the microscopic structure of the medium is considered.

Optical Degradation

With the knowledge of the basis for the optical properties of Black Chrome in hand, it can now be attempted to understand the basis for optical degradation upon furnace heating in air, and solar radiation heating in air. With the optical response of Black Chrome linked to its particulate structure and chemical nature, changes in these quantities upon heating will result in optical degradation.

Harshaw "ChromOnyx" Black Chrome coatings plated on pure nickel substrates were subject to 12 hours of furnace heat in air at 250 C, 350 C and 450 C and in high vacuum ($P < 10^{-7}$ torr) at 350 C. The spectral response of the samples was monitored and showed a marked increase in infrared reflectance after 250 C heat in air with further increases in visible and infrared reflectance after 350 C and 450 C heat in air [7]. The high vacuum heated sample showed no change in optical response after the 350 C heat.

Auger electron spectroscopy (AES) inert-gas ion bombardment depth profiles performed on the air heated samples indicated an increase in the amount of oxygen in the bulk of the coating by over 300% (depending on temperature) whereas the high vacuum heated sample showed no significant changes in the profiles of any of the constituents in the coating (Cr, O, C, Ni). Scanning electron microscopy (SEM) studies along with inert-gas depth profiling however, have indicated that the particulate structure of the coatings is retained. There is a slight indication that some agglomeration of the particles may be occurring in the air heated samples, however, further studies are required to clarify this point.

The retention of the particulate structure in Black Chrome after heating indicates that gross structural changes are not taking place upon heating in air and that therefore the Spheroid Model can be utilized for the study of the optical degradation of the coatings. The large increase of oxygen in the coating with no significant microstructure change is consistent with the possibility that heating the coating in air may result in simply the oxidation of the individual chromium particles constituting the films with the formation of a thick oxide skin on the individual particles. The occurrence of this can be included within the Spheroid Model and the resultant optical response as a function of oxide skin thickness can be generated. Figure 4 shows the effect of increasing oxide skin thickness on the reflectance of the coating. Note the increased visible and infrared reflectance as does occur in experiment.

FIGURE 4.
SPHEROID MODEL CALCULATION FOR REFLECTANCE DEPENDENCE OF
BLACK CHROME ON OXIDE COATING THICKNESS t , ON CHROMIUM
PARTICLES. A: $t = 10\%$ DIA; B: $t = 20\%$ DIA; C: $t = 40\%$ DIA;
D: $t = 60\%$ DIA.

Direct comparison of theory to experiment in Figure 5 indicates that for the 250°C air heated sample an oxide skin thickness of approximately 20% of the particle mean radius is expected and that for 350°C air heated samples a skin thickness of $\sim 40\%$ of the particle mean radius is expected.

It should be noted that the agreement in Figure 5 is not as good as in Fig. 3 and this is possibly due the fact that some agglomeration of particles seems to occur. This agglomeration could possibly change the particle distribution of the black (assumed to be log-normal) and therefore effect its optical response. If agglomeration does significantly occur, the change in distribution would be one toward more spherical particles. Such a change would tend to reduce infrared reflectance, with a slight reduction being called for in the comparison between theory and experiment (c.f. Fig. 5).

FIGURE 5.
COMPARISON OF SPHEROID MODEL CALCULATIONS INCLUDING THICK
OXIDE SKINS ON CHROMIUM PARTICLES TO EXPERIMENT FOR THERMALLY
DEGRADED FILMS. 250° C AIR HEAT -- $t = 20\%$ PARTICLE DIAMETER;
350° C AIR HEAT -- $t = 40\%$ PARTICLE DIAMETER.

CONCLUSIONS

In conclusion, the dependence of a particulate medium's optical properties on its microstructure has been demonstrated. The analysis has been extended to electrodeposited Black Chrome with the results that not only is the basis for Black Chrome's optical properties understood, but preliminary understanding is also obtained for the degradation of these optical properties under furnace heating in air.

ACKNOWLEDGMENTS

Support for this work is acknowledged from the Department of Energy and the University of Houston Energy Laboratory.

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NOTES

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MICROSTRUCTURE AND OPTICAL PROPERTIES OF
BLACK CHROME BEFORE AND AFTER EXPOSURE TO
HIGH TEMPERATURES

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ABSTRACT

The chemical and microstructural stability of the CHROM-ONYX type of black chrome solar coating was investigated at different temperatures and atmospheres. This was done to give a better understanding of the mechanism of solar energy selectivity and its variability when subjected to short term heat treatments. The as-plated structure was found to consist of a suspension of metallic chromium particles within the size range of $100\text{\AA}$ in an amorphous oxide matrix. This assembly was in turn formed into larger particles within the size range of 0.05-0.30 microns. Short term high temperature heat treatments were used to simulate stagnation conditions. Samples were annealed in both air and vacuum, which resulted in similar characteristics. Annealing in air appeared to mildly accelerate optical degradation at high temperatures. For short term heat treatments below 300°C the reflective and microstructural properties appeared to be unchanged. By in situ vacuum annealing of the coating above 400°C microcrystalline Cr_2O_3 was identified. By observation of diffraction patterns it was concluded that a- Cr_2O_3 was transformed into crystalline Cr_2O_3 . The Cr_2O_3 phase continued to grow at higher temperatures at the expense of chromium content. At temperatures above 500°C in vacuum, a new phase identified as Cr_3O_4 formed. It was found that black chrome failed optically between 500 - 600°C for 1 hour heat treatments in both air and vacuum; also the coating heated in air failed mechanically by peeling at 600°C .

INTRODUCTION

Black chrome is one of the major selective surface candidates for use as solar collector absorber coatings. Of the different types of black chrome, the commercial coating "CHROM-ONYX," a jet black finish manufactured by the Harshaw Chemical Company, has been of interest to various investigators and commercial solar collector manufacturers. Although the basic solar selective properties of this material have been investigated [1,2] and life tested relative to other coatings [3-6], very little as yet is known about the physics and microstructure of black chrome. Three major areas remain as fields of current research on black chrome. They are: the investigation of the physical mechanisms of selectivity, its stability upon heating and humidity (both short and long term), and the atmospheric corrosion effects upon black chrome.

However, a simplified absorption mechanism for this coating has been suggested [7] and modeled [8,9] according to Maxwell Garnet theory. Accordingly, there is need to clearly identify the actual absorption mechanism and how it is affected by various operating conditions experienced by solar collectors. It is necessary to understand the effect of stagnation events, humidity, thermal aging, vacuum and air atmospheres upon solar selectivity and stability of black chrome. The following study focuses upon two areas of research, namely the character of as-plated black chrome and the effect of short term heat treatments upon its microstructural and optical properties.

EXPERIMENTAL PROCEDURES

In this study copper test panels were electroplated with black chrome by the Harshaw Chemical Company, according to a conventional procedure. Further details of the as-plated structure and plating parameters are discussed in related research [10]. Throughout this investigation identical samples, consisting of 1.0 micron of black chrome on dull nickel plated copper, were used.

Hemispherical spectral reflectance measurements were used to investigate the optical selectivity of each sample. All reflectance measurements were performed on a Cary 14 integrating spectrophotometer for wavelength range of 0.28-1.8 microns. The measurements for the wavelength range 2.0-2.5 microns (infrared) were done on a Gier Dunkle Model HC 300 heated cavity reflectometer with a directional integrating sphere. All reflectance measurements were taken near normal (20°) incidence.

Both surface and cross sectional morphology were analyzed with the aid of an AMR 1000 scanning electron microscope (SEM). Qualitative elemental analysis was determined by energy dispersive X-ray analysis (EDAX).

Transmission electron microscopy (TEM) was employed to analyze the internal structure and chemical makeup of the coating. A Philips EM 301 research electron microscope was used for this investigation. By use of a heating stage attachment to the TEM it was possible to view the effects of heating upon the morphology and chemistry of black

Figure 1. Wavelength correlation between black chrome spectral reflectance, the solar spectrum and black body spectrum (100°C, 300°C).

chrome. Metallic chromium and oxide particle distributions were revealed by use of gun tilt dark field techniques. A Zeiss particle size analyzer was used to determine the size distribution of these particles.

Heat treating experiments were carried out by one of three methods. Samples heat treated in air were annealed in dry air at 1 atmosphere in a Lindberg tube furnace. Melting point standards and continuous temperature monitoring were used to assure the accuracy of the heat treatment. Vacuum annealing was carried out either in situ within the TEM hot stage at 10^{-4} - 10^{-5} Torr or by vacuum encapsulation.

Samples used for spectral reflectance measurements were encapsulated in long quartz ampules. The encapsulation process consisted of pumping the ampules below 10^{-3} Torr, backfilling with argon and resuming pumping. This process was repeated twice and the ampules were sealed off under vacuum. For purely mechanical strength reasons a partial pressure of argon was allowed to remain in the final encapsulated sample tubes.

RESULTS AND DISCUSSION

The following treatment is divided into three major categories. The first deals with spectral reflectance measurements; the second, scanning electron microscopy and last, transmission electron microscopy including in situ heat treating. These results will be correlated to form a microstructural and chemical model of the black chrome surface to show how it transforms and degrades during short term heat treatments.

Spectral Reflectance Measurements

Hemispherical reflectance measurements are used to derive both absorptance, $a(w,s,t)$ and emittance $e(w,s,t)$ where w is a given wavelength of incident energy at a position (s,t) of the material. An example of a typical reflectance plot and its relationship to the solar spectrum and black body spectra is shown in Figure 1.

In general practice integrated values of absorptance and emittance are useful for solar collector designers. Integrated absorptance (a_i) is

TABLE 1
Integrated Absorptance and Emittance (27°)
for Heat Treated Black Chrome in Vacuum**

Heat Treatment	e_i	a_i	a_i/e_i
None, As-plated	0.12	0.93	7.75
200°C, 1 hr.	0.11	0.93	8.45
300°C, 1 hr.	0.11	0.93	8.45
400°C, 1 hr.	0.12	0.94	7.83
500°C, 1 hr.	0.08	0.92	11.5
600°C, 1 hr.	0.08	0.8	10.0

Values rounded to 2 places. **Residual atmosphere is inert gas.

TABLE 2
Integrated Absorptance and Emittance (27°)
for Heat Treated Black Chrome in Dry Air

Heat Treatment	e_i	a_i	a_i/e_i
None, As-plated	0.12	0.93	7.75
200°C, 1 hr.	0.11	0.93	8.45
300°C, 1 hr.	0.09	0.93	10.3
400°C, 1 hr.	0.10	0.93	9.3
500°C, 1 hr.	0.07	0.90	12.86
600°C, 1 hr.	0.10	0.73	7.3

Values rounded to 2 places.

the average absorptance at each wavelength weighted according to the solar energy intensity distribution. Integrated emittance (e_i) is computed by taking the average emittance at each wavelength weighted according to the blackbody intensity distribution.

In Tables 1 and 2 values for a_i and e_i are tabulated for various short term heat treatments. One hour heat treatments are used for each sample. The data shown in Tables 1 and 2 is derived in part from the curves shown in Figures 2-4. For samples heat treated below 300°C the reflectance plots are fairly identical and resemble the reflectance shown in Figure 1.

Black chrome whether heat treated in air or vacuum for short periods of time appears to exhibit the same characteristic reflectance. A major change in reflectance is noted between the 500°C and 600°C ranges and it

Figure 2. Spectral reflectance for black chrome heat treated in vacuum over the 300-500°C range.

XBL7810-6080

Figure 3. Spectral reflectance for black chrome heat treated in dry air over the 300-500°C range.

XBL7810-6079

Figure 4. Spectral reflectance for both black chrome annealed in dry air and vacuum at 500, 600°C.

XBL7810-6081

appears to be accelerated slightly by presence of air (Figure 4). However, up to and including the 500° range the basic reflectance only exhibits subtle variations.

All samples tested show a characteristic second maxima centered between 1-3 microns. It is fortunate that this maxima occurs close to the cut-off wavelength for the solar and black body spectra. That is, reflectance variations near the cut-off wavelength would have only a slight effect on the a_1 and c_1 values, as shown in Tables 1 and 2. This maxima becomes fairly pronounced at 300°C and subsequently grows in

amplitude with increasing temperature. The presence of air accelerated its growth. The existence of this maxima might be partially explained as a thickness interference effect with its amplitude and position dictated by effective index of refraction and coating thickness, respectively.

Another phenomena is observed from 300°-500°C. At 400°C a noticeable shift of the transition region (2-10 microns) occurs toward the infra-red wavelengths. At 500°C this region shifts back towards the visible region, the overall shift being about 1 micron in wavelength. It is quite possible that structural changes are taking place within the coating to account for this.

Finally a minor infrared absorption, at about 20 microns, is noted commencing with the 400°C samples. This absorption is characteristic of crystalline Cr_2O_3 [11].

To help explain these observed effects it is important to determine chemical and structural changes upon heating within the coating. This will be shown with the aid of both scanning and transmission electron microscopy.

Scanning Electron Microscopy

Typical surface microstructures are depicted in Figure 5 for all short term heat treatments ranging from as-plated to 600°C. By comparing the as-plated structure (Figure 5a) with the 600°C sample (Figure 5b) an increase in surface roughness and particle size, including what appears to be a second phase, has evolved at the higher temperatures. In all cases the surface structure exhibits a porous network of particles, like a sintered powder. From the as-plated to 200°C range of samples

Figure 5. Black chrome examined by SEM at 20 kV, 20° tilt after 1 hour heat treatments. (a) typical surface structure for 27°-200°C heat treated samples. (b) surface structure for 600°C heat treatment, showing formation of bright white particles.

the particle size varies from 0.05-0.30 microns in diameter, with the smaller particles comprising the peak distribution. Beginning at 300°C larger particles, probably an oxide phase (crystalline Cr_2O_3), become apparent. At 400°C particles as large as 1 micron are noticed although the average size is around 0.10-0.20 microns for both phases. Finally at 600°C particle sizes in excess of 1 micron are observed, and the second phase now makes up significant areas of the surface structure. As this second phase grows the surface tends to roughen. The presence of these second phase particles probably accounts for part of the complex reflectance at 600°C.

The effect of air upon the surface structure is not very noticeable until 600°C. Above 600°C the coatings peeled off the samples heated in air, while samples heated in vacuum withstood 700°C for one hour and 800°C for 20 minutes. All coatings form erupted regions which are responsible for mechanical failure above 400°C, which become very apparent at 600°C. These regions appear as glassy phases either in the form of black or white blotches as seen by the TEM. This failure mode will be discussed in detail elsewhere [12]. Energy Dispersive X-ray Analysis (EDAX) was performed on all samples. From this analysis the presence of chromium and nickel (from the substrate) was detected. This method does not specify whether chromium is metallic or part of a compound, or what its structural forms might be. For further analysis of the internal structure Transmission Electron Microscopy must be employed.

Transmission Electron Microscopy

Black chrome on nickel plated copper samples were ion thinned so each sample could be analyzed by conventional TEM techniques. Care was taken to ensure that the ion thinned samples were not altered or heated appreciably during thinning.

As-Plated and Low Temperature Structure

A dark field photograph depicting large agglomerated composite particles containing metallic chromium particles is shown in Figure 6. The diffraction pattern reveals crystalline chromium embedded in an amorphous (a) oxide matrix, presumed to be $\alpha\text{-Cr}_2\text{O}_3$. This analysis is detailed elsewhere [13]. The peak chromium particle size occurred at 72Å with a mean size of 139Å.

In Situ Vacuum Annealed Structure

The vacuum annealed structure is identical to the as-plated structure up to 400°C; starting at 400°C-500°C the appearance of crystalline, Cr_2O_3 is noted, identified from diffraction patterns in Figure 7a. No appreciable decline in chromium content is noted; some agglomeration of chromium is apparent, however. At 600°C many lines of Cr_2O_3 can be identified from the diffraction pattern (Figure 7b) along with a new phase Cr_3O_4 , a high temperature spinel. These conclusions are based on 6 identified lines of Cr_2O_3 and 3-4 lines of Cr_3O_4 and 1 faint line of chromium at 600°C heat treatments. At even higher temperatures both

Figure 6. Agglomeration of chromium particles with matrix material viewed by TEM at 100 kV. The dark field shows metallic chromium particles as white spots. The dense black regions are holes produced by ion thinning.

phases predominate at the expense of metallic chromium which finally depletes. It is uncertain if Cr_3O_4 , an oxygen deficient phase, forms because it is favored thermodynamically to form in vacuum or whether Cr_2O_3 in air would be favored at high temperatures. However, this is of minor consequence because for all practical purposes the coating has failed between 500–600°C when heated for short periods of time. Typical particle shapes and distributions are shown in Figure 8b for Cr_3O_4 and Figure 8c for Cr_2O_3 . This sample was heat treated at 600°C for 30 minutes. The bright field for this pair is shown in Figure 8a and diffraction pattern in Figure 7b.

Annealing in Air

All samples annealed in air up to 300°C exhibit similar morphology and composition to the as-plated structure. At 400°C and higher temperatures, the diffraction pattern for the coating revealed 4 lines of crystalline Cr_2O_3 along with crystalline chromium. These lines in general were more intense than those for vacuum annealed specimens. This may indicate that the amorphous to crystalline transformation of Cr_2O_3 is aided by the presence of air, essentially lowering the transformation temperature. Effects of higher temperatures remain as a current research effort for samples annealed in air.

CONCLUSIONS

From this research the following conclusions appear to be valid for the solar selective absorber, known as CHROM-ONYX.

1. The as-plated structure of black chrome on dull nickel consists of voids and particulate masses within the size range of 0.05–0.30 microns in diameter. These particles are in turn composed of fine chromium

Figure 7. Typical diffraction pattern for 1 hour heat treatment

(a) at 400 and 500°C. Low order Cr_2O_3 and chromium rings are noted along with a diffuse halo region.

(b) Annealed at 600°C. Low order Cr_3O_4 , Cr_2O_3 and faint Cr lines are shown.

particles (mean dia. $139\text{\AA}$) suspended within a matrix of amorphous Cr_2O_3 .

2. After heating for a short period of time (e.g., 1 hr.) in air or vacuum, black chrome does not show appreciable degradation optically, chemically or mechanically up to 300°C .

3. The effect of air upon black chrome appears only to mildly accelerate degradation at temperatures above 300°C , when compared to that in vacuum. However, it may be possible that the coating contains trapped oxygen.

4. At and above 400°C black chrome exhibits a structural transformation within the matrix material Cr_2O_3 . The metallic chromium distribution appears to be unaffected.

a

Figure 8. Morphology of black chrome after 1 hour heat treatment at 600°C, viewed by TEM at 100 kv.

b

(a) Bright field showing particulate coating.

(b) Dark field of region (a) depicting bright white particles as Cr_3O_4 .

c

(c) Dark field of area (a) showing Cr_2O_3 particles.

5. Above 500°C after 1 hour heat treatments, this coating shows growth of Cr_2O_3 particles at the expense of the chromium concentration. At even higher temperatures of 600°C and above the formation of a new oxide phase is noted as Cr_3O_4 .

6. The coating, for practical purposes, optically degrades between 500–600°C after being heated for one hour. In terms of reflectance only minor changes take place above 300°C, although at 400°C infrared

absorption can be noted corresponding to Cr_2O_3 . All of these transformations appear to be permanent and irreversible.

ACKNOWLEDGMENTS

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RECENT DEVELOPMENTS REGARDING ELECTRODEPOSITED BLACK CHROME SOLAR COATINGS*

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ABSTRACT

The thermal stability of electrodeposited black chrome solar coatings, obtained from Harshaw Chemical Co. Chromonyx bath, has been studied as a function of various plating parameters. The composition of the standard bath was determined to be chromic acid (332 g/l), acetic acid (226 g/l), trivalent chromium (16 g/l), iron (8 g/l) and barium (8 g/l). For coatings obtained from the standard bath, the solar absorptance decreased by ~8% when heated above 300°C in air. When the trivalent chromium concentration was reduced to values as low as 8 g/l, the solar absorptance of coatings remained unchanged after aging at 350°C in air for over 1800 hours. Of several other plating variables studied, only the current density and substrate appear to have an effect on the thermal stability. Auger sputter profiles of film composition after thermal aging, indicate a higher metallic chromium content in the coatings plated from the

low trivalent chromium bath as compared to coatings plated from the standard bath.

INTRODUCTION

As reported at the last Selective Absorber Coatings Workshop [1], electrodeposited black chrome solar coatings, obtained from Harshaw Chemical Co. Chromonyx plating bath [2], had experienced a decrease in solar absorptance of ~8% after operation at 310°C in Sandia's Mid-temperature Solar System Test Facility (MSSTF). When coupons that were plated at the same time as the collector receiver tubes were heated in laboratory furnaces in air to 300°C, it was found that some samples were thermally stable (i.e., exhibited no change in solar absorptance) while other samples were thermally unstable. Scanning electron microscopy, sputter Auger composition profiling and ESCA measurements found no significant difference in the coating composition or structure between these stable and unstable coatings [1].

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Therefore, it appeared that electroplating process variations were responsible for the differences between the coatings, and a detailed study of the plating process was initiated. Of primary importance was the determination of the plating bath composition so that the effect of the bath constituents on the coating optical properties and thermal stability could be systematically and reproducibly investigated. In addition, the role of other plating variables, including substrate, current density, bath temperature, etc., needed to be evaluated.

BATH COMPOSITION AND EXPERIMENTAL PROCEDURES

By analysis of make-up addition agents and the plating bath, it was determined that the primary bath constituents were chromic acid, acetic acid, trivalent chromium, iron and barium [3]. The nominal concentration of these constituents in the standard bath and the accuracy of their determination are listed in Table 1. Recently, a new analytical technique has been developed for the trivalent chromium (Cr^{+3}) concentration determination which is more

accurate than the +2 g/l reported in Table 1 [4].

Several materials were used as substrates including nickel foil, 302 stainless steel and electrodeposited sulfamate nickel [5] on mild steel coupons. All substrates were degreased and cleaned with isopropyl alcohol, trichloroethylene and distilled water. Before plating, the substrates were activated in a 50% solution of hydrochloric acid at room temperature for 3-5 minutes for the nickel strates and 1-2 minutes for the 304 stainless steel. Electroplating in the black chrome bath was accomplished using a special cell holder [6] designed to provide a uniform current density on the flat substrates. Although the bath temperature increased during plating, it was kept between 20-26°C. The plating current was maintained at 188 mA/cm² (175 A/ft²) unless otherwise noted (AC ripple less than 0.1%). Thermal aging tests were conducted in laboratory tube furnaces at temperatures of 250°C, 300°C, 350°C, and 400°C. The combined temperature uniformity and accuracy during aging was better than $\pm 8^\circ\text{C}$.

The solar absorptance properties, α_s , of each coating were determined by averaging spectral hemispherical

TABLE 1. COMPOSITION OF STANDARD SOLUTION OF
HARSHAW CHROMONYX BLACK CHROME BATH

<u>Component</u>	<u>Concentration</u>	<u>Accuracy</u>
Chromic Acid (CrO_3)	332 g/l	± 1 g/l
Acetic Acid	226 g/l	± 8 g/l
Trivalent Chromium (Cr^{+3})	16 g/l	± 2 g/l
Iron (Fe^{+3})	8 g/l	± 0.5 g/l
Barium* (Ba)	8 g/l	-----

*The barium in the bath is added only to precipitate any sulfate ions which are detrimental to the plating; its concentration is not critical.

reflectance data obtained using an integrating sphere reflectometer [7]. The normal total emittance $\epsilon(T)$ at $T = 100^\circ\text{C}$ and 300°C was measured using a Gier Dunkle Infrared Reflectometer, Model DB-100, as previously described [8].

agreement with the results obtained with the receiver tubes in the MSSTF (see Table 2). The solar absorptance typically decreased $\sim 5\%$ within ~ 24 hours after heating and remained essentially unchanged after further heating up to 350°C . At 400°C , α_s continued to decrease in long term tests after the initial drop [9].

TRIVALENT CHROMIUM VARIATIONS

Coatings deposited from the standard bath (16 g/l Cr^{+3}) on-to sulfamate nickel substrates were thermally unstable, when heated to 300°C and above in

Because the oxide content in the deposited coatings is influenced by the trivalent chromium in the plating bath, the concentration of Cr^{+3} was varied with all other

TABLE 2. EFFECTS OF TRIVALENT CHROMIUM CONCENTRATION ON THERMAL AGING OF ELECTROPLATED BLACK CHROME

Cr Concentration	Test Temperature	Test time (hr)	α_s	$\epsilon(300^\circ\text{C})$	Plating Time
16 g/l	as plated	0	0.95	0.15	3-1/2 min.
	250°C	64	0.93	0.14	
	300°C	64	0.90	0.13	
	350°C	64	0.89	0.12	

12 g/l	as plated	0	0.97	0.31	3-1/2 min.
	350°C	40	0.97	0.24	
		157	0.97	0.23	
		752	0.96	0.22	
		1849	0.96	0.22	
	400°C	40	0.96	0.23	
		157	0.96	0.23	
		755	0.93	0.21	
		1596	0.88	0.18	

8 g/l	as plated	0	0.97	0.40	5 min.
	350°C	40	0.97	0.32	
		157	0.97	0.32	
		752	0.98	0.31	
		1849	0.98	0.31	
	400°C	40	0.97	0.29	
		157	0.97	0.29	
		755	0.96	0.27	
		1595	0.95	0.24	

bath constituents held constant. Coatings deposited onto the nickel substrates from plating solutions with the trivalent chromium concentration reduced below 16 g/l had improved thermal stability properties. The solar absorptance of coatings obtained from 12 and 8 g/l Cr^{+3} baths remained unchanged after heating to 350°C in air for over 1800 hours (see Table 2). Although the initial $\epsilon(300^\circ\text{C})$ values for these coatings were higher than for the coatings obtained from the standard bath, the emittance of the stable coatings decreased significantly after heating for a short time. After 40 hours at 350°C, $\epsilon(300^\circ\text{C})$ decreased from 0.31 to 0.24 for the 12 g/l Cr^{+3} coating and from 0.40 to 0.32 for the 8 g/l Cr^{+3} coating. With further heating, the emittance values decreased only slightly after 1800 hours. Thus our preliminary results suggest that for coatings with improved thermal stability properties and with solar absorptance values above 0.95, the $\epsilon(300^\circ\text{C})$ values will be initially higher than coatings obtained from the standard bath. However, the $\epsilon(300^\circ\text{C})$ values for the stable coatings decrease significantly after thermally heating for a short time.

At 400°C in air, for the 12 g/l Cr^{+3} coating, the solar absorptance decreased from 0.97 to 0.88 after 1600 hours. For the 8 g/l Cr^{+3} coating, α_s decreased from 0.97 to 0.95 after the same time (see Table 2). If these tests are continued for times as long as 10^4 hours at temperatures of 350°C and higher, the results may be influenced by the thermal stability of the nickel substrate. Nickel begins to oxidize at temperatures above 300°C in air [10]. There has

been some evidence that aging in a solar collector, which combines high temperatures, air, moisture, concentrated sunlight and temperature cycling, may be more severe than the static heating test conducted in our studies [10]. Therefore thermal aging tests in a solar collector are being started.

OTHER PLATING PARAMETERS

Preliminary results have been obtained for the influence of other plating parameters on the thermal stability of plated coatings. These variables include current density, substrate, AC ripple up to 15%, and different rinsing procedures. The laboratory rinsing procedures investigated included the use of distilled water, tap water, sodium metabisulfite solution (frequently used in the rinse to reduce hexavalent chromium) and a dilute water solution containing some of the black chrome bath in order to simulate poor rinsing techniques.

Coatings deposited from the 16 g/l Cr^{+3} bath onto the 302 stainless steel experienced a decrease in α_s of only 0.02 absorptance units after 600 hours at 400°C in air. Thus, coatings deposited on this substrate appeared to be thermally more stable than coatings deposited from the same bath on nickel substrates.

Of the other variables studied, only the current density appears to have an effect on the thermal stability of coatings plated from low Cr^{+3} baths. Coatings plated at a reduced current density 108 mA/cm² (100 A/ft²) from an 8 g/l Cr^{+3} bath show changes in their spectral hemispherical reflectance properties over the solar spectrum when heated to 400°C in air for short times. Although these

reflectance changes decreased the solar absorptance by only 0.02 absorptance units, the changes were similar to changes observed in the hemispherical reflectance properties of unstable coatings [10].

FILM COMPOSITION

The composition of the black chrome coatings was investigated using Auger sputter profiling. The results for coatings deposited from 16 g/l and 8 g/l Cr^{+3} baths onto sulfamate nickel substrates are shown in Figures 1 and 2. Curves for the films both as plated and after heating in air to 350°C for ~70 hours are shown. The interface between the black chrome coating and the substrate was not sharp because of the surface roughness associated with the sulfamate nickel [6] and possibly preferential surface etching caused by the sputtering [9,10]. The interface region indicated with each curve was defined as the region where the peak-to-peak nickel amplitude was between 35% and 65% of its asymptotic value.

Previous composition profile studies using electron spectroscopy for chemical analysis (ESCA) techniques have shown that the chromium in the films exists as metallic chromium and Cr III [1,12]. In addition, transmission electron microscopy confirmed the presence of metallic chromium crystallites within the film [13,14]. For all films examined, the oxygen to chromium ratio (O/Cr) based on peak heights was highest near the outer surface and decreased within each film. Sputter Auger curves obtained from single crystal Cr_2O_3 produced an oxygen to chromium ratio of 2.4:1 [1].

Thus, the outer surface of each film, both before and after heating, is predominately Cr_2O_3 [1,12]. For the 16 g/l Cr^{+3} film, the O/Cr peak-to-peak ratio decreases to a value of 0.4 within the film while in the 8 g/l Cr^{+3} film, this ratio decreases to 0.3. If it is assumed all oxygen is present as Cr_2O_3 and that

(a)

(b)

Figure 1. Auger peak-to-peak amplitude as a function of sputtering time for a black chrome coating electroplated onto a sulfamate nickel substrate from a 16 g/l Cr^{+3} bath. Curves are presented both (a) as plated and (b) after heating in air at 350°C for 70 hours. Sputtering was continued past the time plotted in order to determine the asymptotic nickel signal. Sputter conditions were 5 KV and 25 mA in argon.

(a)

(b)

Figure 2. Auger peak-to-peak amplitude as a function of sputtering time for a black chrome coating electrodeposited onto a sulfamate nickel substrate from an 8 g/l Cr^{+3} bath. Curves are presented both (a) as plated and (b) after heating in air at 350°C for 66 hours. Sputtering was continued past the time plotted in order to determine the asymptotic nickel signal. Sputter conditions were 5 KV and 25 mA in argon.

differential sputtering rates and possible influence of particle size in the heterogeneous, graded composition film do not affect Auger peak intensities, then integrating under the chromium and oxygen curves for each film will give the ratio of total metallic chromium to total chromium oxide. This ratio is 75%/25% (3:1) for the 16 g/l Cr^{+3} film and 80%/20% (4:1) for the 8 g/l Cr^{+3} film. Thus the stable film has slightly more metallic chromium than the unstable film before heating.

After heating to 350°C, both films show a considerable increase in the amount of oxygen in the film. In the unstable coating, the chromium amplitude remains below the oxygen amplitude throughout the film (O/Cr ratio of 1.2), while in the stable coating, the chromium amplitude still increases above the oxygen amplitude. Assuming, as before, that all of the oxygen is in the form Cr_2O_3 , the relative amount of metallic chromium to chromium oxide is approximately 40%/60% (0.6:1) for the unstable film and 55%/45% (1.2:1) for the stable film. Thus only about 30% of the metallic chromium in the stable film was oxidized by heating, while about 50% of the metallic chromium was oxidized in the unstable film. The different amount of oxidation as measured by the Auger sputter profiles suggests that the metallic chromium particle size is larger in the stable coating as compared to the unstable coating.

Examination of the nickel sputter profiles for each film as plated and after heating for 70 hours indicates that there was no appreciable diffusion of

the nickel into the black chrome film. In addition, there was no detectable oxidation of the nickel substrate after the short heat treatment, even though bare nickel oxidizes at this temperature. Note also that the sputtering time required to reach the interface increased by ~20% for both films after heating.

CONCLUSIONS

The primary constituents in the Harshaw Chromonyx black chrome bath are chromic acid, acetic acid, trivalent chromium, iron, and barium. The thermal stability of coatings deposited onto nickel substrates has been significantly improved by reducing the trivalent chromium concentration below its nominal value of 16 g/l. For a coating deposited from an 8 g/l Cr^{+3} bath, the solar absorptance decreased only 2% after heating at 400°C in air for over 1600 hours. Coatings deposited onto 302 stainless steel appear to have better thermal stability properties than coatings deposited onto nickel substrates. The effect of the substrate on thermal stability is currently being investigated. Auger sputter profiles indicate that as deposited coatings from an 8 g/l Cr^{+3} bath have higher metallic chromium oxide content as compared to a coating from the 16 g/l Cr^{+3} bath. After heating to 350°C in air, there is evidence that a higher percentage of the metallic chromium in the unstable coatings oxidizes compared to the stable coatings. While the stable coatings have higher emittance values when deposited, after heating to 350°C in air for a few hours, the emittance values decrease significantly.

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PREPARATION AND DEGRADATION OF REACTIVELY EVAPORATED BLACK CHROME

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ABSTRACT

Preliminary results are described for the preparation of black chrome films by reactive evaporation of chromium in oxygen-18. Chromium coated tungsten rods and an oxygen diffuser are used in a conventional bell jar system to form films up to 110 nm thick. Chromium, black chrome, or Cr_2O_3 films are deposited depending on the chromium flux and steady state oxygen pressure. The films are topographically smooth, but are porous since they range up to 2.5 times the thickness expected for the bulk density. An ISS spectrum is shown of a successfully labelled film with 73% oxygen-18. The valence states of Cr^{+3} and Cr^0 , deduced from ESCA at various ion etched depths below the surface, are consistent with Cr in a Cr_2O_3 matrix.

INTRODUCTION

Electrodeposited black chrome films have desirable optical properties for use as selective solar absorber coatings in applications up to ca. 300°C [1-4]. It has been observed that degradation of the optical properties occurs between 250-400°C [3, 4], but the mechanism of this process is not understood [4]. The purpose of this work is to prepare isotopically labelled reactively evaporated black chrome films and to establish that the films have optical properties similar to those of electrodeposited films. If successful, study of the degradation of the films in oxygen-16 could then be made using gravimetric, optical, SEM, and surface analysis techniques to elucidate the degradation mechanism. Previous work on reactively evaporated black chrome [5] and

rf sputtered films [6] showed the optical properties are comparable to those of the electrodeposited material. Reactive evaporation was chosen as the preparation method because it can be easily adapted to an apparatus that permits the simultaneous measurement of mass change, optical transmittance, and reflectance [7]. Since this project began a few months prior to this conference, only the initial progress of preparing and characterizing the films can be reported.

EXPERIMENTAL

For the preparation of isotopically labelled reactively evaporated black chrome, a standard bell jar vacuum station (Fig. 1), was equipped with feed-throughs for evaporation of chromium from coated rods. To control the uniformity and extent of the oxygen reaction of the chromium flux [5], a circular diffuser tube with holes through the outer wall was erected between the substrate and evaporation source. Oxygen-18 was backfilled into the chamber through a leak valve attached to the supply flask. Steady state ion gauge readings ranging between 10^{-3} to 5×10^{-2} Pa [5] were easily obtained by using the leak valve and partially opening the main valve to the diffusion pump. The mass of deposited material, chromium oxide and chromium, was measured with a crystal oscillator centered in the substrate holder. The initial films were non-uniform in their depth distribution of chromium oxide and chromium, so a rate controller operating with feed-back from the thickness monitor was added. Deposition rates were typically 0.2nm/s. The substrates are located 46 cm (18 in) above the source to provide a thickness uniformity of about 1% in the films.

Composition in depth profiles were obtained using ISS, SIMS, AES and ESCA surface analysis techniques with continuous or incremental ion etching. The ISS data were obtained with a 3-M Model 520 ion scattering spectrometer. Physical Electronics units were used for the ESCA, AES, and SIMS profiles.

The topographical features of the films were determined from SEM photographs made at the Denver Research Institute. The thickness of the films was estimated with an alpha-step profilometer.

RESULTS AND DISCUSSION

Five sets of films ranging in thickness from 20 to 110 nm were prepared at ion gauge readings of 10^{-3} to 5×10^{-2} Pa in a steady state flow of oxygen-18. At the lowest gauge reading, almost pure chromium is deposited and at the highest gauge reading, almost pure Cr_2O_3 is deposited. Thus, control of the gauge reading during reactive evaporation provides the possibility of varying the mixture of Cr in Cr_2O_3 , and confirms the results of Hahn [5].

Using SEM photographs, all films were found to be topographically smooth ranging from chromium to chromic oxide. This is in contrast

with electrodeposited black chrome which exhibits varying degrees of topographical roughness. Films containing the oxide had varying degrees of porosity, as deduced by comparing measured thicknesses with those calculated from the mass deposited and bulk densities. Depending on the $\text{Cr}_2\text{O}_3/\text{Cr}$ ratio prepared, the increase in thickness ranged up to about 2.5 times that expected for the bulk density. No assessment of the chromium particle size in the films has been attempted, but to achieve those typically reported by Ignatiev, et. al. [8], preparation by reactive evaporation in argon and oxygen [9] could be adapted to the present scheme as well as to the apparatus described [7].

From composition in depth profiles, the films were generally found to consist only of chromium and oxygen (AES, ESCA, and ISS), although traces of Na, Mg, Al, Fe and Si were detectable using SIMS. The indicated impurity concentration would be less than 0.1%. The initial films were not uniform in the oxide/metal mixture from the surface to the substrate interface. Oxide concentrations were higher at the surface and interface. The surface oxide probably results from room temperature oxidation during transfer in air. The increased oxide content at the interface most likely is a kinetic effect as the deposition process is building up to the steady state rate of reactive evaporation. Neither of these effects are expected to be of importance when films are prepared in situ on a substrate suspended from a microbalance [7] for studying the reaction of black chrome in degrading gases.

Analysis with ESCA showed that only Cr^{+3} and Cr^0 oxidation states were present, in agreement with a recent analysis of electrochemically deposited black chrome [8]. Furthermore, the ESCA spectra showed that the $\text{Cr}^{+3}/\text{Cr}^0$ ratios were larger where the oxygen content of the films was greatest. Some care must be exercised in drawing conclusions about the quantitative ratios of $\text{Cr}_2\text{O}_3/\text{Cr}$ present in the films [8] because of the action of bombarding ion beams on the valence of exposed chromium [10]. The model of chromium particles in a chromium oxide matrix, proposed by several previous investigators, is qualitatively supported from our composition in depth profiles and the analyses of ESCA, AES, SIMS and ISS spectra.

A most important goal of this project was to prepare black chrome with an oxygen-18 labelled oxide. This has been achieved as shown by the ISS spectrum in Fig. 2. The $^{18}\text{O}/^{16}\text{O}$ peak height ratios [11] indicate that 73% of the oxygen content is oxygen-18, which is greater than that achieved for copper films thermally oxidized by heating in oxygen-18. The tungsten peak in Fig. 2 resulted from continued heating of the chromium coated tungsten rods after the chromium was exhausted. The volatility of tungsten oxides is a well established phenomenon in high temperature-high vacuum technology. The tungsten contamination can be (and has been) eliminated from other film preparations by terminating the reactive evaporation before the chromium coating on the rods is exhausted.

In conclusion, the initial goals of this project have been achieved. Black chrome films, labelled with an oxygen-18 isotope, have been prepared up to "thicknesses" of 110 nm. The films consist of $\text{Cr}_2\text{O}_3/\text{Cr}$ mixtures, contain less than 0.1% impurities, are topographically

smooth, but are porous. The desired ratios of Cr_2O_3 to Cr can be obtained by varying the oxygen partial pressure during reactive evaporation, a technique applicable for depositing black chrome films in situ on substrates suspended from a microbalance.

ACKNOWLEDGEMENTS

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FIGURE 1

Schematic of a High Vacuum Bell Jar System with Components for the Reactive Deposition of Black Chrome Films.

Deposition System and Pumping Station

FIGURE 2

ISS Spectrum of a Black Chrome Film Prepared in Oxygen-18 at an Ion Gauge Reading of $7 \pm 2 \times 10^{-3}$ Pa.

NOTES

STRUCTURE AND COMPOSITION OF BLACK CHROME

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ABSTRACT

Black Chrome is known to consist of chromium and chromium oxide. When electrodeposited under optimum conditions Black Chrome possesses absorptivity greater than 93% and emissivity less than 10% and is also durable against corrosion and 450^oF heat encountered in flat-plate solar collectors. Colors other than black are obtained during Black Chrome electrodeposition. This is thought to be due to the presence of different types of oxides of chromium. Work is in progress at Berry Solar Products to investigate improvements to Black Chrome deposits under a DOE grant.

The purpose of this work is to investigate improvements in selective coatings and test the developed coatings for durability. As the program is still in its infancy - having started in October 1978 - we cannot report significant results to you at this time. But we will try to present our views based on the literature survey we have conducted recently. It is our hope that this forum is the place to exchange ideas and information among different groups working towards a common goal - "Cultivate and Harvest Solar Energy".

A selective surface for solar absorption should have absorptivity greater than 93% and emissivity less than 10% for 20 to 30 years under occasional 500°F temperature and be low cost and easily quality controllable. The candidate materials are very many but it seems that the most practical and economical material to date is Black Chrome. Studies by Lin and others at Honeywell (1) indicate that Black Chrome electrodeposited on 12.7 μm (or 0.5 mil) dull nickel is durable for a period of 30 years. Sowell and Pettit (2) at Sandia observed that the thermal stability of Black Chrome could be increased by lowering the concentration of trivalent chrome in the plating solution. Considerable amount of research is being done on the various aspects of Black Chrome to improve its stability and durability without, of course, losing its optical properties.

As one of the commercial platers of Black Chrome, we observed that there are many unexplained mechanisms at work in Black Chrome plating. One of the aspects of Black Chrome is the surface appearance of powdery substance which everyone refers to as smut. The amount of smut increases with the plating time. It has been said (3) before that the smut does not affect the properties of solid plated Black Chrome. But the scanning electron micrographs of Black Chrome with the smut (Figure 1) and without it (Figure 2) show something different. As can be noticed from the X-ray fluorescence analysis (Figure 3) the amount of chrome decreased by 40% when the smut is removed. This, we feel, is of considerable importance in understanding Black Chrome. We will pursue this study further.

Another aspect of Black Chrome is its nature and composition. Some researchers (3) have reported that our ideal surface is a mixture of chromium metal and its trivalent oxide, Cr₂O₃ in a varying ratio. Our transmission electron microscope study (Figure 4) only reveals that Black Chrome has a fine-grained structure. There are certain other questions listed below about the nature and composition of Black Chrome for whom some answers are needed.

- 1) What should be the optimum proportion of chromium metal to chromium oxide in order for the surface to have the best optical properties and to be greatly durable?
- 2) What is the nature of the chromium oxide?

The electronic structure of chromium is:

Because of the presence of unfilled 3d shell chromium exists in different valence forms. As seen from Table 1, chromium exists in various oxide forms showing different colors. It is possible to obtain different tints like grey, brown, blue and red from the same "Black Chrome" plating solution. Optical properties are affected by these different tints. It is our belief that several chromium oxides are present in the so-called "Black" Chrome to give different tints. Electrode potentials for different reduction reactions are not available in the literature. These potentials could be related to the plating current density using Tafel relationships. It is then possible to control the composition of the chromium oxide.

We believe that unless the complete nature of Black Chrome is understood it is difficult to improve its properties. Therefore our future work involves a study of the nature of chromium metal and chromium oxide in solid Black Chrome deposit and also the nature of the smut.

We are interested in applying Selective Surface on stainless steel and aluminum apart from copper which we are doing at present. It is difficult to plate Black Chrome on stainless steel because of the poor electrical conductivity. Aluminum requires several treatments before Black Chrome is applied and we know that multilayer coatings usually create durability problems. We will be working on multilayers and diffusion in the future. After developing the coatings we will be testing them in an accelerated test box under cyclic temperature conditions.

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CHARACTER OF THE OXIDES OF CHROMIUM

Electronic Structure of Chromium Metal: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

<u>Valence of Chromium</u>	<u>Electrons Needed to Form Metal</u>	<u>Color of Oxide</u>	<u>Electrode Potentials</u>
Bi	2	CrO - Black	(Half reaction potentials $Cr^{2+} + 2e \rightarrow Cr$ -0.91 volts
Tri	3	Cr ₂ O ₃ - Green	(Half reaction potential of $Cr^{3+} + e \rightarrow Cr^{2+} \rightarrow$ -0.41 volts
Tetra	4	CrO ₂ - Brown, Blue	
Hexa	6	CrO ₃ - Red	

Table 1

THE ART OF BLACK CHROME ELECTROPLATING FOR SELECTIVE SURFACE

AT THE ANODE
O₂ EVOLVED

O
X
I
D
I
Z
I
N
G

Factors affecting plating process

- Anode/cathode size ratio
- Electrical resistance - Cr valence - concentrations - addition
- Temperature
- Time
- Anode - cathode distance
($R_B = \text{distance} : I \frac{1}{R_B}$)

AT THE CATHODE
H₂ EVOLVED

R
E
D
U
C
I
N
G

Table 2

SCANNING ELECTRON MICROGRAPHS SHOWING THE STRUCTURE OF BLACK CHROME, WITH SMUT, ELECTRODEPOSITED ON DULL NICKEL. X-RAY FLUORESCENCE ANALYSIS PEAKS OF CHROMIUM AND NICKEL ARE ALSO SEEN.

Figure 1

SCANNING ELECTRON MICROGRAPHS SHOWING THE STRUCTURE OF BLACK CHROME, WITHOUT SMUT, ELECTRODEPOSITED ON DULL NICKEL. X-RAY FLUORESCENCE ANALYSIS PEAKS OF CHROMIUM AND NICKEL ARE ALSO SEEN.

Figure 2

X-RAY FLOJRESCENCE PEAKS WITH AND WITHOUT SMUT
ON BLACK CHROME

Figure 3

TRANSMISSION ELECTRON MICROGRAPH SHOWING A FINE-GRAINED STRUCTURE OF BLACK CHROME.
Figure 4

NOTES

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OUTGASSING STUDIES OF SOME SOLAR ABSORBER COATINGS

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ABSTRACT

As solar collector efficiencies are increased through manufacturing design modifications, an increased demand is placed on the collector system components to withstand higher operating and stagnation temperatures. Recently, the fogging and discoloration of coverplates, which results from outgassing of the system components, has stirred interest in examining the outgassing behavior of various nonselective solar absorber coatings. A reduction in the total amount of radiation striking the absorber surface and a gradual degradation of the coating system results from increased stagnation temperature.

In the present study a series of weight loss measurements were conducted at 149°C, 177°C and 204°C over various time intervals. The reduction in radiation which resulted from the outgassing experiments was approximated by examining the transmittance through a clear coverglass before and after the outgassing experiment. The material balance between that deposited on the coverglass and that lost from the panel was correlated to assess the degradation mechanism.

This comparative study, while preliminary, points out the need to further address the performance requirements of solar absorber coatings depending on their ultimate use requirements. Certain materials may be useful for low temperature applications but may not be satisfactory for medium temperature applications. The described test may be used in classifying various system components.

INTRODUCTION

During the past several years manufacturers of solar collectors have been increasing the collection efficiency of solar absorber systems. By various design modifications the efficiency of the collection system and operating temperature of the solar collector has increased (1,2,3). Improvements in the insulation of the collector assembly, the addition of coverplates to solar collector, and the incorporation of a selective coating have increased the operating temperature of the solar collector unit.

Field studies in recent solar collector systems have shown that some solar absorber paints exhibit a tendency to outgas, resulting in a fogging of the coverglass plate. When seen by the customer of the solar collector, this fogging tendency arouses his concern about the ultimate durability of the solar collector coating and collection efficiency of the coating over an extended period of time. The actual effect of outgassing on collector efficiency has not been fully determined, but it is clear that if the coating system undergoes a significant weight loss, deterioration of the coating has begun. Also, if the coverplate is fogged, reduction in the transmission through the coverplate will be observed, directly affecting collector efficiency.

As a point of reference it is worthwhile to examine the effect of coverplates on the operating temperature of selective and non-selective collector systems. Shown in Table I are the approximate stagnation temperatures of collector systems installed at the Desert Sunshine Test Location in Phoenix, Arizona (4).

TABLE I

Typical Stagnation Temperatures for Non-Selective
and Selective Absorber Plates

<u>Collector Design</u>	<u>Stagnation Temperature</u>	
	<u>Non-Selective</u>	<u>Selective</u>
Unglazed Collector	150 - 200 ^o F	
One Cover Glazing	200 ^o F	250 - 350 ^o F
Two Cover Glazing	200 - 300 ^o F	350 - 400 ^o F
Evacuated Tube		400 - 500 ^o F

From this data one can see the temperature effect with increasing coverplates and the increases due to the selective nature of the absorber coatings. In the present study five non-selective or semi-selective solar absorber paints have been chosen for studies in these outgassing experiments. It is important to point out that the results discussed here are preliminary and no correlation has been made with the data developed in these tests with actual field exposure. For that reason we have chosen not to disclose either the chemical type of the coating

or the manufacturer of the coating system, but instead we are characterizing the systems as either non-selective or semi-selective paints by their absorptivity and emissivity values as reported in the literature. This data is shown in Table II.

TABLE II

Absorptance and Emittance Characteristics
of Some Solar Absorber Paints

<u>Product</u>	<u>Absorptance</u>	<u>Emittance</u>
Commercial I	0.98	0.89
II	0.97	0.92
III	0.96	0.88
IV	0.96	0.84
V	0.97	0.72

It should be further pointed out that all of these systems were recommended by the manufacturers as spray type finishes which could be applied by the solar collector manufacturer in his own operating plant. Some of the systems require baking while others can be applied and cured at ambient temperature. For the purposes of this study each of the systems was applied according to the manufacturers directions and baked to eliminate the possibility of solvent vapors as an outgassing component.

The test method in this study was suggested by personnel from the Chamberlain Corporation and is being presented here as a screening tool for evaluating the outgassing characteristic of various coating systems. In this study, solar collector coatings were heated at various temperatures for varying periods of time. A portion of the outgassing condensate was collected on a glass coverplate and the reduction in direct transmission from this condensate was recorded over the region from 350 nanometers to 1700 nanometers. The amount of the condensate which was collected on the coverplate was compared to the amount of outgassing component released from the collector coating.

EXPERIMENTAL

All coatings were sprayed onto 2x4 inch aluminum coupons and baked according to the manufacturer's directions.

The coupons were suspended in a 400 ml beaker covered with a pre-weighed borosilicate coverglass. This assembly was placed on a thermostatically controlled hot plate. A metal triangle was used to separate the beaker from the hot plate surface.

An iron constantan thermocouple was suspended in the beaker adjacent to the metal test panel to monitor and control the air temperature at 149°C, 177°C and 204°C. (300°F, 350°F and 400°F). The thermocouple was connected to a West "Guardman" thermostatic controller which, in turn, regulated the on and off cycle of the hot plate.

The coating weight deposited upon each coupon was determined by measurements of the coupons before and after coating. The coupon weights were remeasured after specified time intervals at the specified temperatures. The percent weight loss was calculated by comparison to the original coating weight.

The pre-weighed cover plates were reweighed after completion of the test period to determine the amount of outgassing material collected on the coverplate. This weight was compared to the outgassing weight loss of the respective coupon. The material balance was compared to the visible fogging of the borosilicate glass coverplate.

The transmission spectra of the coverplates were recorded over the spectral region of 0.35 μ to 1.7 μ using a direct transmission mode on a Cary Model 14 UV-Visible Spectrophotometer. A borosilicate glass coverplate that was not exposed to the test conditions was used as a reference.

RESULTS AND DISCUSSION

The ability of a coating to function as an absorber surface is a direct function of the solar absorptance, i.e., the fraction of radiation absorbed from all wavelengths. But the coating is only one component of a collector. In maximizing the efficiency of a collector, one must not only optimize the absorptance of the coating, but other materials parameters as well.

A relationship between the collector efficiency and its system parameters is:

$$\eta = F_R \left(\tau\alpha - \frac{U_L \Delta T}{q_i} \right)$$

Where η is collector efficiency, F_R is an overall heat loss factor for the collector, U_L is the collector plate heat removal efficiency, q_i is the incident radiant flux, ΔT is the temperature difference between the collector fluid inlet and the environment, α is the solar absorptance and τ is the transmittance of the coverplate system (5).

The maximum collector efficiency then is:

$$\eta_{\max} = F_R \tau \alpha$$

This equation illustrates the direct dependence of collector efficiency not only on the coating's solar absorptance but also on the coverplate transmittance.

Weight Loss Measurements

Organic coatings vary widely in their ability to withstand elevated temperatures for extended periods of time. In Figures 1, 2 and 3 several solar absorber paints were stagnated at 149°C (300°F), 177°C (350°F) and 204°C (400°F), respectively, for periods up to 96 hours. While these temperatures are higher than that normally observed for an unglazed or one coverplate collector using a non-selective absorber coating, the temperatures are similar to that observed for selective coatings using either one or two cover glazings. It is believed that some non-selective collector systems may also reach these temperature extremes for short periods of time. Therefore, these tests may have utility as an accelerated test method for outgassing experiments.

As is seen by comparison of Figures 1, 2 and 3, only coatings systems III and IV do not appear to undergo a weight loss at the various temperatures. This result is obviously due to the choice of binder in these coating systems. Commercial systems I, II and V show increasing weight losses with time at the various temperatures with obvious decomposition taking place at 177°C and 204°C for Commercial V. This result may be of particular importance since this system has the widest spread in absorptance and emittance values.

FIGURE 1. WEIGHT LOSS OF SOME SOLAR ABSORBER COATINGS AT 149°C (300°F)

FIGURE 2. WEIGHT LOSS OF SOME SOLAR ABSORBER COATINGS AT 177°C (350°F)

FIGURE 3. WEIGHT LOSS OF SOME SOLAR ABSORBER COATINGS AT 204°C (400°F)

In Tables III, IV and V the weight gain observed on the coverplate was compared to the weight lost from the panel after heating at the specified temperature for 96 hours. As can be seen from these tables, the greatest weight gain occurred at the lowest temperature, indicating that oligomeric components were being liberated from the coatings. These materials would deposit at the lower temperatures but would volatilize at the higher temperatures. Further, it is seen from this data that very little of the weight lost from the coated panel actually deposited on the coverglass. In some instances the error in measurement exceeded the weight gain on the coverplate. In these tests the weight of the coverglass (~70 grams) far exceeded the amount of deposit (~0 to 5.4 mg) and small changes in moisture condensate could have a dramatic influence on the accuracy of the material balance evaluation.

Transmission Spectra

Figures 4, 5 and 6 illustrate the reduction in transmission caused by the condensate which appears on the coverglass as a result of the outgassing experiment. It is of interest to note that the greatest effect is noted at the

TABLE III

Material Balance Determinations in the
Outgassing of Some Solar Absorber Coatings @ 300 F

<u>Product</u>	<u>Wt. Loss (mg)</u>	<u>Wt. Gain (mg)</u>	<u>Mat. Bal (mg)</u>
Comm. I	15.5	4.0	-11.5
II	27.6	5.4	-22.2
III	.8	3.1	2.3
IV	31.7	2.7	-29.0
V	2.8	4.3	1.5

TABLE IV

Material Balance Determinations in the
Outgassing of Some Solar Absorber Coatings @ 350 F.

<u>Product</u>	<u>Wt. Loss (mg)</u>	<u>Wt. Gain (mg)</u>	<u>Mat. Bal (mg)</u>
Comm. I	28.4	-1.5	-29.9
II	98.8	0.2	-98.6
III	0.5	-0.7	- 1.2
IV	10.7	-2.0	-12.7
V	9.3	-1.5	-10.8

TABLE V

Material Balance Determinations in the
Outgassing of Some Solar Absorber Coatings @ 400F.

<u>Product</u>	<u>Wt. Loss (mg)</u>	<u>Wt. Gain (mg)</u>	<u>Mat. Bal (mg)</u>
Comm. I	31.2	0.0	-31.2
II	124.3	0.1	-124.2
III	2.1	0.0	- 2.1
IV	17.7	-0.2	-17.9
V	20.4	0.0	-20.4

FIGURE 4. TRANSMISSION CURVE OF A COVERPLATE AFTER CONDENSING VAPORS OF SOLAR ABSORBER COATINGS FOR 96 HRS @149°C (300°F)

FIGURE 5. TRANSMISSION CURVE OF A COVERPLATE AFTER CONDENSING VAPORS OF SOLAR ABSORBER COATINGS FOR 96 HOURS AT 177°C (350°F)

FIGURE 6. TRANSMISSION CURVE OF A COVERPLATE AFTER CONDENSING VAPORS OF SOLAR ABSORBER COATINGS FOR 96 HOURS AT 204°C (400°F)

lowest temperature. This result is consistent with the weight gain observed on the coverplate. At the higher temperatures there is a general reduction in transmission of all the systems as compared to the reference coverglass. Commercial V, which is the most selective, shows the largest spectral transmission reduction at the temperatures expected of a selective coating, and also the largest weight loss, which is totally undesirable. These results indicate that the binder system may not be the most desirable for this selective paint.

Based on the combined observations of the weight loss, weight gain and transmission spectra, one may conclude that most of the outgassing components are not deposited on the glass but exhausted to the atmosphere. However, a sufficient amount of condensate is deposited to cause a noticeable transmission reduction. This reduction amounts to almost 10% in some cases. This effect would certainly have an effect on the efficiency of the collector system.

SUMMARY

The intention of this study was to present an experimental method which may be useful in evaluating the overall ef-

iciency of a collector system. While no reliable statement can be made regarding the relationship of material balance and coverplate transmittance, there appears to be a reasonable relation between weight loss and transmittance decrease. There also appears to be an explainable trend in the relation of operating temperature and weight gain of the collector coverplate possibly due to oligomeric condensates.

Finally, since no actual field data has been made available to correlate with these tests, the data presented should be viewed only as a potential screening method.

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A STUDY OF METAL/INSULATOR COMPOSITE MEDIA AND METAL
SURFACES FOR USE IN SELECTIVE ABSORBER SYSTEMS

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ABSTRACT

A theoretical and experimental study of the optical and selective absorbing properties of composite materials and of the thermal radiative properties of metal surfaces is described.

INTRODUCTION

In the first section of this paper the theory of light wave propagation in a heterogeneous medium is discussed. The Garnett (or Maxwell-Garnett) theory is the appropriate form of effective medium theory for heterogeneous media conforming to the composite topology. It neglects structural effects, but these can be introduced by reformulating the problem in terms of a multiple scattering approach and seeking the solution to this problem in terms of an effective propagation wave-vector. Results are presented for propagation through an infinite periodic array of small spheres immersed in a host of different permittivity (or permeability). The procedure can be generalized to aperiodic systems to include the lowest order corrections associated with pair and triplet correlation functions. In all cases significant effects due to structure-induced multipole fields are seen to occur. A simple parameterization of deviations from the lowest order (Maxwell-Garnett) result is proposed. This permits the direct extraction of information on structural multipoles or clustering effects from experimental data. The dominant features of the average optical constants can therefore be interpreted as modified Mie resonances augmented by noticeable features attributable to structural multipoles which directly reflect the detailed arrangement (according to position, composition, size, and shape) of the particles in the system.

In the second section of this paper design guidelines for the fabrication of optimum selective absorbers are described and their implementation in the construction of selective absorbers using two promising composite materials, $\text{Ni/Al}_2\text{O}_3$ and $\text{Pt/Al}_2\text{O}_3$ is demonstrated.

Measurements of reflectance, solar absorptivity α , thermal emissivity ϵ , and high temperature durability are described.

The Davisson-Weeks expression for the hemispherical emissivity which has long been used to calculate the thermal radiative properties of metal surfaces is in poor agreement with current experiments on copper and aluminum. In the final section of this paper a new expression is developed for the hemispherical emissivity which takes into account the dynamical properties of conduction electrons in the infrared and also includes scattering of the electrons at the metal surface. Since the sum of these two contributions gives the smallest physically allowable emissivity for a given d. c. resistivity one can set a lower limit on the emissivity of any metal once the d. c. resistivity is known at the desired temperature. Finally it is shown that with no adjustable parameters good agreement is obtained between the measured temperature dependent emissivities of copper and aluminum and the values calculated from the known d. c. resistivities.

MULTIPLE SCATTERING THEORY

A: Periodic Systems

We may characterize a periodic composite material (inclusion position $\underline{R}$) by constituent dielectric functions ϵ_i and permeabilities μ_i ; for example

$$\begin{aligned}\epsilon(\omega, \underline{r}) &= \epsilon_1(\omega) \quad (\underline{r} \text{ in host material}) \\ &= \epsilon_2(\omega, |\underline{r} - \underline{R}|) \quad (\underline{r} \text{ in the } \underline{R}\text{-th inclusion})\end{aligned}$$

(and similarly for μ . For such a system the wave equation is

$$\nabla \times (\nabla \times \underline{H}(\underline{r})) - \left(\frac{\omega}{c}\right)^2 \epsilon(\underline{r})\mu(\underline{r}) - \epsilon^{-1}(\underline{r})(\nabla \epsilon(\underline{r})) \times (\nabla \times \underline{H}(\underline{r})) = 0 \quad [1]$$

with a similar equation for $\underline{E}$. Equation 1 can be transformed into an integral equation for $\underline{H}(\underline{r})$ (or $\underline{E}(\underline{r})$) in a single primitive cell, and since $\underline{H}$ is periodic the solution can be described by a (Bloch) wave vector which can be identified as an effective propagation wave-vector. If $\underline{H}$ is expanded in electric and magnetic multipoles (involving multipole coefficients $A_{\ell m}^{\alpha}$, where $\alpha=E$ or H), the integral equation can be shown to lead to a system of linear equations (in the multipole coefficients). The system is homogeneous and possesses a solution only when a standard determinantal condition is satisfied. This condition then relates k and ω , i.e. determines the dispersion relation in terms of the elements of the determinant. These in turn contain 3 physically important pieces of information namely (i) the phase shifts of the single sphere problem, (ii) structural information reflecting the positions $\underline{R}$ of the spheres, and (iii) selection constants related to certain angular momentum components ℓ of the radiation.

With $k=k(\omega)$ obtained from the secular relation an effective product $\overline{\epsilon\mu}$ for transmission is defined by

$$\overline{\epsilon\mu} = k^2(\omega) c^2/\omega^2 \quad [2]$$

If the expansion is truncated at $\ell=1$, for example, and we are in the quasi-static limit, then we have shown [1] that Eq. 2 reduces to

$$\overline{\epsilon\mu} = \epsilon_{MG} \mu_{MG} \quad [3]$$

where ϵ_{MG} and μ_{MG} are the Maxwell-Garnett [2] results. To include higher ℓ values, we can reduce the $\ell>1$ problem to an effective $\ell=1$ problem by the device of matrix folding [3]. An interesting result then emerges, namely that

$$\overline{\epsilon\mu} = \epsilon_{M^3G}^3 \mu_{M^3G}^3 \quad [4]$$

where M^3G stands for multiple Maxwell-Garnett. The expression for $\overline{\epsilon}$ thus obtained is precisely of the Maxwell-Garnett form except that the depolarizing factor departs from the standard value in a way which reflects the concentration of inclusions. This is a necessary consequence of the physical fact that a given inclusion can induce various multipoles in its neighbors in a manner specifically dependent on their mutual arrangement. These corrections to the ordinary Garnett result may be termed structural multipoles. In figure 1 we show MG and M^3G results for the absorption coefficient for a model representation of (20%) fine (Drude) gold particles (ϵ_2) in KBr ($\epsilon_1=2.34$). The arrangement is simple cubic and the significant features are the sharp dips in the curve which occur whenever

$$\frac{\epsilon_2(\omega) - \epsilon_1}{(\ell+1)\epsilon_1 + \ell\epsilon_2(\omega)} \approx 0. \quad [5]$$

These are the multiple resonances and might be regarded as the higher "excited states" of the free spherical inclusion.

FIGURE 1

ABSORPTION COEFFICIENT AS A FUNCTION OF FREQUENCY FOR SMALL ($\sim 50\text{\AA}$) DRUDE GOLD SPHERES IN AN INSULATING HOST (KBr); GOLD VOLUME FRACTION IS 20%.

B: Aperiodic Systems

As a first step in approaching real systems via the periodic analysis given above, we may continue to consider identical inclusions but relax the condition that they be arranged periodically. To model this situation, the aperiodic system can be replaced by a periodic system with a very large basis. An integral equation for $\tilde{H}$ (or $\tilde{E}$) can be determined precisely as before, and except for certain decorative indices denoting basis vectors, its form is unchanged. The resulting system of linear equations in the multipole coefficients is also similar in form but is of course increased in dimension enormously. The implied computational problem is overcome [3] however, by invoking changes in basis of the real space position vectors and using a matrix folding procedure once again to obtain the desired result. The important difference from the periodic case is the necessity to provide structural information (pair, triplet,...etc. distribution functions) for the inclusions in a disordered cermet. These are taken to have the excluded-volume form appropriate to inclusions that do not interpenetrate but are otherwise distributed at random. Again, the major result to emerge is the product rule (4)

$$\overline{\epsilon\mu} = \epsilon_M^3 \mu_G^3$$

where again the effective dielectric constant has the Maxwell-Garnett form, but with an effective depolarizing factor that reflects the structural multipoles appropriate to an aperiodic arrangement. We find these to be more important than in the crystalline system because (a) there is less symmetry, and (b) close approaches of inclusions are permitted in aperiodic systems. Figure 1 shows such aperiodic modifications and compares them to the crystalline case.

Finally it is necessary to consider further disorder arising from distributions of size, composition, and shape. So far as size is concerned, we can set up a multiple scattering problem as before in which the phase shift problem is different for every inclusion. However, if we make the reasonable assumption that size, composition and shape are completely uncorrelated with position we again arrive at a product rule similar to (3) and a M^3G form for ϵ with effective depolarizing factors reflecting, as expected, averages over size, composition, and shape. Experimental information on real cermets can therefore lead to statements on the behavior of such effective depolarizing factors.

COMPOSITE SELECTIVE ABSORBER FILMS

Through the study of the optical properties of metal-insulator composites we have developed guidelines for the design of selective absorber coatings, and implemented these guidelines in the construction of selective surfaces. In particular, through this study we have found composite materials which form surfaces with attractive selective absorber performance and which have high temperature stability in air.

An experimental study of the optical properties of many metal-insulator composite materials reveals that most composites have broad

absorptance characteristics over much of the solar spectrum [4,5,6]. One therefore has a variety of materials from which to design selective surfaces. One can choose materials which have both good optical properties and resistance to thermal degradation.

Some of the most promising films we have examined are composites of nickel or platinum in aluminum oxide, formed by coevaporation of the metal and Al_2O_3 . The deposition by coevaporation facilitates formation of films with graded composition-depth profiles. Since increasing the amount of metal in a composite increases the refractive index, forming the composite film coating with pure insulator on the front surface and metallic content gradually increasing with depth into the film yields a graded index film. The gradual change of the refractive index reduces reflection and increases solar absorptivity. Formation of the coating with a graded refractive index, and with an insulating component of low refractive index, will in general give the best values of the solar absorptivity and thermal emissivity for a thin film (less than 0.5μ thick) [6,7]. The employment of a graded composition profile has several subsidiary benefits. It decreases the amplitude of thin film interference effects, allowing for easier formation of an optimally shaped wave-length-absorptance profile. It also has the effect of improving coating stability since the pure insulator surface layer can play the role of an intrinsic diffusion barrier, protecting the metal from oxidation. Over all, the choice of materials lays heavily on stability requirements which resulted in the choice of Ni, Pt and Al_2O_3 .

FIGURE 2

THE MEASURED REFLECTANCE OF THREE $\text{Pt}/\text{Al}_2\text{O}_3$ FILMS DEPOSITED ON POLISHED Cu.

$\text{Ni}/\text{Al}_2\text{O}_3$ films used for this study were deposited on both polished copper and metal-coated fused quartz. The reflectance spectra of these specularly reflecting films were measured over the range of the solar spectrum. Fig. 2 shows some typical reflectance spectra for

a family of graded Pt/Al₂O₃ coatings on Cu. The primary difference among the films in the figure is thickness, varying from ~0.2 to 0.6μ.

The emissivities ϵ of the coatings on Cu were measured by a calorimetric technique described in refs. [8] and [9]. Figs. 3 and 4 display the emissivity as a function of temperature for these coatings. The curves are labeled with the air-mass two solar absorptivity α , of the films, calculated from the room temperature reflectance data.

FIGURE 3

THE MEASURED TOTAL HEMISPHERICAL EMISSIVITY OF Ni/Al₂O₃ FILMS DEPOSITED ON Cu, AND THE EMISSIVITY OF A BARE Cu SUBSTRATE. EACH CURVE IS LABELED WITH THE SOLAR ABSORPTIVITY OF THE SURFACE AT ROOM TEMPERATURE.

The thermal stability of these Ni/Al₂O₃ and Pt/Al₂O₃ composites was examined by heating to high temperatures in air. Fig. 5 shows the reflectance spectrum of a Ni/Al₂O₃ film after various heat test durations. Figure 6 shows the result of similar tests on a Pt/Al₂O₃ film with heating up to 600°C (1110°F) in air. The Ni/Al₂O₃ composite shows some initial changes upon being heated but then appears to stabilize. The Pt/Al₂O₃ film shows no significant change in reflectance properties.

With these materials we have produced films, with high α (up to 0.94) for both Ni and Pt composite coatings, and have also produced films with low ϵ (less than 0.1). High temperature tests show these films to be quite stable in air.

FIGURE 4

THE MEASURED TOTAL HEMISPHERICAL EMISSIVITY OF Pt/Al₂O₃ FILMS DEPOSITED ON Cu. α IS THE MEASURED SOLAR ABSORPTIVITY FOR EACH SURFACE AT ROOM TEMPERATURE.

LIMITS ON THE EMISSIVITY OF A SURFACE

Recently while making careful hemispherical emissivity measurements, the Cornell Solar Energy Materials Group discovered that the standard expression for the hemispherical emissivity first proposed by Davisson-Weeks was in poor agreement with the experimental measurements. In particular, for good conductors, the Davisson-Weeks expression always predicted an emissivity which was too large. A detailed description of this investigation is given in References [9] and [10]. The new expression for the hemispherical emissivity takes into account the dynamical properties of conduction electrons in the infrared in the free electron limit and also includes scattering of the electrons at the metal surface. Since the sum of these two contributions gives the smallest physically allowable emissivity for a given d.c. resistivity, one can set a lower limit on the emissivity

of any metal once the d.c. resistivity is known at the desired temperature.

The calculated hemispherical emissivities of aluminum, copper and silver are compared with the experimental values in Figure 7. The calculated values for some transition elements are shown. For these materials the measured emissivities are expected to be somewhat larger than the calculated values since we have ignored interband transitions.

To simulate the optical properties of an ideal selective surface we coat the metal with a hypothetical material which does not change the infrared emissivity but causes the absorptivity to be 1 throughout the solar spectrum, and drops abruptly to 0 in the thermal region at longer

FIGURE 5

MEASURED REFLECTANCE OF A $\text{Ni}/\text{Al}_2\text{O}_3$ COMPOSITE DEPOSITED ON A Ni LAYER ON QUARTZ; AS DEPOSITED (—), AFTER 70 HOURS AT 400°C , AFTER 260 HOURS AT 400°C PLUS 350 AT 500°C ●, AFTER 330 ADDITIONAL HOURS AT 500°C Δ.

FIGURE 6

MEASURED REFLECTANCE OF A $\text{Pt}/\text{Al}_2\text{O}_3$ COMPOSITE DEPOSITED ON A Pt LAYER ON QUARTZ; AS DEPOSITED (—), AFTER 50 HOURS AT 500°C ○, AFTER 300 HOURS AT 600°C ●.

wavelengths. We choose a step-like function but one which has a width of a few kT . The high frequency tail of the black body thermal spectrum overlaps the low frequency end of the step function absorptivity and produces a contribution to the emissivity of the composite structure. This contribution to the emissivity from the coating for different cut-off frequencies is also shown in Figure 7. To capture most of the solar spectrum the cutoff should be set near 2 microns (case c).

A figure of merit of such selective surfaces is simply the reciprocal of the hemispherical emissivity. The temperature dependence of this figure of merit for different metal substrates is shown in Figure 8. With a copper substrate at $600^\circ K$ ($620^\circ F$) the largest possible figure of merit is 39. Of course, one could imagine many physical processes associated with pits, oxide coatings, etc. which could make the figure of merit smaller but there is no way to make it larger. Also, if the coating does not have the ideal step function behavior, but turns on more slowly, say as a Lorentzian oscillator, then the figure of merit in the $700^\circ K$ ($800^\circ F$) temperature range will be reduced accordingly. In this temperature region the figure of merit is a sensitive function of the optical properties of the composite structure. By $900^\circ K$ ($1160^\circ F$) the difference between the effectiveness of different metals is small.

We conclude that for high temperature applications the base metal should be chosen for its physical stability not its emittance since

FIGURE 7

TOTAL EMISSIVITY COMPONENTS FOR AN IDEAL SELECTIVE SURFACE VERSUS TEMPERATURE. THE EXPERIMENTALLY MEASURED HEMISPHERICAL EMISSIVITIES ARE REPRESENTED BY DISCRETE VALUES: FOR COPPER 000, FOR SILVER xxx, AND FOR ALUMINUM +++. THE CALCULATED HEMISPHERICAL EMISSIVITY CURVES IN THE FREE ELECTRON APPROXIMATION ARE REPRESENTED BY THE SOLID LINES. THE DOTTED CURVES INDICATE THE CONTRIBUTION TO THE EMISSIVITY FROM A SHARP STEP IN THE SOLAR ABSORPTION SPECTRUM. THE EDGE FREQUENCY IS (A) = 3000 cm^{-1} , (B) = 4000 cm^{-1} , (C) = 5000 cm^{-1} AND (D) = 6000 cm^{-1} .

all good conductors when used in the selective surface mode have about the same high temperature figure of merit.

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FIGURE 8

A FUNDAMENTAL LIMIT TO THE FIGURE OF MERIT VERSUS TEMPERATURE. THE D.C. ELECTRICAL RESISTIVITY OF THE METAL SUBSTRATE AND THE kt WIDTH OF THE BEST SOLAR ABSORPTION EDGE DETERMINE A NATURAL UPPER LIMIT TO THE FIGURE OF MERIT FOR SELECTIVE SURFACES.

NOTES

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IMPROVED SOLAR ABSORBER COATINGS

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INTRODUCTION

The efficient conversion of solar energy to heat requires both a solar absorbing component and an infrared reflecting component on a suitable substrate to allow heat transfer to a working fluid. Typically, the absorber component absorbs solar energy in the 0.35 to 2.2 micrometer wavelength range and should be transparent in the infrared region. These optical properties are observed for black semiconducting metal oxides. The reflector component is typically metallic and maintains a high IR reflectance (or low thermal emittance). The combination of these two components which maintains its optical properties is termed "selective absorber". The theory of selective absorbers is presented in the literature.[1]

The properties of these materials depend on the method of preparation.[2,3] The novel approach to be described in this paper is that of producing thin films of metal and/or metal oxides via decomposition of metallo-organic solutions. Films composed of absorber, reflector and stabilizer components are derived from compatible solutions of respective metallo-organic resins which are typically decomposed in air at temperatures between 500 and 800°C. By varying the ratios of each metallo-organic solution the film composition can be varied. Furthermore, the film thickness can be controlled both by solution rheology and method of preparation.[4]

This paper describes a selective solar absorber development program* directed towards producing materials suitable for industrial process heat applications (~300-700°C). This would make possible moderate to high use temperature, moderate concentration ratio collectors having collector efficiencies superior to competitive units. Black Chrome coatings do not retain their optical properties under these conditions. Our NSF sponsored program was approached with three specific objectives:

- (1) Optimize the "Doped" gold selective absorber film developed in 1962 by Engelhard.
- (2) Investigate the solar optical properties of stable black conducting metal oxide systems (i.e., palladium cobaltate and ruthenium plumbate).

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- (3) Investigate possible replacements of gold with less expensive metals (i.e., silver). This paper is concerned principally with these selective absorbers.

EXPERIMENTAL PROCEDURES

Metallo-organic deposition (MOD) is a process by which thin films of metals or their compounds are deposited on substrates by thermal decomposition, in air or inert or reducing environments, of metallo-organic solutions.[5]

The metal resinate solutions (or formulations) are applied to a substrate by any number of methods including brushing, spraying, spinning, etc. Preliminary studies utilized the spin coating technique in which films were deposited on precleaned 0.15 to 0.18mm thick by 19mm square quartz microscope cover slides. The freshly deposited resinate solutions are then fired in air under controlled heating rates to temperatures in the 500 to 800°C range producing a metal or metal oxide film varying between 1000 and 2000Å in thickness.

The absorptance (α_{25}) is determined by measuring the total reflectance of the test coatings at room temperature in a spectrophotometer (Cary 14) with appropriate attachments. The instrument is calibrated with Eastman White Reflectance Coating (Cat. No. 6080) or smoked MgO. The solar absorptance is calculated from the spectral reflectance data using a numerical integration of the equation:

$$\alpha_{25} = \int_{0.35\mu m}^{2.5\mu m} (1 - R_{25}(\lambda)) F_{AM2}(\lambda) d\lambda$$

Where $R_{25}(\lambda)$ is the room temperature spectral hemispherical reflectance, and $F_{AM2}(\lambda)$ is the fraction of air mass two solar irradiance in the spectral region $d\lambda$.

The $F_{AM2}(\lambda)$ data necessary for the evaluation of α_{25} are published in several sources.[6]

The accuracy and reproducibility of these techniques were evaluated by repeatedly measuring a sample of black chrome solar absorber coating. The standard deviation of ± 0.0025 absorptance units was obtained.

Specular infrared reflectance data were obtained with a Perkin Elmer Model 21 recording spectrophotometer equipped with a Wilks specular reflectance attachment. Agreement between the specular emittance data and hemispherical data

is within the specified range of accuracy of the hemispherical emissometer. For coatings with large diffuse reflectance components, hemispherical emittance ($\epsilon_{25}(100)$) was measured with a Gier Dunkle DB-100 emissometer having an accuracy of ± 0.02 Emittance units and a reproducibility of 0.005 units.[7]

The resistance of these films to degradation in optical properties at elevated temperatures was tested by furnace aging in air at 500°C. Test temperatures were monitored with a multi-point recorder driven by thermocouples located near the samples. Samples were removed at selected intervals from the test furnaces, cooled to room temperature, for α_{25} and $\epsilon_{25}(100)$ measurements and returned to the furnace for a continuation of the simulated aging test.

RESULTS AND DISCUSSION

The early portion of the development program centered on improvements in the optical properties of a film composed primarily of metallic gold and glass forming metal oxides such as Bi_2O_3 , SiO_2 , etc. Both compositional and processing optimization did lead to improvements in α_{25} up to about 0.8 from 0.5 at the contract start. In parallel, a program was carried out to identify possible black conducting metal oxides that, with some modification could be made to have lower emittance values without sacrificing their inherently excellent solar optical absorptive property. Neither of these two approaches showed enough promise to warrant extensive study.

In contrast, the third approach, that of replacing gold with a less expensive metal, did show considerable promise. A detailed search and an extensive screening program of candidate selective solar absorber compositions showed that a film composed of Ag, CuO, and Rh_2O_3 had optical properties considerably better than the materials resulting from the first two approaches. Consequently, considerable attention was focused on optimization and more advanced simulated thermal testing.

The combination of Ag and CuO is derived from the basic optical properties of these materials. Silver, like gold, copper, and aluminum, is a highly reflective metal that should function as the low thermal emitting constituent. The copper oxide, a black semiconductor, should absorb most of the incident solar radiation while maintaining transparency in the infrared region. An optimum mixture of these two species should therefore produce a film of high absorptance and low infrared emittance in the solar regions. The rhodium species, as will be shown below, influences both absorptance and emittance, as well as the durability of the film during thermal aging. The precise stabilization mechanism is the subject of a continued research effort.

The first composition to be studied in some detail was a film composed nominally of 85 wt. % Ag and 15 wt. % (copper oxide and rhodium oxide or rhodium metal). This film, when freshly prepared on polished quartz, had an

α_{25} of 0.85 and an $\epsilon_{25}(100)$ of about 0.04. During thermal aging in air at 500°C, simulating a typical use temperature, the desirable optical properties quickly deteriorated with time as shown in Figure 1, curves 1A (α_{25}) and 1B ($\epsilon_{25}(100)$).

These results were used as a basis for determining the mechanism of deterioration. It was not known at this point which component(s) of the film was (were) most responsible for deterioration of optical performance. The literature indicates that Ag metal is considered the IR reflector component while the metal oxide, CuO, functions as the solar absorber.[8] Consequently, a study was made of varying each of these components while maintaining the Rh₂O₃ content and subjecting the films to thermal aging. The resultant data is shown as curves 2A(α), 2B(ϵ) for the 75 wt. % Ag system and 3A(α), 3B(ϵ) for a system composed of 60 wt. % Ag, 40 wt. % (CuO + Rh₂O₃) on polished quartz. The α_{25} trends show a distinct improvement in stability with decreasing reflector component (or increasing absorber component). However, the reverse trend was found for the emittance; that is increasing $\epsilon_{25}(100)$ with decreasing reflector component Ag. Experiments in which the Rh₂O₃ was not incorporated into the film such that the composition was 60 wt. % Ag/40 wt. % CuO are shown as the broken curves in Figure 1. The α_{25} value is initially unacceptably low ($\sim$.81) and maintains a stable value to 100 hrs. of testing. The $\epsilon_{25}(100)$ is unacceptably high initially ($\sim$.34) and degrades to 0.65 after only 100 hrs. on test. Visible observation of the film after 100 hrs. of test clearly showed an increase in film transparency. Thus it appears as though the Rh₂O₃ acts, to a limited degree, as a stabilizer against Ag agglomeration.

The marked improvement in α_{25} stability of the 60 wt. % Ag system was encouraging and thus an explanation for its poor emittance was undertaken. This film was subjected to more extensive thermal aging at 500°C (Fig. 2) in order to amplify any physical changes occurring in the film. As expected, the trends observed for shorter time exposures at 500°C (refer to Fig. 1) bare out the seriousness of the deterioration in optical performance. Microscopic examination of the film after 800 hrs. onstream showed significant agglomeration of the Ag component.

Optical micrographs were taken of samples before and after thermal testing at 500°C. The micrographic technique used showed both transmitted and reflected light images (Figure 2(a,b)). The solar absorber coating before thermal stability testing is opaque and shows a fine-grained inhomogeneous surface structure (Figure 2(a)). After 800 hours in air at 500°C, a similar coating has a large amount of light transmission and is reflecting at only one location - an agglomerate about 30 μ m in linear dimension (Figure 2(b)). This behavior was confirmed by observing several different samples. Energy Dispersive Analysis (EDA) using a Scanning Electron Microscope showed that the agglomerates were mainly silver.

A stabilizer material was incorporated in the 60Ag/40(CuO + Rh₂O₃) film with the intention of minimizing the agglomeration of the Ag constituent. This proved to be an extremely effective approach towards minimizing $\epsilon_{25}(100)$

increases previously observed at 500°C. The solid curves of Figure 3 show that the α_{25} value of about 0.9 at 500°C is maintained in air, while the $\epsilon_{25}(100)$ was maintained at less than 0.1 after 700 hours on test. This represents a dramatic improvement over the control sample (broken curve, without the stabilizer) which had an $\epsilon_{25}(100)$ of ~ 0.4 for comparable test conditions. Extended testing to 1500 hrs. continued to show superior performance with the stabilizer containing system over that of the stabilizer-free film. However, $\epsilon_{25}(100)$ increases slightly to 0.19 after 1500 hours at 500°C. The α_{25} is showing continuous slight decreases (to 0.88) after 1500 hours at 500°C.

The identification of Ag, CuO, Rh₂O₃ containing films as potential candidates for industrial process heat solar applications is a definite accomplishment of the NSF Grant work. A second accomplishment is the recognition of the mechanism of deterioration after thermal aging as being due to agglomeration of the metallic component. The subsequent minimization of agglomeration by the use of a stabilizer represents a significant improvement in preparing commercially viable films for high temperature solar applications.

Although these newly developed films are substantially superior to those available earlier, the problem of slightly decreased optical performance after thermal aging at 500°C in air is still unsolved. The needed improvements and the rationale for a permanent solution are the subject of a continued research at Engelhard.

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FIGURE 1 SOLAR ABSORPTANCE (α_{25}) AND THERMAL EMITTANCE ($\epsilon_{25}(100)$) VS. TIME

CONDITIONS: 773°K (500°C), Air, Quartz Substrates
 — [Ag-(CuO+Rh₂O₃)] - - - [Ag-CuO]

OPTICAL MICROGRAPHS OF 60Ag/39.5CuO/0.5Rh₂O₃
SOLAR ABSORBER COATING - 390X

FIGURE 2 (b) AFTER 800 HRS. AT
773°K (500°C) IN AIR.

FIGURE 3 SOLAR ABSORPTANCE (α_{25}) AND THERMAL EMITTANCE ($\epsilon_{25}(100)$) VS. TIME

CONDITIONS: 773°K (500°C), Air Quartz Substrates

COMPOSITION: [60Ag - 40(CuO + Rh₂O₃)]

NOTES

CVD MOLYBDENUM FILMS OF HIGH INFRARED REFLECTANCE

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ABSTRACT

Molybdenum thin films deposited by pyrolytic decomposition of molybdenum carbonyl attain, after anneal in a reducing atmosphere at 1000 C, infrared reflectance values within 0.7% of the reflectance of super-smooth bulk molybdenum. These films exhibit both the refractory nature of molybdenum and the high infrared reflectance generally associated with conventional mirror materials. The entire production sequence proceeds at 1 atm and requires less than 1 h. Films deposited under oxidizing conditions exhibit a solar absorptance of $\alpha = 0.77$ and a thermal emittance of $e = 0.44$. Absorptances of $\alpha = 0.82$ with $e = 0.08$ are obtained by first annealing and then overcoating these black molybdenum films with an antireflecting layer. Changes in the optical properties during annealing are related to compositional and structural properties of the films, as determined by x-ray diffraction, electron microscopy, and Auger spectroscopy. The results of anneals in air at 500 C are reported for the most reflective films which have been coated with either thin passivators or complete photothermal stacks.

INTRODUCTION

The most common photothermal solar converters operate on the principle of the absorber-reflector tandem. The solar flux penetrates into the topmost layer, which is absorbing over the solar spectral range. Toward longer wavelengths the absorber is transparent, so a reflector layer underneath can "look through" the absorber on top and minimize the reradiative loss in the infrared by its low emittance.

Efficiency of the solar conversion depends on the absorptance for solar radiation of the top layer and the low emittance of the reflector layer in the infrared, with both quantities sustained at the operating temperature. Operation at 500 C or above presents a problem in particular for the reflector. Materials of high infrared reflectance, such as the noble metals, agglomerate at temperatures as low as 250 C, causing the reflector to deteriorate.

The problem is aggravated for converter stacks that are fabricated at high temperatures. Previous work has established the feasibility of depositing spectrally selective stacks from the vapor phase [1]. This fabrication by chemical vapor deposition (CVD) proceeds at atmospheric pressure, offering the potential of large-scale continuous flow-through manufacture. Since deposition temperatures are in excess of 700 C, CVD fabrication pre-screens the stacks against catastrophic thermal deterioration processes.

Stabilization of thin silver films up to temperatures in excess of 800 C has been accomplished by overcoating them with oxide films [2]. Nevertheless, the process is not quite satisfactory because the noble metals are difficult to deposit by CVD, rendering a sequential all-CVD fabrication cumbersome. The situation can be improved and the inherent potential of CVD fabrication of selective surfaces realized, if a temperature-stable material of sufficient infrared reflectance can be found that is readily laid down by CVD.

The obvious candidates are the refractory metals, which in bulk form are prohibitively expensive. When polished to a supersmooth finish, bulk molybdenum has an absolute reflectance of from 97.1% at 3 μ m to 98.4% at 15 μ m [3]. Molybdenum thin films prepared by physical vapor deposition reflect considerably less than the bulk form, unless excessive and lengthy preparations are employed [4]. The strong chemical reactivity of molybdenum, and a structure different from that of the bulk, are suspected causes of the reduced reflectance of these films. Thin films of the refractory metals deposited from the vapor phase have been studied extensively for their hardness and electrical conductivity [5,6], but little is known about their optical properties. Recent work has demonstrated the possibility of preparing molybdenum films of improved infrared reflectance by chemical vapor deposition (CVD) [7]. Subsequent studies have determined those compositional and structural properties which influence the infrared optical properties of CVD molybdenum, and have led to the development of the procedure reported here for producing films of an even higher infrared reflectance.

In developing CVD reflector films that not only compete in their infrared reflectance with standard mirror materials but also have a promising solar absorptance of their own, previous concepts of the absorber-reflector tandem can be changed. The nearly perfect wideband reflectance of silver is not desirable, if operating in tandem with a marginal solar absorber such as silicon. The absorptance of polycrystalline silicon drops without trapping the near-infrared insolation, and moreover, an indirect gap results in a shallow absorption edge. In contrast, amorphous silicon exhibits a steep absorption edge located somewhat further into the infrared [8]. There is still room for improvement in the stack performance, however, by boosting its solar absorptance through a reflector material underneath that reflects considerably less than does silver in the spectral range of the solar emission's infrared tail. The reduced reflectance of molybdenum in the near-infrared will achieve this improvement of the stack's performance. The improvement will be particularly pronounced if the technology of "black molybdenum" described in the following sections is utilized.

EXPERIMENTAL PROCEDURE

Deposition of Molybdenum Thin Films

Films were deposited by the pyrolytic decomposition of molybdenum carbonyl:

This reaction does not go to completion at temperatures below 400 C [9]. Incomplete decomposition results in the inclusion of carbon and oxygen within the growing film and increases the electrical resistivity [6]. Attempts to deposit at temperatures above 400 C under 1 atm result in gas phase decomposition and powdery, non-adherent films [5].

Films discussed in this paper were deposited at temperatures between 200 and 400 C under 1 atm of argon carrier gas. Although adherent to polished quartz substrates, these as-deposited films contain, as mentioned above, substantial amounts of carbon and oxygen and exhibit only moderate infrared reflectance. The films were grown in a horizontally fed, radiatively heated reactor at growth rates on the order of 3 Å per second at 300 C.

Black molybdenum films, with significantly lower reflectance in both the infrared and visible wavelength ranges, were deposited at 300 C while under 1 atm of argon by introducing oxygen at a flow rate equal to or less than 0.5% of the argon flow.

Post-Deposition Anneal

In recent studies of the passivation of CVD molybdenum films against oxidation, we sometimes observed reflectance increases after anneals in air at 500 C [10]. The effect is ascribed to outgassing and/or structural changes in accordance with observations on bulk molybdenum [11]. For thin films, DeRosa [12] has observed changes in x-ray diffraction patterns of CVD samples after anneal, while Oikawa [13] used high-temperature treatments to improve the electrical conductivity of evaporated molybdenum.

Results presented here involve changes in the optical properties of deposits which have been exposed to post-deposition anneals in flowing forming gas (90% helium, 10% hydrogen) at temperatures from 700 to 1000 C for different durations. Measuring the temperature to within 10 degrees, the anneal time begins after a 4-min warm-up and excludes a 5 to 10 min cool-down period.

EXPERIMENTAL RESULTS

Highly Reflective CVD Molybdenum

Films deposited by CVD without oxygen additions reflect up to 85% of 10 μ m radiation before anneal. Near normal specular reflectance is measured to within 1% on a Perkin-Elmer 137 Spectrophotometer, and is plotted in Figures 1 and 2 relative to the reflectance of an aluminum reference. Figure 1 shows the relative reflectance of films deposited at 300 C, and annealed for 5 min at different temperatures. Figure 2 plots relative reflectance of a similar set of films as a function of anneal duration at 750 C. Similar profiles are obtained for films deposited at temperatures from 200 C to 450 C, establishing the insensitivity of the effect of the anneal to the initial deposition temperature. It follows from Figures 1 and 2 that anneals of from 5 min at 1000 C to 30 min at 750 C are capable of producing films which approach

FIGURE 1. RELATIVE REFLECTANCE, AT 10 μ m, OF CVD MOLYBDENUM FILMS PLOTTED AGAINST THE TEMPERATURE OF A 5-MIN ANNEAL.

FIGURE 2. RELATIVE REFLECTANCE, AT 10 μ m, OF CVD MOLYBDENUM FILMS PLOTTED AGAINST THE DURATION OF ANNEAL AT 750 C.

the infrared reflectance of the aluminum reference. Scatter in the data points may be caused by variation in thickness from 1200 Å to 3000 Å, affecting the occurrence of outgassing and structural changes during anneal.

Since the reflectance traces of the fully annealed films coincide with that of the aluminum reference on our reflectometer, films were deposited on two quartz optical flats, annealed for 25 min at 1000 C, and submitted to H. E. and J. M. Bennett at the Michelson Laboratory, China Lake, California, for measurement in their Precision Absolute Reflectometer. This instrument is capable of determining absolute reflectance values to an accuracy of $\pm 0.1\%$ [14]. The results are shown in Figure 3. One CVD film is bare, while the other has been passivated with 300 Å of Si_3N_4 to prevent any reflectance reduction by exposure to air. Included in the figure are the absolute reflectances of bulk molybdenum polished to a supersmooth finish [3], as well as a molybdenum film sputtered under ultraclean conditions [4]. Note that the CVD films have absolute reflectances within 0.7% of the reflectance of super-smooth bulk molybdenum from 3 to 15 μm . Note also that the CVD films, prepared and annealed within less than 1 h, are superior to the sputtered sample which requires lengthy and careful pre-deposition preparation [4]. The CVD film of higher reflectance is passivated with Si_3N_4 , as is required for further processing during the fabrication of spectrally selective solar converters.

FIGURE 3. ABSOLUTE REFLECTANCE, FROM 3 TO 15 μm , OF SUPERSMOOTH BULK MOLYBDENUM, UNPROTECTED AND PASSIVATED CVD MOLYBDENUM AFTER ANNEAL, AND SPUTTERED MOLYBDENUM.

Abrupt changes in reflectance during annealing are accompanied by large increases of electrical conductivity. The conductivity of bulk molybdenum, however, is not attained. Sheet resistance was measured with a General Radio Resistance Bridge across a molybdenum square of known geometry using both silver paint and a grid of evaporated silver contacts. The non-rectifying character of the contacts was established through their I-V characteristic. Thickness was measured by FECO interferometry. Table 1 compares conductivity and reflectance values for an unannealed and a completely annealed film with the values for bulk molybdenum.

TABLE 1. THICKNESS, ELECTRICAL RESISTIVITY AT 20 C, AND ABSOLUTE REFLECTANCE AT 10 μm OF AN AS-DEPOSITED FILM, AN ANNEALED FILM, AND SUPERSMOOTH BULK MOLYBDENUM

Sample	Thickness (μm)	Resistivity at 20 C ($\mu\Omega\cdot\text{cm}$)	Absolute reflectance at 10 μm (%)
As-deposited	0.154 ± 0.006	250 ± 25	85.0 ± 1.0
Annealed	0.134 ± 0.007	9 ± 2	97.4 ± 0.1
Bulk Mo	---	5.7^a	98.1 ± 0.1

^a Handbook of Chemistry and Physics, 52nd edition, The Chemical Rubber Co., Cleveland, Ohio, 1971, p. E-72.

Three changes in film composition and structure occur in coincidence with the enhancements of reflectance and conductivity. First, the anneals change crystal structure significantly. As-deposited films show fcc-MoOC [15] structure in x-ray diffraction, which upon anneal is first replaced by hcp-Mo₂C, and finally, after complete anneal, by a bcc-Mo response. The abrupt reflectance increase shown in Figure 1 occurs in coincidence with the disappearance of the MoOC structure.

Second, micrographs taken with an electron microscope show that annealed films contain grains which are over 50 times the size of the grains in as-deposited films. Electron diffraction patterns concur with x-ray measurements by exhibiting the transition from a fcc to a bcc ring pattern which occurs during anneal. The fcc rings are more densely populated than the bcc rings, as is expected, due to the growth in grain size caused by the anneal.

Finally, compositional changes resulting from outgassing during anneal have been measured by several techniques. Auger spectroscopy can quantify C and O levels in a molybdenum matrix to within only ± 30 to 50% [16]. A direct measurement for each of the three constituents by other techniques has therefore been used to calibrate the Auger results. Measurements were made for carbon with a Perkin-Elmer 240 Elemental Analyzer, for oxygen with Rutherford backscattering, and for molybdenum by absorption spectroscopy. These determinations indicate that high temperature anneals of reflecting molybdenum change molybdenum

content from 62 ± 15 to 94 ± 4 atomic percent. Figure 4 shows oxygen and carbon levels, measured by Auger spectroscopy, superimposed on the reflectance profile. It must be emphasized that these data are to be interpreted in a relative sense only. Figure 4 demonstrates that the reflectance increases occur in conjunction with the outgassing of oxygen. As deposited, and again after complete anneal, the Auger sputter profiles indicate that the films are homogenous. Partially annealed films, however, contain a nonuniform distribution of impurities with depth.

FIGURE 4. OXYGEN AND CARBON CONTENT OF A SET OF MOLYBDENUM FILMS ANNEALED FOR 5 MIN AT DIFFERENT TEMPERATURES. SHOWN FOR COMPARISON IS THE REFLECTANCE PROFILE OF FIGURE 1.

Lifetime Tests

Previous work at the Optical Sciences Center has attempted to integrate as-deposited reflective CVD molybdenum films into complete photo-thermal stacks. Stacks which consisted of amorphous silicon over silicon nitride over molybdenum over fused silica have been annealed for over 1000 h at 500 C in air. These long-term anneals have shown that the as-deposited films survive the CVD of Si_3N_4 and a-Si, and that the reflectance of the molybdenum does not deteriorate during the 1000 h if pinhole and crater growth in the stack surface is avoided. Outgassing of the as-deposited molybdenum has been related to crater growth.

Identical stacks deposited on highly reflective, fully annealed molybdenum have been exposed to air for over 1000 h at 500 C. A set of stacks using as-deposited molybdenum was tested with the new stacks, as a control. Crater growth was not observed on the stacks containing

annealed molybdenum while serious growths occurred on the control set. After 1000 h at 500 C in air the silicon layer was etched from the successful stacks such that the emittance of the molybdenum surface could be re-evaluated. An emittance of 0.045 of the 500 C blackbody spectrum resulted.

An analysis of other potential long-term failure modes in these stacks is in progress. These involve stresses induced by the crystallization of the amorphous silicon layer or by pinholes in the silicon nitride which permits oxidation of the underlying molybdenum. Use of nickel substrates which bond well to molybdenum films [17] will increase stack adherence.

Using silicon nitride films to passivate as-deposited molybdenum against reflectance loss [10] has been extended to highly reflective annealed molybdenum. Films of the highest reflectance, which have been passivated with Si_3N_4 , retain their reflectance throughout 2 days at 500 C in air.

CVD Black Molybdenum

Figures 5 and 6 summarize solar absorptance and thermal emittance of films which were obtained by pyrolyzing $\text{Mo}(\text{CO})_6$ in the presence of oxygen. The evaluation of absorptance and emittance is based on "distorted- λ plots." These plots graph hemispherical reflectance against an abscissa which is linear in either fractions of the total solar flux or of the reradiation loss [18]. Since solar absorptance α and thermal emittance e are given by

$$\alpha = \frac{\int_0^{\infty} \alpha(\lambda) \cdot \Phi_s(\lambda) d\lambda}{\int_0^{\infty} \Phi_s(\lambda) d\lambda} ; \quad e(T) = \frac{\int_0^{\infty} \epsilon(\lambda) \cdot \epsilon_{BB}(\lambda, T) d\lambda}{\int_0^{\infty} \epsilon_{BB}(\lambda, T) d\lambda} ,$$

their values can be obtained from distorted- λ plots by simple planimetry. Air mass 2 is used in Figure 5 for the solar input $\Phi_s(\lambda)$, and a temperature of 500 C in the blackbody emittance $\epsilon_{BB}(\lambda, T)$ of Figure 6. Assuming the samples to be opaque and Kirchoff's law to be valid, the absorption $\alpha(\lambda)$ and the emittance $\epsilon(\lambda)$ can be approximated by $1 - R_{\text{hem}}$. Although the evaluation of the solar absorptance in Figure 5 is actually based on a hemispherical reflectance measurement, it should be noted that nearly the same values are obtained for specular reflectance. This suggests that the absorptance of black molybdenum is not based on surface texture, but represents an intrinsic property of the material. Note further that the thermal emittance derived from Figure 6 is based on a specular reflectance measurement, giving an upper limit for e , so the actual thermal emittance may be even smaller.

In both figures, Curve 1 represents α and e for CVD molybdenum films deposited without the intentional presence of oxygen, and subsequently annealed for 20 min at 1000 C. Curve 2 gives α and e for black molybdenum, as obtained by CVD in the presence of oxygen, and subsequent anneal for 5 min at 1000 C. Curve 3 shows the profiles for as-

FIGURE 5. DISTORTED λ -PLOT OF THE SOLAR ABSORPTANCE α OF A SET OF THIN MOLYBDENUM FILMS. SEE TEXT FOR THE DIFFERENT TREATMENTS OF THE SAMPLES.

FIGURE 6. DISTORTED λ -PLOT OF THE THERMAL EMITTANCE ϵ FOR A BLACKBODY TEMPERATURE OF 500 C FOR THE SAMPLE SET OF FIGURE 5.

deposited black molybdenum. Antireflecting the anneal black molybdenum of Curve 2 by a layer of Si_3N_4 of proper thickness results in the profiles marked 4 in Figure 5 and Figure 6.

It follows that the presence of oxygen during deposition raises the solar absorptance to 0.77 and the thermal emittance to 0.44. Subsequent anneal of black molybdenum decreases the emittance to 0.06, while lowering the solar absorptance to 0.58. Although not yet optimized, over-coating with silicon nitride produces respectable selectivity ($\alpha = 0.82$, $e = 0.08$). Substantial selectivity has also been obtained by overcoating with 500 Å of silicon. Antireflected black molybdenum is deposited by two simple CVD steps. The films are expected to demonstrate durability at 500 C, since they are subjected to anneal above 700 C during production. Table 2 summarizes trends in α and e which are observed in response to annealing black molybdenum at different temperatures. Higher temperatures of anneal result in lower values for the solar absorptance as well as the thermal emittance. An optimal anneal temperature exists near 800 C.

Analogous to the studies performed on highly reflecting films deposited without the intentional presence of oxygen, we have followed the structural and compositional changes of black molybdenum through the anneal. The pattern of x-ray diffraction changes from monoclinic MoO_2 to bcc molybdenum during the anneal. The oxygen-rich as-deposited black films outgas during anneal, as indicated by Auger spectroscopy, and become nearly as pure as the most reflective films deposited in the absence of oxygen. Although scanning electron microscopy indicates that black molybdenum films are slightly rougher than the highly reflective species, comparison of hemispherical and specular reflectance suggests that the slightly higher surface texturization is not the cause of their blackness. Unlike selective blacks that operate on the basis of their surface texture, the solar absorptance of black molybdenum is not affected by wiping the surface.

CONCLUSIONS

Depending on the choice of process parameters, pyrolytic decomposition of molybdenum hexacarbonyl can result either in reflecting or black films of molybdenum. High temperature anneal significantly enhances the infrared reflectance of both types of films. After anneal the reflecting films reach reflectance values within 0.7% of super-smooth bulk molybdenum, competing with the optical properties of conventional mirror materials such as aluminum in the infrared range. Annealed black molybdenum nearly rivals this infrared reflectance, but retains substantial solar absorptance. An antireflective layer of Si_3N_4 raises the absorptance to 0.82, with the thermal emittance kept at 0.08 of the 500 C blackbody profile. These performance values establish a good approximation to a single-layer spectrally selective converter of promising temperature stability. Reflecting molybdenum can be passivated with Si_3N_4 against oxidation-induced reflectance loss for a 2-day period at 500 C in air. Removal of the silicon layer from complete stacks, which have been exposed to air at 500 C for 1000 h, reveals a

TABLE 2. SOLAR ABSORPTANCE AND THERMAL EMITTANCE OF CVD MOLYBDENUM

	Solar absorptance (% of AM = 2 solar flux)	Thermal emittance (% of 500 C blackbody radiation)
Reflective Mo, annealed 20 min, 1000 C	37	3
As-deposited Black Mo	77	44
Black Mo annealed 5 min, 700 C	76	14
Black Mo annealed 5 min, 800 C	72	8
Black Mo annealed 5 min, 900 C	56	6
Black Mo annealed 5 min, 1000 C	58	6
(Anti-reflected) Black Mo annealed 5 min, 1000 C	82	8

a molybdenum surface with an emittance of 0.045 of the 500 C blackbody spectrum.

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AMORPHOUS SILICON ABSORBERS FOR PHOTOTHERMAL SOLAR ENERGY-CONVERSION

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ABSTRACT

Crystalline silicon is a poor absorber of solar photons, requiring thick films for complete absorption. In contrast, amorphous silicon has a much stronger absorption, permitting absorbers to be of a considerably smaller thickness. In order to optimize the use of amorphous silicon in our converter stacks, we simulated the performance of twin pairs of multilayer stacks. These twins were identical in their fabrication, except that one stack used amorphous silicon and the other used polycrystalline silicon. The results of these simulations indicate that stacks containing amorphous silicon perform better than stacks using polycrystalline silicon, and, in addition, that silicon-on-molybdenum stacks perform better than silicon-on-silver stacks. Experimental results verify these predictions with values for the solar absorptance of molybdenum-based amorphous silicon stacks of up to 0.77, compared to a value of 0.70 for silver-based stacks. Thin amorphous silicon layers on black molybdenum have produced absorptance values to 0.79, all values being taken at room temperature. They are expected to be higher at 500 C.

INTRODUCTION

Photothermal converters utilizing amorphous silicon as the absorbing medium have several advantages over polycrystalline silicon absorbers, requiring thicker films for complete absorption. Amorphous silicon is a much stronger absorber of solar photons with an absorption edge located further into the infrared, resulting in the absorption of a larger fraction of the solar insolation for an equivalent thickness. In the thermal infrared amorphous silicon has an absorption lower than that of polycrystalline silicon due to a smaller number of free carriers, reducing the thermal emission losses (1,2).

To better define the role of the structure, amorphous vs. polycrystalline, of the silicon absorber, we designed twin stacks that were essentially identical, except that one employed amorphous silicon as the absorber and the other a polycrystalline layer. In order to optimally design the dimensions of the twin stacks, we began simulations of their

performance. We were especially interested in determining how the thickness of the absorber might be tailored to take full advantage of amorphous silicon's higher absorption.

We then fabricated an actual twin sample set to test the predictions of the simulation using the parameters suggested in the optimizing process. These samples did show gains in the solar absorptance of the amorphous stack over its polycrystalline twin, and supported the trends found in the preceding simulation.

CVD AMORPHOUS SILICON

Amorphous Silicon as Photothermal Absorber

The potential of amorphous silicon as a solar absorber has been realized by our group since 1974 (3). It was known, however, that electron beam evaporated or sputtered amorphous silicon crystallized at 550 C, precluding Chemical Vapor Deposition (CVD), which requires a minimum deposition temperature of 580 C for reasonable deposition rates. Consequently, our work used only polycrystalline silicon as the absorber. Recent work with radio frequency (RF) glow-discharge-produced amorphous silicon has resulted in films that are temperature stable against crystallization to 680 C (5). These films contain substantial amounts of hydrogen which evolve as the crystallization temperature is approached (5).

At this point we realized the possibility of producing amorphous silicon by CVD, and began investigations into the nature of our CVD silicon deposited at 600 C. We found that these films are amorphous and remain so until 670 C, presumably due to the stabilizing action of inclusions of trace impurities such as hydrogen and oxygen.

Preparation

Our amorphous silicon films are prepared by the pyrolytic decomposition of silane (SiH_4) in a radiation-heated horizontal reactor. The carrier gas is helium at a nominal flow rate of 10 l/min, with a silane concentration of 0.25% to 1.0%. The deposition temperature range is 550 C to 800 C, with deposition rates of 100 Å/min to 1500 Å/min, depending not only on temperature, but also on silane concentration. Thickness ranged from 0.100 to 2.00 microns (6, 7).

Properties

Figures 1 and 2 show data for the refractive index and absorption coefficient, respectively, for both amorphous and polycrystalline silicon. These were determined from spectral transmission and reflection measurements together with film thickness measurements (6).

Films produced at temperatures of 550 C to 650 C are amorphous and show, within experimental error, the same values for their optical constants independent of deposition temperature. The temperature of crystallization is 670 C, which was determined by annealing amorphous silicon

Fig.1. Refractive index for a sample annealed at 650 C for successive annealing times (See Ref. 6).

Fig.2. Absorption coefficient for different deposition temperatures (Ref. 6).

Fig.3. Hydrogen content of CVD amorphous silicon, as determined from SIMS by C.W. Magee.

Fig.4. Comparison of absorption edges for amorphous and polycrystalline silicon for a thickness of 2.0 μm .

films at various temperatures for a fixed length of time and measuring by X-ray diffraction the onset of crystallization.

It can be speculated that impurities incorporated into our films raise the crystallization temperature to 670 C. SIMS measurements taken by C.W. Magee at the RCA Laboratories, Princeton, NJ, have established the hydrogen content of our films to be 0.2 to 0.7 atomic percent (Figure 3) leveling off at the temperature of crystallization.

PHOTOTHERMAL CONVERTER DESIGN AND MATERIALS

Our stacks are designed after the dark mirror concept using the tandem action of a highly reflective thermal infrared reflector overlaid with a solar absorber transparent in the thermal infrared. In the past we have used polycrystalline silicon and silver as the absorber and reflector, but are now looking to amorphous silicon as a more absorbing material, and to molybdenum as a more stable, refractory reflector.

The Absorber Layer

The absorber layer would ideally have a step function profile for its absorption edge, with this step located at 2.0 μm . Polycrystalline silicon poorly approximates this step function with a broadly sloping absorption edge centered at 0.700 μm , reflecting in this profile its indirect band gap absorption. In contrast, the absorption edge of amorphous silicon is much steeper than that of polycrystalline silicon and is located further into the near infrared, at 0.775 μm . For an equivalent thickness, amorphous silicon should show an increased solar absorptance relative to polycrystalline silicon. Figure 4 shows that this is indeed the case. This comparison of absorption edges for a film thickness of 2.0 μm gives an absorptance of 56% for amorphous silicon and 49% for polycrystalline silicon. These values are representative only of the silicon absorber layer, and not for a complete photothermal stack.

It is also important to realize that although amorphous silicon has a larger absorption coefficient at the wavelength of interest than does polycrystalline silicon, the solar absorptance results as a function of both absorption coefficient and film thickness,

$$A \sim \exp(2ad) \quad (1)$$

where A is the film absorptance, a is the absorption coefficient, and d is the film thickness. In addition, the lineshape of the absorption edge is also significant. As the film becomes thicker, the absorptance increases exponentially. This increase is significant, however, only in cases where the absorption edge is shallow, as for polycrystalline silicon (Figure 4). For amorphous silicon with its much steeper absorption edge, increased thickness changes the absorptance much less past some minimum thickness, and much thinner films can be used than in the polycrystalline case.

The Reflector Layer

Previously, we have used silver as the infrared reflector because of its high reflectivity. However, it must be evaporated and stabilized against agglomeration at temperatures above 250 C. Molybdenum on the other hand is a refractory metal, and is capable of high infrared reflectance (8) in thin film form. The agglomeration problem is reduced. Thin molybdenum films can be produced by CVD and possess reflection properties in the near infrared that enhance stack absorption. Molybdenum, while having a high reflectance in the thermal infrared, has a low reflectance in the visible of $R \sim 0.50$ which increases to 0.97 at 2.5 μm . In this region where silicon is transparent, the low molybdenum reflectance promotes the absorption of solar photons that have passed through the silicon absorber.

DETERMINATION OF OPTICAL CONSTANTS FOR SIMULATIONS

The programs performing the simulations required knowledge of the refractive index and absorption constant of the amorphous and polycrystalline silicon, and of the silver and molybdenum. In addition they required the experimental determination of reflectance of the silver and molybdenum.

Figures 1 and 2 show the experimental values for the refractive index and absorption coefficient of amorphous and polycrystalline silicon (6). These constants were extrapolated beyond the range of measurements to shorter and longer wavelengths as required by the programs.

The optical constants for both silver and molybdenum were taken from the AIP Handbook (third edition). These bulk constants for molybdenum are in error for thin films as they do not reproduce the reflectance measured on thin molybdenum films. They result in reflectances that are lower than the reflectances we measure on thin films, and as a result produced simulated solar absorptances that were too large. Reflectance values for silver were taken from Kingslake (9), while reflectance values for molybdenum were measured on our CVD molybdenum films.

SIMULATIONS

Models

In order to model our stacks, two types of simulations were performed. The two models are shown schematically in Figure 5.

In the "bulk" model we simplified the operation of the stack in order to observe the intrinsic absorption processes of the silicon-reflector tandem. We assumed no front surface reflection, interference effects were disregarded, and all reflections were assumed specular. The stack absorptance due to the silicon was calculated according to Beer's Law

$$I = I_0 \exp(-ad) \quad (2)$$

Figure 5. Two stack models for simulations.

where a is the absorption coefficient and d the film thickness. By assuming that the absorption due to the reflector layer was unity less the reflectance, the stack absorptance became

$$A(\lambda) = 1.0 - R(\lambda)\exp(-2a(\lambda)d) \quad (3)$$

where $A(\lambda)$ is the absorptance, $R(\lambda)$ is the reflectance of the metal layer, $a(\lambda)$ is the absorption coefficient of the silicon, and d is the absorber layer thickness.

In the "interference" model (Figure 5) we assumed the full stack configuration. We also assumed radiation at normal incidence, specular reflectance at all interfaces, finite front surface reflection, and interference effects. Using the optical constants and thickness of each layer, the reflectance and transmittance at each interface was sequentially calculated beginning at the air interface and working into the film, using the appropriate Fresnel equation. A spectral reflectance was calculated and the spectral absorptance was calculated as unity minus the spectral reflectance. The transmittance was assumed to be zero due to the presence of the opaque reflector.

Solar Absorptance Calculations

In both models the method of calculating the solar absorptance was the same, based on the Thomas-Richmond 100 Selected Ordinate Method (10). This method uses 100 wavelengths chosen such that they divide the Air Mass 2 (AM2) solar insolation profile into 100 equal sections. The solar absorptance integration process then becomes one of calculating the absorptance at these 100 points, summing and dividing by 100. This method does require that the reflections vary slowly compared to the sampling frequency of the 100 Ordinates. This condition is well satis-

fied for silicon thicknesses less than 1.00 microns. In order to extend this calculation procedure to thicker stacks, where interference effects lead to rapid fluctuations in the absorptance over a small wavelength increment, and in order to insure accurate calculations on the thinner films, the 100 Selected Ordinate Method was extended to 200 points by interpolating once between each of the original 100 points. To verify that these computations were indeed accurate, initial results from computer calculations were compared to a test case calculated by hand and planimetered on distorted wavelength paper. The differences in the two results were generally less than 0.5%.

Parameter Variations

Parameter variation consisted of adjusting the thickness of the silicon absorber layer from 0.060 to 6.00 microns. In the "bulk" model, this increase in thickness produced a monotonic increase in solar absorptance. In the "interference" model, the absorptance at first increased and then began to oscillate as interference effects became effective.

SIMULATION RESULTS

Studies were first done for silicon on silver stacks, where it was found that the solar absorptance of the stack increased only with an increase in the thickness of the silicon absorber layer. This resulted from a mismatch of the optical constants of the silicon and silver in the region of silicon transparency. The constants for silver and silicon in this region (0.8 to 2.6 microns) are approximately $n = 0.1$, $k = 6.0$ and $n = 3.7$, $k = 0.0$, respectively. The reflectance of this interface was calculated according to

$$R = \frac{(n_{Si} - n_M)^2 + (k_{Si} - k_M)^2}{(n_{Si} + n_M)^2 + (k_{Si} + k_M)^2}, \quad (4)$$

where n and k are the real and imaginary parts of the refractive index, and where Si and M refer to silicon and the metallic reflector layer, respectively. The result showed that the stack's reflectance remains close to unity in the 0.8 to 2.6 microns range due to the disparity in the values of these constants. Thus, once the region of silicon transparency is entered, the high reflectance of silver results in a loss of absorptance.

The situation is much different when a material with better matched constants of $n = 4.0$, $k = 4.0$ such as Mo is overlaid with Si (Figure 6). Then reflectance values at interference fringe minima approach zero and the silicon effectively "antireflects" the material, in the region of silicon transparency, thus adding the reduced reflectance of the molybdenum to the absorptance of silicon. Solar photons that penetrate the increasingly transparent absorber are trapped by the "reflector" underneath. We see in Figure 7 experimental reflectances of Ag, Mo, and Black Mo, and the "transparency" edge of silicon. In contrast to silver, we see molybdenum's lower near infrared reflectance permitting the absorption of photons that have passed unabsorbed through the transparent silicon layer, thereby increasing the stack's absorptance. The

Fig.6. Comparison of simulated reflectances of Ag- & Mo-based stacks indicating the effect of the lower infrared reflectance of Mo.

Fig.7. Experimental reflectance values of Ag, Mo, and Black Mo with the "transparency" edge of Si shown for reference. Dashed areas indicate increases in solar absorptance.

dashed area of Figure 7 shows the gains in absorptance by using molybdenum, while the crosshatched region indicates the additional absorptance gained by using Black Mo as the reflector layer.

This study indicates that an optimal stack should consist of a very thin layer of amorphous silicon, 1000 Å to 2000 Å thick, deposited on a reflector with high n 's and k 's, such as Mo. The match in optical constants of amorphous silicon and molybdenum permits amorphous silicon to antireflect the molybdenum in the near infrared. This thin layer of amorphous silicon is sufficient to absorb the incident radiation in the visible, and reflection losses from the silicon are reduced by an antireflection coating. This configuration will also enhance the stack performance by reducing thermal emittance. Amorphous silicon of this thickness produces no interference fringes in the thermal infrared.

The major results of the computational studies are that amorphous silicon performs better than polycrystalline silicon in two respects: It is a better absorber of solar insolation in the visible, and it serves as an antireflection material for the molybdenum reflector in the near infrared. Amorphous silicon on molybdenum stacks also perform substantially better than polycrystalline silicon on silver stacks. Lastly, the amorphous silicon layer should be less than 2000 Å in thickness. This last result is important for several reasons. Silicon of this thickness produces no interference fringes in the thermal infrared and allows the stack reflectance to approach that of the molybdenum, on the order of 97% absolute. This produces stacks of very low emittance. It can be further determined that thin silicon will be more resistant to crystallization, less susceptible to thermal stresses that

degrade stack lifetimes, and more economical in terms of material cost and fabrication.

EXPERIMENTAL RESULTS

To verify the results of the above calculations, actual twins were prepared based on the guidelines from the simulation studies for an optimal stack. We found that amorphous silicon performed better than polycrystalline silicon by up to 0.04, for silicon thicknesses less than 2.0 microns. Silicon on molybdenum stacks performed better than silicon on silver stacks for all matched thicknesses. Values up to 0.77 for silicon on molybdenum stacks were obtained, and the thicknesses of the silicon in these stacks were less than 0.60 microns. Another stack made on Black Mo showed a solar absorptance of 0.79 (Figure 8). This stack used a very thin silicon layer, approximately 500 Å thick, and has not been antireflected in the visible. A similar design made with a silicon thickness of approximately 800 Å and an antireflection coating should produce solar absorptances greater than 0.80 by increasing the stack's absorption in the visible.

Fig.8. Experimental hemispherical reflectance of a Si-Black Mo stack which has a solar absorptance of 0.79.

CONCLUSIONS

Silicon on molybdenum stacks are better solar absorbers than silicon on silver stacks without the technical difficulties inherent in depositing and overcoating silver films. This is a result of molybdenum's lower reflectance in the near infrared that permits it to absorb those solar photons that penetrate the increasingly transparent silicon absorber layer. Molybdenum-based photothermal stacks are more refractory than are silver-based stacks, and hence are more stable at elevated temperatures.

Silicon on molybdenum stacks have shown solar absorptances of up to 0.79, even without the benefit of an antireflection layer. By optimizing the silicon thickness, silicon on molybdenum stacks should produce

absorptances greater than 0.80. Noting that these values were determined at room temperature, we can expect an additional increase in absorptance of 0.05 at 500 C. This is a result of electron-proton interactions at elevated temperatures that produce a shift in the absorption edge of silicon towards lower energies, increasing the fraction of the solar spectrum absorbed. This has been observed for polycrystalline silicon, and preliminary results indicate that amorphous silicon shows the same shift to longer wavelengths of the absorption edge (11). We thus can expect solar absorptance values for our photothermal stacks of 0.85 or larger at an operating temperature of 500 C.

It is now possible to use amorphous silicon absorber layers less than 1000 Å thick in conjunction with a molybdenum reflector. These stacks have no interference fringes in the thermal infrared, and thus a reduced thermal emittance. These stacks have better mechanical properties, are less susceptible to thermal stresses that degrade lifetimes, and are easier to fabricate.

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NOTES

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INHOMOGENEOUS SURFACES AS SELECTIVE SOLAR ABSORBERS

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ABSTRACT

An outstanding problem in the collector field is the development of selective solar absorbers. The best surfaces currently available are serendipitous discoveries which derive their properties from the microscopically inhomogeneous distribution of metal and dielectric particles.

We saw a need to obtain a generalized understanding of the optical behavior of inhomogeneous surfaces. In lieu of analytic solutions, we developed a computer code which uses mean field approximations to accurately describe the reflectance of inhomogeneous surfaces. This approach enables us to use realistic materials parameters and surface topologies, and arbitrary angles of incidence in our calculations.

We found that the impression of a texture with depth D and texture size $2a$ on the surface of an otherwise shiny metal would lead to a sharply defined low reflection window for $\lambda_{II} < \lambda_I$, $\lambda_{II} \sim 20a$, and $\sim \lambda_I / 6D$.

We also found that particle track etching could create a surface satisfying these criteria and produce a new type of selective absorber.

INTRODUCTION

There exist a variety of solar absorbers whose optical properties are determined by their surface topology. One surface in widespread use is electroplated black chrome. It was initially made accidentally and used as a decorative surface finish (1), but has since been refined into a very good selective absorber (2, 3). Recent work (4, 5) has shown the film to consist of a porous mixture of very fine metal and oxide particles deposited so that most of the metal particles are on the bottom and the oxide on top. The reflection spectrum is substantially specular and very selective (α/ϵ about 5) (2).

Another absorbing surface is dendritic tungsten (6). For this, one uses vapor transport to grow a dense forest of tungsten whiskers on a flat surface. These whiskers are considerably larger than the wave-

Graded Surface Topologies

FIGURE 1. THREE TOPOLOGIES FOR INHOMOGENEOUS SURFACES:
a) ROUGH, b) SPONGY, AND c) HAZY.

One retains information on the topology of the surface by the choice of the approximation (11). For instance, a surface made up of metal particles surrounded by an oxide layer (12) or uniformly spaced in a dielectric matrix (13), is most appropriately treated by the Maxwell Garnett approximation. The statistical nature of the actual distribution of particles is handled by a simple generalization of the approximation (14). A random mixture of dielectric and metal particles, on the other hand, would be better handled by Bruggeman's approximation (13), and a rough surface would best be treated by the form of the Maxwell Garnett approximation which describes cylinders aligned normal to the surface. Furthermore, in the cases in which the topology depends on the metal/dielectric ratio (15), it is necessary to use several approximations, each applying to a different depth in the surface. In that case one must be careful not to introduce an artificial discontinuity in $\epsilon(z)$ at the boundary between the approximations (16).

Having made the above approximations, it is conceptually possible to solve for the reflectivity analytically (17). That approach is not very useful in practice, however, because of the complicated behavior of the effective dielectric constant in any realistic situation (18).

length of visible light. The reflection spectrum is diffuse and only slightly selective.

Superficially, these surfaces look and behave very differently. In most surveys of absorber coatings, they are listed in separate categories. Our point of view is that they represent two extremes of a continuum of possible surfaces - which we call inhomogeneous - and that the optical properties of these surfaces can be understood by reference to a universal curve using only a few parameters.

Our purpose in this paper is 1) to describe a unified treatment of the optical properties of inhomogeneous surfaces, 2) to use it to generate benchmark optical standards and to compare them to achievable surfaces and 3) to show how this treatment can then be used to generate criteria for the development of new surfaces.

MODELLING

Topologically, there are three distinct kinds of inhomogeneous surfaces (Figure 1): a) singly connected (rough), b) multiply connected (spongy), and c) unconnected (hazy). An exact description of the interaction of light with any of these surfaces is totally out of the question; they present an impossibly complex boundary value problem. Some progress has been made on statistically rough surfaces (7), and on simple geometries (8), but we have chosen to treat these surfaces as two dimensional aggregates of independent particles because of the ease with which they can be arranged to simulate any type of surface by varying their shape, distribution, and orientation (9). In addition, good approximations exist to describe the interaction of light with small particles (10). The problem is to apply them in such a way to retain a maximum of information.

We do this by separating the problem into two parts. For the first analysis, we use only space averaged optical properties, yielding a surface which has only a specular reflectance. In the second, we treat the effects of the fluctuations around the average which causes the diffuse reflectance. The optical properties resulting from each analysis are treated as independent. We add them up at the end to give the total reflectance. First we will describe the procedure for calculating the average properties.

Specular Reflectance

We use an effective medium approximation to replace the exact inhomogeneous structure at every point with an average medium; we have then an effective dielectric constant ϵ_{eff} with planar symmetry; (i.e. $\epsilon_{\text{eff}} = \epsilon(z)$). At the surface ($z = 0$), $\epsilon(0)$ has the value of the dielectric; deep within the material ($z = \infty$), $\epsilon(\infty)$ has the value of the bulk material; in between there exists a smooth (though highly nonlinear) transition between transparent dielectric and reflective metal characterized by some distance D .

FIGURE 2. CALCULATED REFLECTANCE OF AN AIR/GOLD INHOMOGENEOUS SURFACE. BRUGGEMEN'S APPROXIMATION WAS USED FOR A LINEAR VARIATION IN CONCENTRATION OF SPHERICAL PARTICLES OVER A DEPTH OF A) $1.0\mu\text{m}$, B) $0.1\mu\text{m}$ AND C) $0.001\mu\text{m}$. THE SOLID LINE IS FOR THE CASE OF NORMAL INCIDENCE OF LIGHT, THE DASHED LINE FOR 57° FROM NORMAL.

In order to surmount this obstacle, we make a further approximation by approximating the continuously varying surface layer with a set of n homogeneous thin films (19). We use enough layers ($n > 100$) that this has no effect on the computed optical properties. This part of the problem is now reduced to the straight-forward one of adding the multiple reflections from $n + 1$ interfaces, which can be done (with the help of a computer) for arbitrary grades, polarizations, and angles of incident light (19, 20).

We have done reflectance calculations for linear grades between a number of specific material combinations (18, 19) (air and/or glass with gold, Ni, Cr, Ag, Si, SiO_2 , Ti; and Cr_2O_3 with Cr). We find that they have a reflectivity whose wavelength dependence is quite general and, to a large extent, independent of the approximations used. Reflectance curves for air/gold surfaces of different depth are shown in Figure 2. Reflectance curves for different topologies of glass/chrome surfaces are shown in Figure 3. These curves are all basically step functions, with high reflectance, $R_0 > .9$ at long wavelengths, a low reflectance, $R_L \sim .05$, at short wavelengths, and a rather sharp transition at about λ_I . R_0 is approximately equal to the smooth surface reflectivity of the metal of which the grade is made. R_L , on the other hand, may be very low; for grades in which $\epsilon(z)$ goes continuously to (1), at $z = 0$

$R(\lambda)$ may be less than 1% at $\lambda_c/2$ (21) and continue to lessen as the wavelength shortens (Figure 2). In many cases it is necessary to stabilize the graded surface by using a dielectric filler to replace the air. In that case, R_L is limited to about 4% by the reflection from the air/dielectric interface on the front of the grade (Figure 3). λ_I depends almost entirely on the grade depth. It varies from material to material, the transition occurs at relatively shorter wavelengths for more reflecting metals, but a good rule of thumb is that the reflectance is substantially reduced at $\lambda_I \sim 6D$. The shape and breadth of the transition between R_L and R_0 are determined by the topology of the surface as indicated by the form of the mean field approximation used and the details of the grade (22).

FIGURE 3. CALCULATED REFLECTANCE OF A GLASS/CHROME SURFACE. IT CONTAINS A LINEAR VARIATION IN CONCENTRATION OF METAL OVER A DISTANCE OF $0.3\mu\text{m}$. $\epsilon(z)$ WAS CALCULATED FROM BRUGGEMAN'S APPROXIMATION FOR SPHERES (1) AND FROM MAXWELL GARNETT'S APPROXIMATION FOR METAL SPHERES (2), FOR SPHERES OF THE MINOR CONSTITUENT (3), AND FOR ALIGNED METAL CYLINDERS (4).

Diffuse Reflectance

Now we have to go back to consider the fluctuations which we separated out of the first analysis. In order that our initial assumption of independence be valid, we must assume here that the total light scattered from the incident light beam as it propagates through the grade, is much smaller than that lost through absorption (18). For that, the particles' radius, a , must be quite small compared to the light wavelength and one need only consider the lowest order real term from Mie's multipole expansion for a particle's extinction cross section (Rayleigh scattering cross section):

$$Q/\pi a^2 = \text{Re} \left\{ \frac{8x^4}{27} \left| \frac{\epsilon_p - \epsilon_{\text{eff}}}{\epsilon_{\text{eff}} + L_p(\epsilon_p - \epsilon_{\text{eff}})} \right|^2 \right\} \quad (1)$$

where $x = \frac{2\pi a \epsilon_{\text{eff}}^{1/2}}{\lambda}$ and L_p is the depolarization factor (1/3 for spheres).

One can integrate this to obtain the total scattering from the particles in the grade to get (21)

$$\frac{I_{\text{sc}}}{I_0} = \frac{2}{9} \left(\frac{2\pi a}{\lambda} \right)^4 \frac{\ell_0}{a} \int_0^1 \exp \left[- \left(\frac{4\pi \ell_0}{\lambda} \right) \int_0^x \text{Im}\{\epsilon_{\text{eff}}(x')^{1/2}\} dx' \right] \text{Re}\{\epsilon_{\text{eff}}(x)^{1/2}\} \sum_i c_i(x) \left| \frac{\epsilon_i - \epsilon_{\text{eff}}(x)}{\epsilon_{\text{eff}}(x) + L_i(\epsilon_i - \epsilon_{\text{eff}}(x))} \right|^2 dx \quad (2)$$

where both the metal and the dielectric are assumed to be particles of radius a whose dielectric constant and distribution within the grade are given by ϵ_i and $c_i(x)$ respectively. The grade depth is ℓ_0 . The exponential takes account of the absorption of light in passing through the grade on the way to and from the scattering particle. In addition it was assumed that only half of the scattered light is deflected back out of the surface. These last two factors certainly overestimate the light escaping the surface, and have only their simplicity to recommend them. Note that the scattering strength of these particles varies as a^3/λ^4 (23) so that light scattering from the particles should have a very rapid onset on going to shorter wavelengths.

The scattered light will spoil the low specular reflectivity of the graded film and define a short wavelength edge to the low reflectivity region described earlier. We place this edge, somewhat arbitrarily, at

the wavelength λ_{II} at which the light scattered out of the grade is 1/4 of the very short wavelength reflectivity of the inhomogeneous surface (24). Table I shows the calculated scattering strengths for spherical metal particles whose density varies linearly in a grade 0.25 μ m deep. $\epsilon_{eff}(z)$ was calculated from Bruggeman's symmetric mean field approximation (25). The radius of the particles was picked so that λ_{II} occurs at about 0.25 μ m. You can see that the scattering strength depends on the material, but in the spirit of this analysis, it is reasonable to put λ_{II} at about 20a for metals.

FIGURE 4. UNIVERSAL CURVE FOR THE REFLECTANCE OF INHOMOGENEOUS SURFACES.

Total Reflectance

Putting together the specular and diffuse reflections from our graded surfaces, we find a universal curve (Figure 4) which potentially exhibits three distinct reflectivity regimes. In region I, the reflectivity is specular and approaches the smooth surface reflectivity, R_0 , of the metal making up the grade. The short wavelength boundary to this regime is determined by the depth of the grade. A good rule of thumb is that $\lambda_I \sim 6D$. In region II, the reflectivity is diffuse and equals R_0^n where n depends on the topology but is often between 2 and 3. The long wavelength edge to this region is determined by the inhomogeneity size. We put λ_{II} at 20a. If $\lambda_I \sim \lambda_{II}$, there can exist a third, very low reflectivity region. The residual reflectivity here is mainly induced by the experimental inability to have $\epsilon_{eff}(z)$ go continuously to the dielectric constant of air at the surface.

TABLE 1. DIFFUSE REFLECTANCE R_D OF A GLASS ($n = 1.5$)/METAL SURFACE CALCULATED USING EQUATION 2. THE METAL DENSITY VARIES LINEARLY WITH DEPTH IN A GRADE 0.25 μm DEEP. $\epsilon_{\text{eff}}(z)$ IN THE GRADE WAS CALCULATED USING BRUGGEMAN'S APPROXIMATION. THE PARTICLE RADIUS, a , WAS PICKED SO THAT $R_D = 1/4 R_0^2$ AS $\lambda = .25\mu\text{m}$.

WAVELENGTH (μm)	DIFFUSE REFLECTANCE		
	GOLD $a = .016\mu\text{m}$	NICKEL $a = 0.11\mu\text{m}$	CHROME $a = .012\mu\text{m}$
.25	.042	.074	.044
.35	.018	.017	.036
.45	.008	.004	.018
.55	.009	.008	.013

In order for the solar spectrum to be contained in this low reflectivity region, one requires $\lambda_I \sim 2\mu\text{m}$ and $\lambda_{II} \sim .3\mu\text{m}$. These requirements imply a grade depth $D \sim .3\mu\text{m}$ and a particle radius $a \sim 0.015\mu\text{m}$. It is perhaps not surprising that this prescription fits the current ideal selective absorber black chrome fairly well. One empirically optimized recipe results in a film about 0.7 μm thick containing Cr particles whose mean diameter is 139 Å (5). Neither the distribution of particles nor their size are directly under the experimenter's control: the particle size distribution for instance is a very broadly peaked function, and the distribution of Cr within the grade is highly nonlinear (26). In addition, its properties depend on the existence of an absorbing oxide film between the metal substrate and the particles for its properties. Because of these limitations, the current experimental values for D and a are probably as close as one can get to the optimum using this particular technique. The optical properties of these films, however, are quite good (Figure 5), and the incentive for continuing work on them is to change their structure in such a way as to improve their stability.

There are, for instance, other possible geometries. If one were to make an ideal selective surface with a rough topology, that is the pores (or peaks) would have to be much deeper than their diameter ($D \sim 20a$). This geometry is very similar to that produced in dendritic tungsten except that the scale of the dendritic surface is too large by an order of magnitude ($D = 25\text{--}80\mu\text{m}$ and $a = 1\text{--}5\mu\text{m}$ (6, 27)). There are many other techniques for producing roughened surfaces, but very few combine the fine scale and deep relief required to make them selective.

FIGURE 5. REFLECTANCE OF GLASS/CHROME SURFACE $0.3\mu\text{m}$ DEEP: A. COMPUTER CALCULATION OF A LINEAR METAL DENSITY GRADE USING BRUGGEMAN'S APPROXIMATION FOR SPHERES. B. EXPERIMENTAL MEASUREMENT OF DUPONT BLACK CHROME (26).

A technique which potentially does meet these requirements is particle track etching (27). During the study of damage tracks ($50\text{\AA}$ diameter) left by high energy particles, Fleischer *et al* discovered that the tracks were chemically very active and could be etched out as conical holes whose depth, D , was very large compared to their base diameter (49).

Inorganic glasses typically have a $D/4a < 7$ and so are not suitable for making a selective absorber. The holes in polymer glasses, however, may have $D/4a > 30$. A high density of such holes, overlapping on a surface would produce the required topology, which could then be metallized by a number of means to form a selective absorber.

We have demonstrated this concept in vitreous silica by bombarding the surface of a 1" square slide with $63\text{ MeV } ^{63}\text{Cu}^{8+}$ ions to a density of about $10^{12}/\text{cm}^2$ (28), and etching for a few minutes in a 2.5 wt% ammonium hexafluoride solution. The conical hole resulting from each track is then about $1500\text{\AA}$ deep and has a base diameter of $1200\text{\AA}$ (a cylinder radius (half width at half maximum) of $300\text{\AA}$). En mass, these tracks create a roughly linear grade for which $\lambda_I \sim .9\mu\text{m}$ and $\lambda_{II} \sim .6\mu\text{m}$ and which reduces the air/glass reflectivity by a factor of two in the visible spectrum (Figure 6).

Moreover, this surface has a very low reflectivity even when metallized. Curve B in Figure 7 shows the reflectance of a vitreous silica slide whose rear surface has been particle track etched as described above, and then metallized by the vacuum evaporation of tellurium. Since the air/silica interface, contributes .04 to curve B, one can see that the silica/Te interface must reflect only a few percent of the incident light throughout the visible (compared to 45% for a smooth interface - curve A). One can see also that this interface is potentially selective; its reflectance steadily increases with increasing wavelength, but this trend is negated at about $3\mu\text{m}$ by the onset of the SiO_2 absorption bands. In practice, then this slide is not selective; its black body emissivity at 100°C is nearly 1 because of the thick layer of glass on top of the graded interface. That is not a major barrier, however. It should be straightforward to put a similar grade on a 1 mil film of a plastic like polyethylene which is nearly transparent throughout the infrared. An assembly like that could have a solar absorptivity greater than .9 and a thermal emissivity (100°C) less than .2.

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FIGURE 6. SURFACE TRANSMISSION LOSSES FOR AN AIR/SILICA INTERFACE.

FIGURE 7. REFLECTANCE OF TELLURIUM COATED SILICA SLIDE: A) SMOOTH INTERFACE, B) ROUGH INTERFACE.

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NOTES

HIGH TEMPERATURE SOLAR ABSORBER PAINTS

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Summary of Presentation

A program to develop high temperature solar absorber coatings for central receiver applications was initiated under DOE Contract EG-77-C-02-4270A000 and continued under SERI subcontract XJ-9-8009-1.

For central receivers of the external cylinder design operating at high temperatures (1000°F) and high solar concentration ratios (1000X and above) maximizing the solar absorptance α of the solar absorber coating is more beneficial from a standpoint of net energy gain than minimizing the radiant energy loss by minimizing the IR emissivity. In terms of net energy gain, a 2% increase in α from 0.95 to 0.97 is equivalent to a reduction in ϵ from 0.90 to 0.24 when operating at 1000°F and a concentration ratio of 1000X. The objective of this program is therefore to develop high temperature solar absorber coatings exhibiting maximum solar absorptance ($\alpha \geq 0.95$) with long term, high temperature optical and mechanical stability. No specific goal has been set with respect to the emittance level of the coating. Projected coating costs, ease of application and repair, as well as environmental considerations are additional criteria in selecting the optimum coating.

Coatings developed in this program are based on paint formulations, i.e. dispersions of selected high α , metal oxide pigments in selected paint vehicles. A series of pigments have been identified which are thermally stable at 700°C and yield a solar absorptance of 0.95 to 0.97 when formulated in silicate and silicone matrices. Ferro Corporation's F-6331 pigment, a mixed oxide of (Fe-Mn-Cu) has been identified as the preferred pigment. Coatings have been formulated with (1) ortho-ethyl silicates, (2) silicones and (3) water-base alkali silicates. All paint formulations cure to totally inorganic coatings. Cure of the ortho-ethyl silicate binder takes place at ambient temperature but requires humidities in excess of 50%. The silicone based coatings require cure temperatures in excess of 300°C to decompose the silicone to $(\text{SiO}_2)_x$. Paint formulations based on alkali silicates are fast, self-curing, totally inorganic as formulated and require neither high temperature cure nor humidity to affect cure. Coatings formulated with ortho-ethyl silicates and silicones are stable at 700°C in air for at least 500 hours. Alkali silicate based paints have not been tested yet for long term thermal stability.

SOLAR ABSORBER COATINGS FOR CENTRAL RECEIVERS
OF THE EXTERNAL CYLINDER DESIGN

IMPORTANCE OF MAXIMIZING α
RATHER THAN MINIMIZING ϵ .

RECEIVER OPERATING TEMPERATURE: 1000°F

CONCENTRATION RATIO: 1000:1

	<u>α</u>	<u>ϵ</u>	<u>EQUIVALENT TO</u>
COATING BASE CASE	0.95	0.90	=
IMPROVED COATING I 1% INCREASE IN α	0.96	0.90	$\alpha = 0.95$ $\epsilon = 0.57$
IMPROVED COATING II 2% INCREASE IN α	0.97	0.90	$\alpha = 0.95$ $\epsilon = 0.24$

THERMALLY STABLE, HIGH α PIGMENTS

ACCEPTANCE CRITERIA

- $\alpha \geq 0.95$
- NO CHANGE IN α AFTER HEATING IN AIR AT 500°C FOR 24 HOURS

STABLE, HIGH α PIGMENTS

- (Fe - Mn - Cu)Ox; FERRO'S 6331
 - 12.6% FeO
 - 56.4% MnO
 - 31% CuO
- Co_3O_4
- CoO
- (Cu-Cr)Ox; METEOR 789o
- Mn_3O_4
- Mn_2O_3

BINDERS (VEHICLES) FOR HIGH TEMPERATURE SOLAR ABSORBER PAINTS

ORTHO-ETHYL SILICATES

SILICONES

R = ALKYL GROUPS

WATER-BASE ALKALI OXIDE SILICATES

COMMON FEATURES AND SIGNIFICANT DIFFERENCES BETWEEN BINDER TYPES

COMMON FEATURES

- ALL CURE TO TOTALLY INORGANIC COATINGS

DIFFERENCES

SOLVENT TYPE

- ORTHO-ETHYL SILICATES AND SILICONES REQUIRE ORGANIC SOLVENTS
(ALCOHOLS, ETHERS, ESTERS, AROMATICS)
- ALKALI OXIDE SILICATES ARE AQUEOUS SOLUTIONS
 - TOTALLY INORGANIC AS FORMULATED

CURE MECHANISM

- ORTHO-ETHYL SILICATES
SOLVENT EVAPORATION AND HYDROLYSIS BY INTERACTION WITH
MOIST AIR - ROOM TEMPERATURE CURE
- SILICONES
SOLVENT EVAPORATION FOLLOWED BY HIGH TEMPERATURE (1000°F)
VITRIFICATION (DECOMPOSITION)
- ALKALI OXIDE SILICATES
FAST, SELF-CURING BY EVAPORATION OF WATER; REQUIRE
NEITHER HIGH TEMPERATURE CURE NOR HUMIDITY TO AFFECT
CURE

Figure 1: Microphotograph of (Fe-Mn-Cu)Ox Coating in Lithium/Sodium Silicate at Low PV Ratio of 0.75. Extensive Mud Cracking; 110 X.

Figure 2: Microphotograph of (Fe-Mn-Cu)Ox Coating in Lithium/Sodium Silicate at High PV Ratio of 3.15. No Evidence of Mud Cracking; 110 X.

Figure 3: Microphotograph of (Fe-Mn-Cu)O_x Coating in Lithium/Sodium Silicate Showing Surface Clusters of Pigment/Silicate; 110 X; $\alpha = 0.98 - 0.99$.

Figure 4 : Spectral Hemispherical Reflectance Measurements of (Fe-Mn-Cu)Ox Coating in Lithium/Sodium Silicate; No Surface Clusters

Figure 5 : Spectral Hemispherical Reflectance Measurements of (Fe-Mn-Cu)Ox Coating in Lithium/Sodium Silicate with Surface Clusters

Figure 6 : Spectral Hemispherical Reflectance of Meteor 7890, (Cu-Cr)Ox in Silicone

Figure 7 : Spectral Hemispherical Reflectance of Meteor 7890, (Cu-Cr)Ox in Ortho-Ethyl Silicate

Figure 8 : Spectral Hemispherical Reflectance Measurements of CoO and Mn_3O_4 Pigmented Silicones after Vitrification

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INSTRUMENTATION FOR THE EVALUATION OF SELECTIVE SURFACES AT THE UNIVERSITY OF ARIZONA

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ABSTRACT

The Measurement Laboratory at the Optical Sciences Center remains deeply involved in the evaluation of selective surfaces for photo-thermal energy converters. Recently, we have significantly improved two of our instruments, the Integrating Sphere Reflectometer (ISR) and the High Temperature Spectrophotometer (HTS) and are adding a Bennett Absolute Reflectometer (BAR).

- 1) The ISR provides critical reflectance data on non-specular selective surfaces. It operates in the indirect (hemispherical-directional) mode. The radiation passes through a monochromator and arrives at a two-color detector with a range of 0.40 to 2.70 microns. Data acquisition is based on a background-corrected sample-and-hold system.
- 2) When operational, the HTS will supply information on temperature dependent properties of thin films. The HTS has been limited to reflectance measurements by a simple two-beam comparison to a beam reflected from a room temperature reference. We have added a transmittance cell, built onto the high vacuum cavity containing the reflectance optics. A data acquisition system similar to that of the ISR is being implemented.
- 3) A double-reflection Bennett absolute reflectometer is being made operational, as well.

INTRODUCTION

The Measurement Laboratory at the University of Arizona's Optical Sciences Center remains deeply involved in the evaluation of selective surfaces for photothermal energy converters. Recently, we have sig-

nificantly improved two of our instruments, the Integrating Sphere Reflectometer (ISR) and the High Temperature Spectrophotometer (HTS), and added a Bennett Absolute Reflectometer (BAR).

INTEGRATING SPHERE REFLECTOMETER

The ISR provides critical reflectance data on non-specular selective surfaces. Scattering from rough surfaces can cause spectrophotometers measuring reflectance at near-normal incidence to err by neglecting the diffuse component of the reflectance. A hemispherical measurement not only takes scattering into account, but allows the non-specular component to be estimated by comparison with the specular component. Our ISR operates in the indirect, or hemispherical-directional mode. As shown in Figure 1, a tungsten-halogen source is mounted at a side port of the integrating sphere; the sample is placed in the center of the sphere and is illuminated hemispherically. The sample is baffled to prevent its direct illumination by the source. The sphere is coated with Eastman White Reflectance Coating, a material which maintains a diffuse reflectance of above 70% up to around $3\text{ }\mu\text{m}$. In order to observe the directional reflection at various angles, the sampleholder is supported by a shaft which can be rotated by a knob outside of a second sphere port. The radiation reflected from the sample at the chosen angle emerges from the sphere through a third sphere port and encounters a relay mirror and a collimating mirror before entering the dual beam monochromator as the sample beam. A reference arc on the sphere wall is reflected onto a second collimating mirror by a cylindrical mirror mounted in the exit port; the collimating mirror then directs the reference beam into the other arm of the monochromator.

The monochromator, part of a heavily modified Perkin-Elmer 21 Spectrophotometer, is shown in Figure 2. The beam-combining optics employ a three-phase chopper: One 120° sector is cut-away and passes the reference beam, a second 120° sector is reflective and directs the sample beam into the same path, and a third 120° sector is coated with Nextel black paint and serves as an indicator of the background level. Figure 3 schematically presents this chopping arrangement. After the beams are combined, a Littrow-mounted prism disperses the radiation. The entrance and exit slits are mechanically linked and are servo-controlled by the electronics to keep the reference beam constant. The radiation is then focussed on the detector, a two-color device consisting of a UV-enhanced silicon photovoltaic detector and a lead sulfide detector. The former absorbs and detects radiation from 0.4 to about $1.0\text{ }\mu\text{m}$ and transmits longer wavelengths, which are detected by the underlying lead sulfide. The detector, made by Infrared Industries, covers 96% of the Air Mass 2, $\alpha=1.3$, $\beta=0.04$ insolation computed by Thomas and Richmond[1].

Figure 4 reproduces the optical components and shows in flow chart form the overall sample-and-hold scheme for measuring signal levels. The actual electronics in the dashed rectangle are shown in Figure 5. The monochromator is stepped to a specific wavelength, and synchronizing pulses from LED-phototransistor pairs at the chopper trigger a gate which sequentially selects one of three lines for each of the three phases. The signal is integrated by an RC network utilizing the sample-

FIGURE 1. INTEGRATING SPHERE AND RELAY OPTICS OF ISR.

FIGURE 2. MONOCHROMATOR OPTICS OF ISR. DASHED CIRCLE IS PROJECTION OF INTEGRATING SPHERE.

FIGURE 3. THREE-PHASE CHOPPER AND PHASE-SYNCHRONIZATION SYSTEM IN THE ISR.

FIGURE 4. GENERAL FLOW CHART OF ISR COMPONENTS.

FIGURE 5. SCHEMATIC OF ISR SAMPLE-AND-HOLD ELECTRONICS.

FIGURE 6. EXAMPLE OF STRIP CHART RECORD FOR INTEGRATING SPHERE REFLECTOMETER. THE CALIBRATION AND SAMPLE RUNS ARE INDICATED ON THE FIGURE. WAVELENGTH RANGE FOR EACH RUN IS 0.4 TO 2.7 μm .

and-hold capacitor, and the resulting analog level is transferred by a second gate to a dual-slope A/D converter. The BCD output moves to a Southwest Technical Products 6800 microcomputer and to a front panel LED display. After data at this wavelength are analysed, the monochromator is stepped to the next wavelength, and the process is repeated until the entire spectrum is scanned.

Data analysis proceeds in the following fashion. Before the sample series is run, black glass and evaporated aluminum standards are measured and the results are stored in the computer's memory. It should be noted that all measurements are made with respect to the reference arc on the sphere wall, the reflectance of which is carried by the reference beam of the ISR. Background is removed by first removing the stray radiation due to the monochromator, indicated by the blackened chopper sector, from the aluminum's reflectance factor. Then, by comparing the known and measured reflectances of the black glass standard, the remaining background is calculated and subtracted. At this point, a background-corrected aluminum reflectance factor has been compiled. The sample is then run, and both the background indicated by the blackened chopper sector and the residual background revealed by the black glass standard are subtracted, leaving a background-corrected sample reflectance factor.

This procedure provides corrected reflectance factors for both the sample and for the aluminum standard; the former is divided by the latter, causing the sphere wall's reflectance to cancel. The last step is the multiplication of this ratio by the absolute reflectance of aluminum, which is presently presumed to be equal to the published data on the absolute reflectance of laboratory aged aluminum films. This dependence on external data sources will end shortly when a double reflection Bennett absolute reflectometer, described below, is made operational in the summer of 1979. The spectral reflectances are sampled at 240 points; reflectances at wavelengths corresponding to the selected ordinates of Thomas and Richmond [1] are summed and divided by the total number of ordinates to yield the solar absorptance "a". Figure 6 shows a strip chart output for a series of molybdenum films made in our chemical vapor deposition laboratory. It is followed by a trace of the aluminum standard, which tests the system's accuracy. If the true absolute reflectance of aluminum is reproduced, we can be reasonably sure that the optical and computer components are acting properly.

HIGH TEMPERATURE SPECTROPHOTOMETER

Our second major project has been the three-part improvement of the High Temperature Spectrophotometer (HTS):

- 1) A cell for measuring high temperature transmittance has been installed.
- 2) The source and vacuum chamber optics have been improved.
- 3) A microcomputer controlled sample-and-hold data acquisition system very similar to that of the ISR has been added.

Figure 7 shows the overall layout of the HTS. A source, either a tungsten-halogen lamp for the visible or a Globar for the infrared, is

FIGURE 7. OPTICAL LAYOUT OF HIGH TEMPERATURE SPECTROPHOTOMETER -- ONLY ONE OF THE TWO BILATERALLY SYMMETRICAL LIGHT PATHS IS SHOWN FOR CLARITY. MIRRORS MARKED "A" ARE SPHERICAL, THOSE MARKED "B" ARE FLAT.

FIGURE 8. CHOPPER AND PHASE SYNCHRONIZATION OF HTS.

imaged at two points in the plane of the transmittance cell by symmetrical sequences of relay mirrors. A chopper near this focal plane switches the beams, provides timing signals to the electronics, and reveals the background level when both beams are blocked by the opaque blackened sector. The source is imaged again at the heated and ambient reflectance cells on opposite sides of the vacuum cavity. After the beams are recombined, as shown in the figure, the resulting beam leaves the cavity and enters a Leiss NaCl monochromator. The dispersed radiation, with a range of 0.38 to 15 μm , falls on either a silicon PIN detector for wavelengths up to about 1 μm or a Golay cell for the longer infrared wavelengths.

The instrument will be operated in two modes. In the reflectance configuration, the transmittance cell will be empty, and a heated reflecting sample is compared to a room temperature reference in the opposite beam. In the transmittance mode, the reflectance cells will be unheated and will contain aluminum relay mirrors, while the transmittance cell will contain nominally identical, heated substrates in each beam, with one of the substrates coated with the film to be measured.

The data acquisition system is essentially identical to that of the ISR, with the same microcomputer and peripherals. (See Figures 8, 9, and 10) Among the differences are a slightly different chopper and the lack of a controllable slit. We may implement the latter in the near future. Temperature limits for both cells are about 800 C; chromel/alumel and platinum/platinum-10% rhodium thermocouples will be attached to, or directly adjacent to sample substrates. The HTS should become operational with its new capabilities by March 1979.

The microcomputers for the ISR and HTS can be linked to the Optical Science Center's Data General Eclipse Minicomputer, as charted in Figure 11. This interconnected system will be expanded to accommodate additional instruments as they are automated. We have already benefited from much faster analysis of ISR data and look forward to similar improvements on the HTS.

BENNETT ABSOLUTE REFLECTOMETER

The Bennett Absolute Reflectometer (BAR) mentioned above is depicted schematically in Figure 12.[2]. A tungsten-halogen lamp and a Globar will serve as sources for the appropriate spectral regions. A Perkin-Elmer 99 monochromator with interchangeable prism assemblies follows. The dispersed radiation emerges and is injected into a somewhat complex optical system made up of identical, symmetrical banks of three spherical mirrors on either side of a rotating sampleholder. Four separate measurements are necessary to determine the absolute reflectance of a sample. With the sampleholder facing one bank of mirrors, one measurement is performed with the sample in place; the facing bank of mirrors generates two reflections of the monochromatic beam from the sample and then directs the beam to the exit mirrors and the detector. The second measurement is made with the sample removed, so that the beam is returned by a mirror in the opposite bank and is then directed along the same path to the detector. Thus, a ratio between the incident beam

FIGURE 9. GENERAL FLOW CHART OF HTS COMPONENTS.

FIGURE 10. DETAILED FLOW CHART OF COMPONENTS IN DASHED BOX OF FIGURE 9.

FIGURE 11. FLOW CHART OF COMPUTER SYSTEM CURRENTLY AVAILABLE TO THE MEASUREMENT LABORATORY.

FIGURE 12. OPTICAL LAYOUT OF BENNETT ABSOLUTE REFLECTOMETER SHOWING BASIS FOR ABSOLUTE REFLECTANCE MEASUREMENTS.

intensity, I_0 , multiplied by a series of relay mirrors and I_0 multiplied by other relay mirrors and the sample reflectance squared is set up. The third and fourth measurements are done with the sampleholder rotated 180 degrees, thereby setting up a second, similar ratio. When the two ratios are multiplied, all of the relay mirror reflectances and I_0 cancel out, leaving the sample reflectance to the fourth power. Taking the fourth root provides the absolute reflectance.

In order to push this instrument into the middle infrared, three measures may be taken.

- 1) A cesium iodide prism would carry the monochromator out to beyond 50 μm .
- 2) A large plexiglass enclosure is being assembled so that purging by dry gases can be carried out, since atmospheric absorption would be serious.
- 3) A far-infrared detector, possibly a bolometer, must be acquired. When operational, this instrument will serve to calibrate our standards for our dual-beam instruments and to measure some of our very reflective films to be incorporated into tandem solar stacks.

ACKNOWLEDGEMENTS

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"Chemical Vapor Deposition of Refractory Metal Reflectors for Spectrally Selective Solar Absorbers", Department of Energy, Advanced Technology Branch, #EY-76-S-04-3709.

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NOTES

COMPOSITION PROFILING OF SOLAR COATING MATERIALS

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Abstract

About 60% of our efforts were devoted to Auger analysis service for other DOE solar grantees. They will discuss the results in their own reports.

With help from Honeywell, we measured the optical properties of various surfaces such as cone-covered Cu surfaces, chromic oxide coatings prepared by plasma spraying [$\alpha = 90\%$]. Sputter deposited Mo films prepared under such low background pressure that their Auger analysis shows only negligible amounts of C and O gave excellent IR reflectivity values [between 2.5 and 40 μm wavelength $\sim 96\%$].

In longer duration vacuum heat treatments of Mo films on oxidized SS, difficulties arose with C entering into the Mo from the vacuum side due to C containing background gases. Sputter coating of the Mo-Cr₂O₃-SS samples with Al₂O₃ eliminates this problem and longer lifetime tests in good and poor vacuua of this coating stack are now in progress.

ANALYSIS SERVICE

Auger Analysis service to outside DOE grantees was rather substantial. Our customers were primarily the University of Arizona [Prof. Seraphin's Group] and to a minor degree Honeywell, Inc. and Dr. Czanderna, SERI. Altogether this service amounted to about 60% of our efforts. We analyzed more than 150 samples [about 450 Auger spectra and 150 composition vs. depth profiles]. Presently our backlog has piled up to 36 samples from the University of Arizona, Honeywell and some mirror samples from Suntek [Robert Cornia] are expected.

Details about results will, as in the past, be reported by those who made use of this service.

Some of the film stacks from the University of Arizona had a fairly thick Si coating on top. With our sputtering rate in the Auger system limited to 100 $\text{\AA}/\text{min}$, the depth profiling became very time consuming. This problem was solved with a new "sputter angle lapping" technique. For this the samples were presputtered, before transfer into the Auger

system, in a Hg plasma [ion current densities of several mA/cm²]. Near the edge of the samples where the ion sheath curves around the [negative] target, the bombarding ions become focused and cause much more intense sputtering than in the flat areas of the sample. With the resulting depth gradient, one can spread out the layered stack laterally and switch to line or point analysis without the need for sputter profiling and can collect useful composition data as a function of depth.

For Honeywell we analyzed some black Ni and black Cr films, and for Czanderna [SERI] we studied the differences between corroded and uncorroded areas of Ag mirror samples. These latter samples came covered with a protective polymer coating which needed to be removed in order to collect valid depth profiles. By rubbing the samples with a champagne cork (which has high friction but no abrasive properties) soaked in methanol the polymer coating can be readily removed without damage to the underlying films.

OWN STUDIES

Optical Properties of Sputter Deposited Mo

The major part of the work for Arizona concerned the quantitative analysis of CVD deposited Mo films with respect to their C and O content. This, in turn, stimulated some efforts of our own: We wanted to compare the composition and the optical properties of our sputter deposited Mo films with those deposited by CVD in Arizona. Arizona supplied us with four quartz blanks onto which we sputter deposited Mo under as clean vacuum conditions as we could possibly achieve. Three of those coated samples were sent back to Arizona for their optical evaluation. On the other sample we first checked with Auger the C and O content and found both to be barely detectable as shown in Figure 1. We then forwarded this sample to Bill Durand (a graduate student in our group who works at Honeywell). The average reflectivity amounted to at least 96% in the range between 2.5 and 40 μ m wavelength as shown in Figure 2. This result certainly disproves the validity of such graphs [as recently shown at the AVS meeting in San Francisco] in which sputter deposited Mo films, when compared to various other film deposition methods, gave the poorest measured IR reflectivity. Beyond doubt, the secret is that the films need to be deposited at a high rate in a clean noble gas plasma. We anticipate that the films could be even further improved with negative biasing of the substrate during the sputter deposition which preferentially resputters oxygen from the film.

Fig. 1. Auger spectrum of sputter deposited Mo on quartz.

Fig. 2. Reflectance of sputter deposited Mo on quartz in the wavelength range 2.5μ to 40μ as measured with Beckman IR-4240 at Honeywell.

Optical Properties of Various Other Surfaces

In order to get an idea of what typical values of α and ϵ are achievable, we investigated these optical properties of various absorbing surfaces with the help of Bill Durand at Honeywell. For instance, the edge-on surface of stacked razor blades gave $\alpha = 98\%$, $\epsilon = 53\%$.

Three samples, which METCO had prepared for us by plasma spraying with chromic oxide powder, showed for coatings of various thickness the following values: 25 μ : $\alpha = 90\%$, $\epsilon = 85\%$; 50 μ : $\alpha = 89\%$, $\epsilon = 82\%$; 100 μ : $\alpha = 90\%$, $\epsilon = 82\%$.

Cu samples on which we had created densely-spaced cones produced by Mo seeding during sputtering gave an average of $\alpha = 95\%$ and $\epsilon = 52\%$.

We found that the possibly simplest and most economical way of producing a high absorber coating [not very selective] consists of heating SS304 for 45 minutes at 900°C in air. Such samples showed $\alpha = 91\%$ and $\epsilon = 80\%$. It is interesting that subsequent heating of this coating in vacuum improved the selectivity such as: 4 hrs. heating at 725°C in vacuum gave $\alpha = 90\%$, $\epsilon = 64\%$.

Black Cobalt

A remarkable selective solar absorber coating is described in a German patent application "Offenlegungsschrift 2526716" of 6/30/77. The high selectivity is achieved by choosing a material which has such a high absorption in the solar spectrum and that one can make this coating so thin (1000 Å) that the reflectivity of the metal underneath remains the dominating factor in the IR. The values given for this coating on a Cu substrate covered with an electrolytically-deposited 1000 Å cobalt sulphide layer are $\alpha=97\%$, and $\epsilon(90^\circ\text{C})=6\%$. The same coating on a Ag covered glass substrate gave values of $\alpha = 96\%$, and $\epsilon = 4\%$. With the detailed recipes given in the patent, we should have no difficulty in depositing this coating on our high IR reflectivity sputter deposited Mo and to subsequently study with Auger and optical measurements the lifetime versus operating temperature limits.

The Chromium Oxide Diffusion Barrier

We had shown that a short (about 15 minutes) heat treatment of stainless steel at about 900°C produces a dense chromium oxide coating [1] which is an excellent diffusion barrier. We proposed to continue to study the effectiveness of this

barrier as a function of temperature and in particular for longer times. At a temperature of 725°C in a 10^{-5} torr vacuum, the chromium oxide diffusion barrier holds up to 165 hours as well as it did after 1 hour. Figure 3 and 4 show the corresponding Auger depth profiles of air oxidized stainless steel 304 samples over which Mo was deposited by Argon triode sputtering. There is no evidence of diffusion of any of the stainless steel components through the chromium oxide coating. However, all the stainless constituents diffused through the barrier when an air oxidized sample was heated to 825°C for 100 hours as shown in Figure 5. A serious problem arose during longer term heating: We noticed that carbon from the vacuum environment combined with Mo to form molybdenum carbide at the Mo surface as shown in Figure 6. A piece of clean Mo was vacuum heated along with the air oxidized samples. A molybdenum carbide coating of comparable thickness was formed, confirming our suspicion that carbon containing gases in the vacuum system are the source of this carbon.

The next step was to cover the Mo with Alumina or silica so that carbon diffusion from outside can be eliminated. Al_2O_3 was deposited on Mo/ Cr_2O_3 /stainless 304 in a mercury plasma system by RF sputtering as shown in Figure 7. Vacuum heating of these samples is in progress in order to extend the life time studies of this coating stack to much longer times. We are aware that we are somewhat behind in our long term heating studies, mostly caused by the heavy demand in our service to other DOE grantees and the difficulties with C from the vacuum system. We hope, however, that in the remaining 3 months of this grant (in particular with the Al_2O_3 protective layer) we will be able to come up with much more accurate predictions about the service life for much longer time periods.

We have recently achieved a breakthrough in understanding the phenomenon of cone formation of sputter metal targets during seeding with foreign atoms. It was demonstrated that whisker growth plays an essential role in this process. It will be of much interest to investigate the optical properties of whisker covered metal surfaces.

We have succeeded in producing densely-spaced steep cones on a Si wafer substrate by seeding the wafer during sputtering with minute amounts of Mo. The multiple reflections of the visible light back and forth between the cones could possibly make an anti-reflection coating on Si unnecessary. Has any reader of this paper an application idea for such Si cones? Possibly in photovoltaic devices.

Fig. 3. Composition-depth profile for a sample of Mo/Cr₂O₃/SS304 after a vacuum ($\sim 10^{-5}$ torr) heat treatment of 1 hour at 725°C.

Fig. 4. Same as in Fig. 3; 165 hours at 725°C.

Fig. 5. Same as in Fig. 3; 100 hours at 825°C.

Fig. 6. Same as in Fig. 3; 260 hours at 700°C.

Fig. 7. Composition-depth profile for a sample of Al₂O₃/Mo/Cr₂O₃/SS304.

Acknowledgements

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DIRECTIONAL ABSORPTANCE SPECTROCALORIMETRIC
MEASUREMENT AND SPECTRAL PROFILE PARAMETRIZATION
OF SOLAR ABSORBERS AT ELEVATED TEMPERATURES[†]

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ABSTRACT

A testing program is developed to optically and thermally characterize spectrally selective solar absorbing layers of different types under experimentally simulated operating conditions at high temperatures. Parametrized spectral profile modeling with the Fermi model, the solar reflectance-infrared emittance method and with direct spectrocaltoric measurements are considered. The application of a new type of directional absorptance spectrocaltorimeter presently under test is described.

I. INTRODUCTION. The emphasis in the present testing program is to optically and thermally characterize spectrally selective (SS) solar absorbing layers of different types under experimentally simulated operating conditions at elevated temperatures (T_x). In most SS layers, the absorptance spectral profile, of prime importance in governing the solar-thermal conversion efficiency, shifts with T_x , incident flux direction, thermal cycling and environmental exposure. Problems exist both in producing layers having the required thermochemical stability with thermal cycling and in making reliable optical properly measurements at high temperatures (HT). Parametric analyses of the effect of the spectral profile on the solar-thermal conversion efficiency of SS layers at different levels of hierarchy are studied; including the Fermi spectral profile model for spectral adsorptance (or reflectance), the solar reflectance-infrared emittance method and directional absorptance and emittance by spectrocaltorimetry. The present uncertainty in HT optical data in certain cases emphasizes the need for controlled HT measurements at T_x , where both the spectral absorptance and hemispherical emittance are measured in situ. Direct calorimetric measurements are possible with a new type of vacuum spectrocaltorimeter, which has been designed and is presently under test. This calorimeter is described and the extent of its measurement capability when operational is evaluated.

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II. PARAMETRIZED SPECTRAL PROFILE MODELING. In an analysis of the behavior of the spectral profile with wavelength and temperature, the five-parameter Fermi model was developed[1] and fitted to the $\alpha_\lambda (T_x)$ data, as converted from the spectral reflectance ($\alpha_\lambda = 1 - \rho_\lambda$) measured at T_x . This model is shown in Fig. 1,

Fig. 1. Fermi model spectral profile.

and given by,

$$\alpha_\lambda = B + \left\{ \frac{(A-B)}{\left[\exp \left(\frac{\lambda' - \lambda_0}{TK} \right) + 1 \right]} \right\} , \quad (1)$$

where the five parameters include A the short-wavelength absorptance limit approaching 0.3 μm , B the long-wavelength absorptance limit approaching 40 μm , λ_0 the half-height absorption shoulder wavelength at $(A+B)/2$, TK the shoulder broadening factor and S the skew factor. The wavelength λ can be skewed to λ' about λ_0 with the power-law skewing function,

$$\lambda' = \lambda_0 - \frac{\lambda_0}{S} \left[1 - (\lambda/\lambda_0)^S \right] , \quad (2)$$

including restrictions that at λ_0 , $\lambda' = \lambda = \lambda_0$ and $d\lambda'/d\lambda = 1$. The sense of the skewing is determined such that for elongation in the wavelength region beyond λ_0 , $S > 1$ and for contraction beyond λ_0 , $1 > S > 0$.

Representative spectral profiles of different types of 33 absorbers are shown in Figure 2. These include intrinsic semiconductor absorbers, such as hydrogenated amorphous silicon (A-Si) as deposited by sputtering (SP) and by CVD on polished Nb substrates and a crystalline silicon stack (C-Si) deposited on Ag by CVD[2]; interference multilayers, such as $\text{MgF}_2\text{-M}_0\text{-CeO}_2$ evaporated on M_0 (MMC)[3] and $\text{Al}_2\text{O}_3\text{-Mo-Al}_2\text{O}_3$ evaporated on M_0 (AMA)[4]; and the mixed-type absorbers, black chrome electroplated on bright Ni from Sandia (BCr)[5] and black nickel from Honeywell (BNi).[5] The A-Si, C-Si, BCr and BNi coatings

Fig. 2. Spectral absorptance profiles of spectrally selective solar absorbing layers with Fermi model fits. Interference fringes are smoothed for A-Si and C-Si. References to selective layer measurements are given in the text.

were measured by normal specular reflectance and the MMC and AMA coatings by directional-hemispherical reflectance. The fits obtained with the Fermi model are also shown in the figure. In the fitting process, the parameter A was adjusted with a weighted fit about the solar envelope peak wavelength λ_s (0.57 μm for AM2). B was adjusted to fit in the infrared emission peak range for typical absorber operating temperatures. A comparison of the CVD deposited amorphous silicon A-Si and crystalline silicon C-Si coatings shows a shift of λ_o from 0.93 μm to 1.30 μm . Also, a potentially higher solar absorptance α_s for the amorphous material (A-Si curves shown in Figure 2 are without AR overcoats) is possible, due to its higher absorption coefficient. An investigation is underway to develop a hydrogenated amorphous silicon-on-Nb composite for hybrid photovoltaic-photothermal solar conversion.[6]

With increasing T_x , the spectral profiles in Figure 2 typically show an increase in B in the infrared and hence ϵ_T . In the case of intrinsic absorbers such as C-Si, the shift in λ_o with T_x is most prominent. The high-temperature curves are shown dashed to indicate their approximate behavior, due to irreversible shifts with thermal cycling.[5] Difficulties arise in measuring ρ_λ at HT and in controlling the thermal, structural and environmental history of the SS layer-substrate composite. Those HT curves shown represent the approximate intrinsic reversible behavior, where available. The effects of these shifts with temperature are shown parametrically in Table I. The B shift affects ϵ_T most strongly in C-Si, MMC and BNi, which have relatively lower λ_o wavelengths. With BCr, having a small B shift but a large λ_o , the resulting ϵ_T shift is almost entirely due to the emission spectrum shift itself. For MMC and BCr, ϵ_{TH} was measured independently at elevated temperatures and a comparison with the integrated ϵ_T values shows significant discrepancies. Here again, irreversible reactions in the SS layers with thermal cycling are possible, as well as discrepancies between measurements of unequal hemispherical averaging. It should be noted that there is also a problem with comparisons between measurements at different temperatures such as $T_{p\lambda}$, the reflectance measurement temperature; T_x , the solar-thermal operating temperature; and T'_x , the total hemispherical emittance measurement temperature.

The resulting solar-thermal conversion efficiencies obtained from a computer simulated solar concentrator system with typical optical losses[1] are also shown in the table. The efficiency η_{ss}^* represents the maximum Carnot efficiency at the optimum T_x for a given SS absorber. η_{FM}^* is computed from the fitted Fermi model profile, where it will be noted the agreement is typically within 1%. The figure-of-merit $X\alpha_s/\epsilon_T$ is also shown in the table for comparison. Whereas there is a qualitative agreement at low T_x between η_{ss}^* and $X\alpha_s/\epsilon_T$ as to the ranking of the different SS absorbers shown here, the validity of $X\alpha_s/\epsilon_T$ breaks down at high T_x , due to the non-uniqueness of the ratio and the algebraic subtractive feature of the $\sigma\epsilon_T T_x^4/X$ emissive loss term in the radiation transfer equation.

Table I
Solar-thermal conversion efficiency and spectral profile parameters

	$T_x (^{\circ}\text{C})$	α	α_s	$\lambda_o (\mu\text{m})$	$T_x (^{\circ}\text{C})$	$B(T_x)$	$\epsilon_T(T_x)$	$\epsilon_{TH}(T_x)$	$X\alpha_s/\epsilon_T$	$\eta_{ss}^*(Z)$	$\eta_{TH}^*(Z)$
C-Si	20	0.990	0.735	0.93	180(1X)	0.122	0.134		6	17.0	17.6
	500	0.990	0.781	1.01	480(32X)	0.186	0.196		130	41.0	41.1
E-Ni	20	0.947	0.865	1.74	280(1X)	0.022	0.045		19	29.6	29.7
	500	0.957	0.872	1.67	480(32X)	0.067	0.122		230	48.7	48.7
Ni-C	20	0.984	0.903	1.44	180(1X)	0.070	0.081	0.053(260 $^{\circ}\text{C}$)*	11	25.5	25.5
	538	0.982	0.900	1.46	480(32X)	0.105	0.149	0.062(538 $^{\circ}\text{C}$)*	190	49.5	49.4
ECr	20	0.952	0.928	3.21	180(1X)	0.096	0.131		7	23.6	23.6
	300	0.952	0.925	3.18	330(10X)	0.100	0.191	0.24(300 $^{\circ}\text{C}$) [†]	48	40.3	40.4
	500	0.952	0.923	3.16	530(100X)	0.109	0.314		290	53.6	53.9

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Due to the uncertainty of true hemispherical averaging and of using ρ_λ data for SS layers in the infrared, where $\rho_\lambda \rightarrow 1$ and $\alpha_\lambda \rightarrow 0$, a method was developed and applied to black chrome[8], involving the measurement of the solar spectral reflectance up to λ_o and the infrared total hemispherical emittance, both at T_x . These results, when joined by iterative integration using the Fermi model, then give a complete spectral profile, as shown schematically in Figure 3A. This method is limited, however, in that if one sample is used for both measurements, it must have no irreversible shifts with thermal cycling or if two "identical" samples are used, that they undergo an identical thermal cycling temperature/time sequence in the two separate measurements, which is difficult at best to accomplish. In practice then, the method may be restricted to a relatively low temperature range, perhaps less than $\sim 300^{\circ}\text{C}$ depending on the SS material being tested.[9]

III. DIRECTIONAL ABSORPTANCE SPECTROCALORIMETER. Accurate spectral profile modeling at HT is most reliably carried out where the directional spectral absorptance $\alpha_\lambda(T_x, \theta, \phi)$ is directly measured calorimetrically at T_x with monochromatic illumination under controlled environmental conditions. This approach is shown in Figure 3B. In addition, the simultaneous measurement of ϵ_{TH} at T_x in situ in the same instrument along with α_λ closely simulates experimentally the actual conditions of the full-scale absorber-receiver of a solar collector. As a result, a new type of vacuum spectroradiometer was designed and is under test to measure the high temperature ($\rightarrow 700^{\circ}\text{C}$) directional spectral absorptance and total hemispherical emittance of test selective coatings. This spectroradiometer is shown schematically in Figure 4. The test sample disk is mounted within a high-vacuum chamber C. It is located at O, as suspended by its thermocouple and heater lead wires at the center of a joule-heated thermal guardring TG. The sample disk is independently joule heated to T_x , ranging from -20°C to 700°C . Concurrently, the guardring temperature is kept approximately equal to T_x through differential

Fig. 3. High-temperature spectral profile evaluation methods -
 A. Solar reflectance-infrared emittance method with Fermi model fit and
 B. Directional spectral absorptance by spectroradiometry.

thermocouple sensing. TG acts as a thermal isolation anchor, allows for rapid initial scanning to T_x and minimizes conductive heat losses from the sample. This assembly in turn is suspended, and thermally isolated from, the double goniometer rings G. These rings may be rotated with respect to the incident beam I_λ through the polar angle ($\theta = 0^\circ - 85^\circ$) and the azimuthal angle ($\phi = 0^\circ - 360^\circ$). The rings are also thermally anchored to the cooled radiation shield, which is black and kept at a low ambient temperature T_0 , ranging between -196°C and 20°C to maintain the inequality, $T_0^4 \ll T_x^4$. Throughout the range of polar and azimuthal rotations, the sample disk, dimensionally small compared to the ambient shield, sees a low and effectively constant blackbody radiation from the ambient background.

As shown in Figure 4, the sample disk may be directionally illuminated by a parallel monochromatic beam I_λ of wavelength ranging from $0.3 \mu\text{m}$ to $21 \mu\text{m}$. Intense illumination is provided in the $0.3 \mu\text{m} - 3 \mu\text{m}$ wavelength range by a 1 KW tungsten-halogen lamp with infrasil optics as shown at A.

In the $2\mu\text{m} - 21\mu\text{m}$ infrared range, a 275 watt blackbody cavity with reflection and ZnSe optics, as shown at B, is used. Depending on the given wavelength operating range, a combination of selective long-pass, short-pass, hot mirror (HM) and liquid-cell filters are inserted for heat dissipation and higher order interference rejection. The double monochromator is of the off-axis Ebert design, with a bandwidth $\leq 0.025 \lambda$. Measurement of the I_λ incident at the sample disk is made with a pyroelectric detector located at D, when translated into the sample position at O. An in situ calibration also can be made at temperature using a reference monitor layer deposited on the reverse side of the sample disk. Alternate measurements of α_λ for each surface of the disk can be made in place by a θ rotation. Also, since the operating temperature may be extended below room temperature, a direct comparison is possible with room temperature ρ_λ measurements made on a given sample surface.

Fig. 4. Directional absorptance spectroradiometer.

With this instrument, the spectral absorptance measurement involves the thermal response of the sample absorber disk due to internal joule heating P_J and incident monochromatic flux I_λ at wavelength λ . In general, the dynamic thermal power equation for an absorber subject to radiative, conductive and convective energy transfer specified at $\lambda, T_x, \theta, \phi$ and t is given by,

$$\pm m C_p \frac{dT_x(t, \lambda)}{dt} = P_J + \alpha_\lambda(\lambda, T_x, \theta, \phi) A_x I_\lambda(\lambda) \quad (3)$$

$$- \sigma \epsilon_{TH}(T_x) A_T [T_x^4(t, \lambda) - T_o^4] - \dot{Q}_D - \dot{Q}_V, \quad ,$$

where (+) represents the heating mode and (-) the cooling mode and C_p = sample specific heat, m = sample mass, A_x = absorber area exposed to I_λ , A_T = total sample area, $\dot{Q}_D$ = net conduction heat loss rate and $\dot{Q}_V$ = net convection heat loss rate. The transient behavior with time t is shown in Figure 5, where the marker times indicate the switching sequence for P_J and I_λ .

Fig. 5. Transient temperature response sequence for sample disk with joule heating P_J and monochromatic flux I_λ .

The steady-state case in the dark is represented by region D, where at thermal equilibrium $T_x \rightarrow T_{eq}$. For this case, a measurement of the total hemispherical emittance $\epsilon_{TH}(T_x)$ is given by,

$$\epsilon_{TH} = K_1 / \sigma A_T (T_{eq}^4 - T_o^4) \quad , \quad (4)$$

where $K_1 = P_J - \dot{Q}_D - \dot{Q}_V$. Here $\dot{Q}_V$ is negligible in the vacuum chamber ($\leq 10^{-7}$ Torr) and $\dot{Q}_D$ is small when using the thermal guarding technique.

The transient case under monochromatic illumination I_λ for a given wavelength λ is shown by region B. For this case, the directional spectral absorptance $\alpha_\lambda(\lambda, T_x, \theta, \phi)$ at thermal equilibrium is given by,

$$\alpha_\lambda = [\epsilon_{TH} A_T (T_{eq}'^4 - T_o^4) - K_1] / A_x I_\lambda \quad (5)$$

In practice, accurate measurements of T_{eq} and T_{eq}' are required, as facilitated here by the use of the thermal guardring. In addition, the sample disk is designed for a minimum thermal response time with a low mC_p/A_T ratio. Digital readout and computer data reduction facilitate response with time measurement in this system. For high-temperature chemical stability, tungsten and niobium are used as substrate metals, as formed into 22 mm diameter disks. A nichrome heater laminate and chromel-constantan thermocouple wires are embedded within the two disk halves and sealed to form a final sample disk 0.76 mm thick having a 1-3 gm. mass. The disk rim area represents 6.5% of the total sample disk area A_T . Provision is then made to deposit the test selective coating as the last operation in the sample preparation.

When operational in this testing program on selective solar absorbing layers, the present spectroradiometer will add the capability for direct in situ measurements at high temperatures to 700°C of both the spectral absorptance and the total hemispherical emittance. It will combine in one instrument,

- A. Spectral behavior - $\alpha_\lambda(T_x)$ at $\lambda = 0.3 - 21 \mu m$ and spectrally integrated behavior - $\epsilon_{TH}(T_x)$ in the infrared.
- B. Spatial behavior - $\alpha_\lambda(T_x, \theta, \phi)$ and hemispherically integrated behavior - $\epsilon_{TH}(T_x)$.

For analysis, the Fermi parametrized model will provide a coordinating bridge between spectral dependence and integrated behavior, with a minimum number of parameters.

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9. See reference 5. for instance, where these spectral shifts with temperature for black chrome and black nickel are seen.

NOTES

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DESIGN AND CONSTRUCTION OF A HIGH TEMPERATURE VACUUM SPECTROMETER FOR MEASURING TEMPERATURE AND WAVELENGTH DEPENDENCE OF HEMISPHERICAL EMISSION

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ABSTRACT

A vacuum spectrometer for measuring the wavelength (1-20 μm) and temperature (100-700°C) dependence of the hemispherical emittance has been designed and is under construction. The sample is at the focus of a 12-inch paraboloidal reflector with a 180° collection angle. The central 60° emission cone is collected by an off-axis ellipsoidal reflector that directs the beam toward a series of plane mirrors, focusing it on the detector. The annular beam (30 to ca. 90°) is reflected by the 180° paraboloid and collected by a 12-inch paraboloid with a collection angle of 90°. A second off-axis ellipsoidal reflector with a collection angle of 90° concentrates the annular beam on the same detector. The spectrometer is enclosed in a vacuum chamber and the optics are kept at constant temperature. The spectral analysis of the beam is made by conventional means. The instrument operation modes are discussed in the text.

INTRODUCTION

The radiation loss of a solar thermal collector is given by

$$L = \int_{\theta} \int_{\lambda} \epsilon(\lambda, T, \theta) B(\lambda, T) d\lambda d\theta, \quad (1)$$

where

$$B(\lambda, T) = \frac{C_1}{\lambda^5 [\exp(C_2/\lambda T) - 1]}, \quad (2)$$

and $\epsilon(\lambda, T, \theta)$ is the emittance of the collector's surface at T and λ , in the direction θ . In most cases, the angular integration may be avoided by using the hemispherical value of the emittance, $\epsilon_h(\lambda, T)$, in which case eqn. 1 reduces to

$$L = \int_{\lambda} \epsilon_h(\lambda, T) \cdot B(\lambda, T) d\lambda. \quad (3)$$

An instrument has been designed and is under construction to measure the hemispherical emittance as a function of wavelength and temperature, in the range of expected applications.

INSTRUMENT DESCRIPTION

The instrument collects the thermal emission of a sample over a hemisphere, focusing it on a detector. Figure 1 shows a schematic drawing of the optics. The sample — a 22.5-mm disk — is heated to the measuring temperature, at the focus of a 12-inch paraboloidal reflector P_1 with a collection angle of 180° . A black-body cavity R at the same temperature is used for calibration. The radiation emitted by the sample within the normal 60° cone is collected by an off-axis ellipsoidal reflector E_1 that focuses the deflected beam on the same detector. The annular beam reflected by P_1 is sent by a second 12-inch paraboloid to a second off-axis ellipsoid E_2 which extracts the annular beam and focuses it on the detector. The separation of the sample's emission into two beams eliminates the shadow that would otherwise be cast along the optical axis of the hemispherical reflector P_1 .

The reflectors are commercial units shaped to order, made of nickel-plated brass coated with bare gold, and have a copper tubing on the back for cooling purpose. The optics are enclosed in a vacuum chamber evacuated with a diffusion pump and a cold trap. The collected beams leave the chamber through an appropriate window with a 6° divergence, with the focus outside the chamber.

Three options are at present being considered for the spectrometric analysis of the beam, namely:

1. Band pass interference filters,
2. Monochromator, and
3. Fourier transform spectrometry.

The options will be developed in this order. The first step will consist of chopping and filtering the beam with narrow-band pass filters up to $11.6 \mu\text{m}$, extending the region to $20 \mu\text{m}$ by using wide-band pass filters whose characteristics are shown in Table 1.

FIGURE 1. SCHEMATIC DIAGRAM OF THE SPECTROMETER OPTICS.

The use of filters has, however, two disadvantages. On the one hand, the background radiation integrated over the emission spectrum is not negligible, as shown in Table 2, where the filtered power of a 5-cm² sample is given for several temperatures. On the other hand, the limited number of filters may partially hide the interference fringes making an accurate determination of the actual emittance difficult. The second option - a monochromator - would be better due to the continuous scan of the spectrum, but it would probably imply a lower sensitivity, being therefore more appropriate for higher temperatures. The best solution is the use of Fourier transform analysis, in which case high resolution and high sensitivity are both simultaneously achieved. This option, however, is particularly expensive and will have to be postponed to a near future.

TABLE 1. CHARACTERISTICS OF SELECTED OCLI FILTERS.

Filter ^a	λ (μm) ^b	$\Delta\lambda$ (μm)	τ ^c
NO0903-7	0.903	0.04	0.73
NO1266-5	1.266	0.02	0.54
NO1570-6A	1.570	0.13	0.80
NO1996-6	1.996	0.07	0.85
NO2886-9	2.886	0.22	0.75
NO4387-9	4.387	0.28	0.83
NO5620-8	5.620	0.43	0.78
NO7211-9	7.211	0.52	0.81
N11676-9	11.68	0.53	0.80
W15000-9A	15.00	1.80	0.55
W19183-9	19.18	2.00	0.33

^aBackground transmission is ca. 0.1% of total radiation.

^bPeak transmission wavelength.

^cAverage transmission between half-power points.

TABLE 2. RADIATION OF A 5-cm² SAMPLE AFTER FILTERING, AT SELECTED TEMPERATURES.
THE POWER IS EXPRESSED IN WATTS AND CALCULATED FOR UNIT EMITTANCE AT AN
AMBIENT TEMPERATURE OF 300K.

Filter	100°C	200°C	300°C	400°C	500°C	600°C	700°C
N00903-7	2.6E-15	2.2E-11	7.0E-09	4.8E-07	1.0E-05	1.1E-04	7.1E-04
N01266-5	3.7E-11	2.3E-09	1.5E-06	2.9E-05	2.6E-04	1.4E-03	5.3E-03
N01570-6A	4.4E-08	7.9E-06	2.3E-04	2.5E-03	1.5E-02	5.6E-02	1.7E-02
N01996-6	1.4E-06	8.5E-05	1.2E-03	5.0E-03	3.1E-02	9.1E-02	1.7E-01
N02886-9	2.3E-04	4.1E-03	2.5E-02	1.0E-01	2.4E-01	5.1E-01	9.2E-01
N04387-9	3.6E-03	2.6E-02	8.7E-02	2.1E-01	3.9E-01	6.4E-01	9.5E-01
N05620-8	9.5E-03	4.8E-02	1.3E-01	2.5E-01	4.2E-01	6.3E-01	8.7E-01
N07211-9	1.4E-02	5.5E-02	1.2E-01	2.1E-01	3.3E-01	4.5E-01	5.9E-01
N11676-9	7.8E-03	2.3E-02	4.2E-02	6.4E-02	8.7E-02	1.1E-01	1.4E-01
W15000-9A	9.8E-03	2.7E-02	4.6E-02	6.7E-02	8.9E-02	1.1E-01	1.4E-01
W19183-9	3.1E-03	8.0E-03	1.3E-02	1.9E-02	2.5E-02	3.1E-02	3.7E-02
Background with one filter	3.2E-04	1.2E-03	2.8E-03	5.6E-03	9.9E-03	1.6E-02	2.5E-02

MODES OF OPERATION

Three modes of operation, as shown in Figure 2, are anticipated. The reflection mode will be used for room temperature measurements, at which the emission mode cannot operate. This mode will also be used to determine the optical absorption in the solar spectrum, as well as the IR absorption of films deposited on polished substrates.

The luminescence mode will be available to study any possible photoexcited radiation characterizing candidate materials for solar conversion, and will include facilities to measure lifetimes and annealing kinetics.

Additional ports will allow measurements performed on films never exposed to uncontrolled atmospheres, by attaching the spectrometer to deposition equipment already designed.

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FIGURE 2. THE THREE FUNDAMENTAL MODES OF OPERATION OF THE INSTRUMENT DESCRIBED IN THE TEXT.

NOTES

Appendix I

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U. S. Patents

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Appendix II

1. International Absorber Developments*
2. New U. S. process/materials*

*includes only process/materials not discussed at conference;

*information presented as received and has not been evaluated; list is not considered exhaustive

International

Dornier-System GmbH

(W. Scherber and G. Dietrich)

*Solarox

- $\alpha_s \approx 0.91-0.96$, $\epsilon_t \approx 0.10-0.20$
- $T_{stab} \approx 200^\circ\text{C}$ (5000 hrs)
- aluminum substrates
- two stage electroplating process

*Solartex

- $\alpha_s \approx 0.94-0.96$ (AMO), $\epsilon_t \approx 0.14-0.18$ (100°C), $\epsilon_t \approx 0.20$ (300°C)
- $T_{stab} > 400^\circ\text{C}$ (>3000 hrs), 700°C (5 minutes)
- electroplated coating (Co) plus heat treatment

Philips GmbH (Hamburg)

*Electroplated CoS with $\alpha_s \approx 0.96-0.97$

- $\epsilon_t = 0.06-0.07$ on copper
- $\epsilon_t = 0.07-0.08$ on nickel
- $\epsilon_t = 0.04$ on silver-coated glass
- $T_{stab} \approx 300^\circ\text{C}$ (>1000 hrs in vacuum)

New South Wales Institute of Technology

(B.S. Thornton, School of Mathematical Sciences)

*Electrodeposited black chrome on "chromised" steel

- $\alpha_s \approx 0.90-0.95$, $\epsilon_t \approx 0.20$, $T_{stab} \approx 150^\circ\text{C}$
- eliminates nickel layer

Yazaki Co. (Japan)

*Chemical treatment of stainless steel

- mixed Cr and Fe oxides and sulfides
- $\alpha_s \approx 0.92$, $\epsilon_t \approx 0.10$
- inexpensive, durable
- 4000 panels/month

Showa Aluminum Co. (Japan)

*Anodized aluminum

- $\alpha_s \approx 0.94$, $\epsilon_t \approx 0.07-0.10$
- 1 year accelerated H_2O , UV, water spray

University of Delft, Netherlands (M. van der Liej and
C. J. Hoogendoorn)

*Spray coated $SnO_2:F$ on black enamel

- $\alpha_s \approx 0.92$, $\epsilon_t \approx 0.15$
- $T_{stab} \approx 400^\circ C$ in air, $200^\circ C$ in vacuum
- extremely rugged

New U. S. Developments

NASA-Lewis/Harshaw (G. McDonald)

*Electroplated Co/CoOx from std.

Watts plating solution plus oxidizing agents

- $\alpha_s \approx 0.92$, $\epsilon_t \approx 0.15$
- $T_{stab} \approx 500^\circ\text{C}$ in Air

NPD Energy Systems (W. Dryer)

*Electrodeposited black chrome on blue chrome
on copper, steel, or aluminum

- $\alpha_s \approx 0.92-0.97$ $\epsilon_t \approx 0.04-0.15$
- eliminates nickel layer

Climax Molybdenum Company (J. D. Redmond)

*Sodium dichromate (ebonized) treatment of steels

- $\alpha_s \approx 0.90$, $\epsilon_t \approx 0.15$
- no direct thermal stability data
- inexpensive

Ergenics (MPD Technology Corporation)

*Maxorb solar/foil (selective surface on thin nickel foil
with adhesive)

- $\alpha_s \approx 0.97$, $\epsilon_t \approx 0.10$
- $T_{stab} \approx 150^\circ\text{C}$ (>3000 hours)

OCLI (Santa Rosa, California)

*Developmental multilayer film on foil with adhesive

- $\alpha_s \approx 0.95$, $\epsilon_t \approx 0.10$

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