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Selective Surfaces for Solar-Thermal Conversion*

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Selective surfaces are used to obtain high absorption of the incident solar flux and simultaneously suppress losses due to thermal radiation from the hot converter surface. Whether or not the reduction of these losses leads to more economical energy production depends on several factors, the most important being the cost of the selective surface and the concentration ratio of the collector system. The allowable limits for the costs of a selective surface are derived for examples of a flat plate hot water heater, a distributed collector, and a central receiver system. The several basic methods for obtaining selectivity are discussed. Material science and physical chemistry enter strongly into their further development and reduction in costs. Even so, the best estimates for fabrication costs using presently available mass production techniques indicate that selective surfaces can be economically competitive for each of the discussed applications.

Introduction

My original intention was to cover a wide range of coatings with applications to mirrors and windows as well as to selective surfaces. However, time limitations dictated that the topic be restricted to just selective surfaces. A good reference for the wider range of applications is a recent article by Mattox (*1*).

The first thing we must do is to make sure everyone understands what we mean by a selective surface for thermal conversion of solar energy. As shown in Fig. 1, such a surface has high absorptance over the wavelengths spanning the spectrum of the incident solar flux. It also has a low emittance across the spectral region where the radiation from a blackbody with high surface temperature is located. The low emittance suppresses the losses due to thermal reradiation and makes it possible to operate the collector at higher efficiencies and higher temperatures.

This idea is not new. Although it was recognized even before 1955, presentations by Tabor (*2*) and Gier and Dunkle (*3*) 21 years ago at the Conference on the Use of Solar Energy established the connection to collector performance characteristics.

In the last few years much of the early work has been repeated. However, the emphasis has been on new or improved materials which have superior durability and performance at elevated temperatures. The purpose of this paper is to briefly review the economic advantage implied by using selectivity on the absorber surface, the basic designs for their

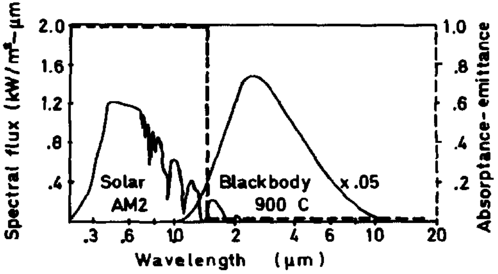

FIG. 1. Spectral flux distribution for the sun and a blackbody at 900°C. The spectral absorptance of an ideal selective surface is shown by the dashed line.

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implementation and some recent advances in materials and fabrication techniques.

Relationship between Performance and Selectivity

If the selective surface is used to increase the collector's efficiency, the desirable end result is actually a reduction in the cost of energy available for the *intended use.* For instance, in some process heat applications the necessity of obtaining high temperatures may dictate additional energy costs. The cost C of the energy collected is given by

$$C = (v + w/x)/\int \phi\eta\, dt, \qquad (1)$$

where

v = cost of the facility per unit area of solar flux intercepted. This includes mirrors, support structures, piping, power plant, financing cost, etc., but excludes the cost of the coating on the surface of the absorber.

w = cost per unit area of the coating on the surface of the absorber.

x = concentration ratio of light at the absorber surface.

ϕ = the instantaneous solar flux at the aperture of the system.

η = the instantaneous conversion efficiency. In general, this is the product of subsystem efficiencies such as transmittance of the optical components, thermal conversion at the absorber, efficiency of generating system if used, etc.

The integral is to be taken over the lifetime of the system. Many of the terms in Eq. (1) are too vaguely known to make accurate cost projections. Collector costs are highly dependent on production volumes; the solar flux curves are poorly known for most local areas, and the conversion efficiency is highly dependent on the system's design and its operating temperature which in turn depends on solar flux, fluid flow, and position along the collector.

This paper is restricted to a consideration of selective surfaces for increasing conversion efficiency. The conversion efficiency η_{st} for the selective surface can be obtained from the energy balance equation at the converter, namely,

$$\overset{\substack{\text{energy}\\ \text{absorbed}}}{\phi x\tau\alpha} = \overset{\substack{\text{energy}\\ \text{to}\\ \text{working}\\ \text{fluid}}}{Q} + \overset{\substack{\text{radiation}\\ \text{losses}}}{K_1(T_s^4 - T_a^4)} + \overset{\substack{\text{conduction}\\ \text{and}\\ \text{convection}\\ \text{losses}}}{K_2(T_s - T_a)}, \qquad (2)$$

where

α = solar absorptance of converter surface.

τ = transmittance of optical components.

T_s = temperature of absorber surface.

T_a = temperature of surroundings.

K_1 = transfer coefficient for radiative losses. It includes the emittance of the surfaces, Stefan–Boltzmann constant, and configuration factors.

K_2 = transfer coefficient for conduction and convection.

Hence

$$\eta_{st} = Q/\phi x\tau = \alpha - (1/\phi x\tau)[K_1(T_s^4 - T_a^4) + K_2(T_s - T_a)] \qquad (3)$$

Flat plate collectors for space and water heating represent most of the present solar thermal market. They operate at relatively low temperatures, and their conversion efficiency is limited primarily by convection and conduction losses. Nevertheless, selective coatings can be shown to substantially improve performance. Data from Meine (*4*) for a water heater with a single cover window and operating at a temperature 50°C above 10°C ambient shows

$\eta_{st} = 0.52$ for $\alpha = \varepsilon = 0.98$, while

$\eta_{st} = 0.63$ for $\alpha = 0.90$ and $\varepsilon = 0.00$.

This compares well to values of Hottel and coworkers (*5*) for a similar system. Explicit forms for the loss terms for this system may be found in references (*4–8*).

Using these values as average efficiencies and assuming collectors with and without selective surfaces operating side by side with the same solar flux, one can obtain from Eq. (1) a maximum incremental cost $\Delta w = w_2 - w_1$

which could be tolerated for the more efficient collector, without raising the energy costs. The results for a flat plate collector with the above operating conditions is

$$\begin{aligned}\Delta w &= x((\eta_2/\eta_1) - 1)(v + w_1 x)\\ &= 1((0.63/0.53) - 1)(\$100/\text{m}^2)\\ &= \$19/\text{m}^2. \qquad (4)\end{aligned}$$

The cost used here for a single glazed flat plate collector falls in the range of recent quotes obtained from various suppliers. However, by the time installation is complete the cost about doubles. Incidentally, prices quoted for collectors with selective surfaces are anywhere from 12 to 50% above their nonselective counterparts.

A similar analysis can be carried out for central receiver systems that are characterized by concentration ratios of 500 or more. The large concentration ratios can be utilized to produce high temperatures even in the absence of selective surfaces. They also dilute the losses due to radiation, convection, and conduction. However, as operating temperatures rise the control of radiation losses, which go as the fourth power of the temperature, becomes more advantageous. In addition, a relatively expensive coating can be tolerated since its cost is also diluted by the concentration ratio. For example, for operation at 500°C with $x = 500$ and a solar absorption $\alpha = 0.90$, the reduction in thermal efficiency due to radiation losses would be $\varepsilon\sigma T^4/\phi x\tau = 0.05$ for an emittance $\varepsilon = 0.9$ and only 0.005 for $\varepsilon = 0.1$. Assuming losses of 3% for conduction and convection gives

$$\begin{aligned}\Delta w &= ((0.87/0.82) - 1)(500)(\$1324/\text{kW}_e)\\ &\quad \times (0.18\ \text{kW}_e/\text{kW}_{\text{solar}})(\text{kW}_s/\text{m}^2)\\ &= \$7200/\text{m}^2,\end{aligned}$$

where the cost per kW_e output and the 18% total conversion efficiency are from recent literature (*9, 10*). Hence, a durable coating with the high absorptance and low emittance values which could be supplied in low volume at costs less than $\$7200/\text{m}^2$ would appear to be economically competitive. Since the total market for such coating would be low, cost reductions through high volumes might not be obtained.

Distributed collector systems utilizing long parabolic troughs and concentrations of 10–100 are also being studied (*11*). The absorber tube is housed in an evacuated glass cylinder to prevent losses due to convection and condition. The remaining loss is by radiative exchange with the cooler vacuum jacket and has been calculated for a selective surface ($\alpha = 0.9$, $\varepsilon = 0.11$) operating at 263°C by Thodos (*12*). Using his results together with $x = 30$, $\tau = 0.79$, and $\phi = 630\ w/\text{m}^2$ the converter efficiency given by Eq. 3 is 0.86. Repeating the calculation for a nonselective surface ($\alpha = \varepsilon = 0.9$) gives a lower efficiency of 0.66. Again applying Eq. 1 to find the maximum incremental costs acceptable for such a coating

$$\begin{aligned}\Delta w &= ((0.86/0.66) - 1)(30)(\$300/\text{m}^2)\\ &= \$2700/\text{m}^2.\end{aligned}$$

The rather high acceptable cost of the coating arises because of the high cost of the remainder of the system, brought about partially by the large piping costs and the necessity to maintain the vacuum jacket. The moderate concentration ratio helps to offset this.

The analyses done above are shown in Table I to facilitate comparison of the three systems.

TABLE I

SUMMARY RESULTS—MAXIMUM ALLOWABLE COSTS OF SELECTIVE SURFACES ($\alpha = 0.9$, $\varepsilon = 0.1$) FOR FLAT PLATE, DISTRIBUTED COLLECTOR, AND CENTRAL RECEIVER SYSTEMS

	Flat plate	Distributed collector	Central receiver
Concentration	1	30	500
Efficiency			
No selectivity	0.53	0.66	0.82
With selectivity	0.63	0.86	0.87
$(\eta ss/\eta gb) - 1$	0.19	0.30	0.06
System costs ($\$/\text{m}^2$)	200	300	240
Limit of acceptable coating cost ($\$/\text{m}^2$)	38	2700	7200

Coatings

We turn now to review the techniques for obtaining selective coatings. There are several optical systems which lead to selectivity. The simplest is a single material which in bulk has the desired high absorptance below 1.5–2 μm and a low emittance at longer wavelengths.

The spectral reflectance of ReO_3 shown in Fig. 2 approximates the desired profile (*13*). Although the reflectance in the visible region is too high and the edge is at too short a wavelength the possibility if finding a single material, or of engineering a material which more nearly approaches the desired spectral characteristics is intriguing (*3*, *4*). Other candidate materials can be found in the references but as in the case of ReO_3 do not by themselves have the desired selectivity.

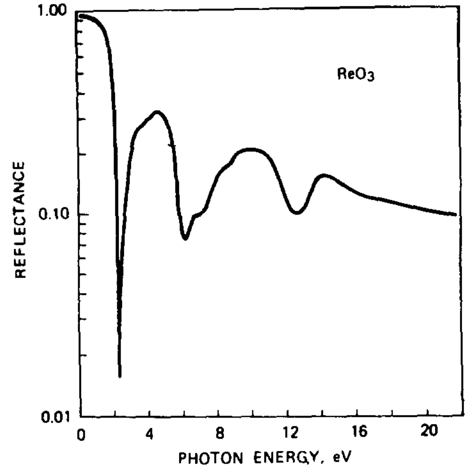

FIG. 2. Reflectance of rhenium trioxide at near-normal incidence.

At the opposite end of the complexity scale are the thin-film interference coatings. To my knowledge no purely dielectric stacks have been advocated for solar–thermal conversion. A successful design (*15*) which gives high absorptance and good emittance control is typified by Honeywell's $Al_2O_3/Mo/Al_2O_3$ (AMA) coating on a molybdenum reflector (*16*). A similar coating using Cr between the dielectrics and Ag as the reflector layer is reported by Helio Associates to give a solar absorptance of 0.94 and an emittance of only 0.04 (*17*). The spectral reflectance of the Helio "black chrome" is shown together with curves for electroplated black chrome in Fig. 3. The absorption in the thin (50 to 200 Å) metallic layer is strongly enhanced by standing waves set up by the dielectric spacers. The lifetime for AMA coatings operating at 800°C was estimated to be over 20 years (*16*). The Cr–Ag combination was stable at 600°C for a few

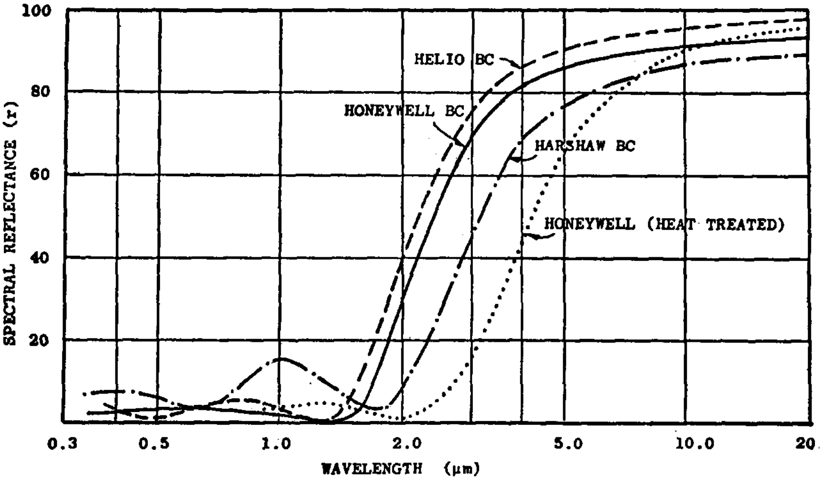

FIG. 3. Reflectance of some black chrome selective surfaces. The Honeywell and Harshaw coatings are electroplated while the Helio coating is a vacuum evaporated interference stack consisting of glass substrate + Cr (10 nm) + Ag (159 nm) + Al_2O_3 (165.3 nm) + Cr (10.0 nm) + Al_2O_3 (206 nm) (*16*).

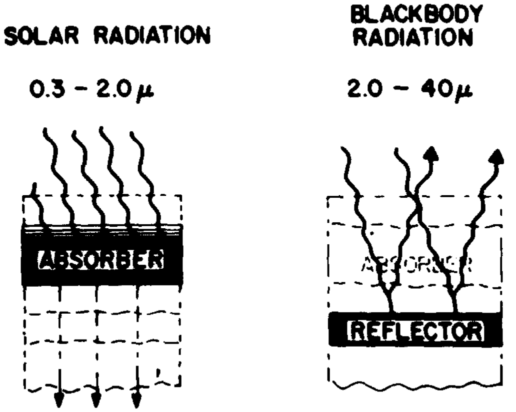

FIG. 4. Basis of absorber–reflector tandem type of selective surface. The absorber is transparent in the infrared allowing the emittance to be determined by the reflector characteristics.

hours during tests we ran in our high-temperature reflectometer. Unfortunately, the interference coatings are sensitive to "detuning" because of changes in the optical path lengths as the angle of incidence increases. This causes a reduction in the absorption of solar flux with off-normal incidence.

These films have traditionally been produced in small quantities by vacuum evaporation or sputtering. A recent cost estimate for sputtered films done at high volume in large capacity units was about \$3/m^2 (*1*, *18*). A large coating laboratory presently markets a "dark mirror" produced by sputtering with good selectivity for about \$16/m^2. This price would appear to be cost effective in distributed collector or central receiver applications. The \$3/m^2 price would of course depend on market volume and production yields.

The tandem, absorber–reflector selective surface shown in Fig. 4 is intermediate in complexity between a single material and an interference stack. The incoming solar flux is absorbed in the top layer which is a material with high bulk absorptivity for wavelengths less than 2.5 μm. However, at longer wavelengths in the infrared the top layer becomes

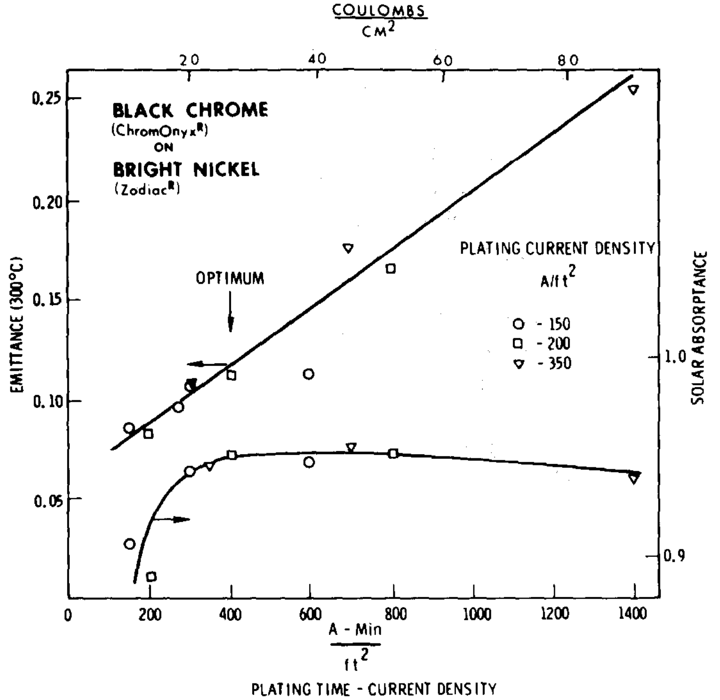

FIG. 5. Total hemispherical emittance and solar absorptance of Chrom–Onyx black chrome on bright nickle as a function of thickness (~current density × time) (from Ref. *20*).

transparent, allowing the shiny underlying reflector to provide the low emittance.

Semiconductors including many metal oxides and some sulfides have optical properties desirable for the absorber layer. Some of the earliest work (*19*) on selective surfaces was done using an absorber–reflector tandems and today they command most of the commercial market. One of the most promising materials is the "black chrome" (*20*) produced by electroplating.

Figure 5 shows optical characteristics as a function of plating current for one such process. The coatings can be improved by varying the plating current during the deposition to provide an inhomogeneous film composition. Auger analysis of coatings produced in this manner show that they consist of Cr_2O_3 and free Cr with the Cr : O ratio varying from 10 : 1 at the reflector interface to 1 : 1 at the air interface (*20*). The resulting graded index of refraction serves as an impedance matching mechanism to reduce front surface reflection and also effectively couples radiation from a large range of incidence angles into the absorber. When properly deposited the black chrome coatings have solar absorptance greater than 0.95 and an emittance of approximately 0.2 at a stable operating temperature of 350°C. At higher temperatures in a poor vacuum or in air the free chromium in the film begins to oxidize and the solar absorptance decreases (*21*).

Actual fabrication costs are difficult to obtain. Batch-type electroplating could run about $\$3/m^2$ while a cost of several cents per square meter might be reached in a devoted facility with flow-through baths and high volumes (*1*). With today's high costs for installed collectors, these coating costs are well within the limits of economic feasibility for many low to intermediate temperature applications.

At the University of Arizona Optical Sciences Center we have been using silicon as the bulk absorber together with silver for the reflector film (*22*). the unique aspect of our research is that chemical vapor deposition (CVD) is being used to obtain thin films of optical quality. This process is ideally suited for adaptation to large volume flow-through production methods. Figure 6 shows the spectral reflectance of a typical coating with a 1.75-μm thick silicon layer. Because of the high index of refraction of silicon the stack also has an antireflection coating consisting of a single $\frac{1}{4}$-wave thickness of Si_3N_4 which was also deposited by CVD. The CVD coatings are deposited with the substrate at 600–700°C and subsequently show excellent thermal stability. We have samples which have endured 2000 cycles between 150 and 500°C plus 100 hr at 600°C without significant degradation. The coatings have also withstood a few hours at 800°C during high-temperature reflectance measurements. As evident in Fig. 6 the absorption edge shifts to longer wavelengths at elevated temperatures. This is actually desirable and increases the solar absorptance. There is a slight degradation in the infrared emittance which is most evident at the positions of the interference fringes. The solar absorptance and infrared emittance at 500°C for a typical coating of this design are 0.76 and 0.07, respectively.

Our present work is to extend the use of CVD to produce infrared reflectors of tungsten and molybdenum which are stable for very

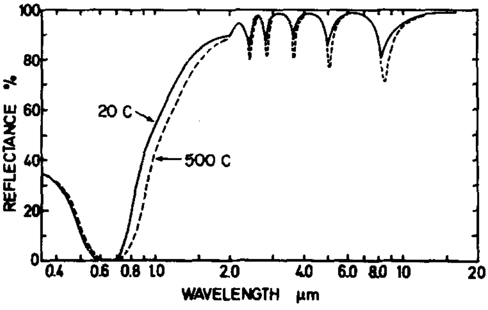

FIG. 6. Spectral reflectance at 20 and 500°C of a silicon–silver tandem selective surface. The silicon thickness is 1.75 μm and is antireflected by a 0.07-μm-thick silicon-nitride film. (In the region of rapidly oscillating fringes between 0.7 and 2.0 μm the effective coating reflectance is plotted.)

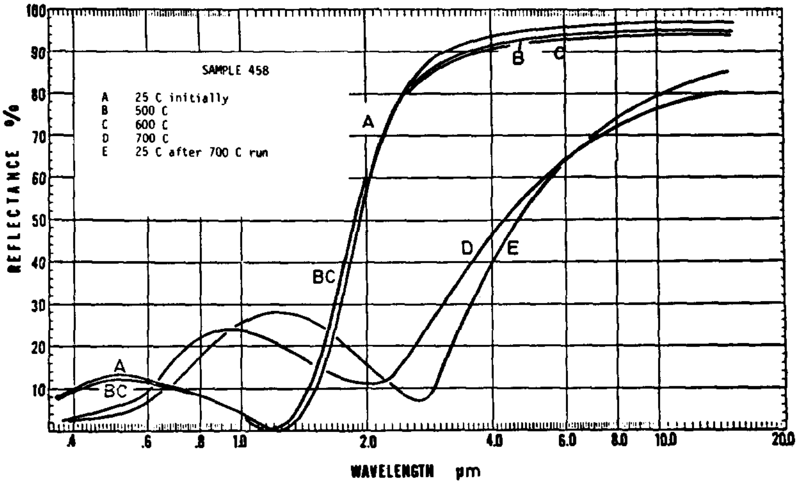

FIG. 7. Room-temperature and high-temperature reflectance of a ZrC_xN_y–aluminum tandem selective surface from U.S. Bureau of Mines, Albany Metallurgical Research Center. The reflectance measurements were made at the Optical Sciences Center.

high-temperature operation. Preliminary studies indicate that deposition of these refractory metals in a reducing atmosphere produces infrared reflectance that matches the high values for the bulk materials. Although we have not done detailed cost studies for this system, preliminary estimates indicate that CVD coatings will be less expensive than those deposited under vacuum.

Absorber layers utilizing ZrC_xN_y have also been under investigation (*23*). Figure 7 shows the room temperature and high-temperature reflectance of one of these coatings with an aluminum reflector layer on a stainless-steel substrate (*24*). Stability of the selective properties was maintained at temperatures of up to 600°C when maintained under a good vacuum ($<10^{-5}$ Torr). It degraded at 700°C which surpasses the melting point of the aluminum used as the reflector. The high absorption coefficient of this material allows the use of films thin enough to avoid interference fringes in the infrared. This absorber is fabricated by sputtering Zr in an atmosphere containing carbon and nitrogen.

An absorber–reflector tandem fabricated by reactively sputtering stainless steel onto a polished copper substrate in a methane atmosphere has also been reported (*25*). The resulting thin layers of metal carbides had solar absorptances ranging from 0.75 to 0.90 and low emittances (0.07 at 600°C). The coatings were stable at 600 C under a vacuum but degrade at lower temperatures in air.

A fourth method for obtaining selectivity is by controlling the surface morphology of the film. This is sometimes called wavefront discrimination or a reflective-absorber. Figure 8 shows an electron micrograph of a rhenium film which has a desirable structure (*26*). Since the dimensions of the whiskers are less than infrared wavelengths, the surface appears specular with low emittance for thermal radiation. Dendrites of tungsten have been grown by CVD (*27*) and show strong absorption of normally incident solar flux. Unfortunately the absorptance decreases rapidly as the angle of incidence increases, and the measured emittance of these surfaces is high (0.25–0.30). The emittance may increase substantially if the tungsten is allowed to oxidize by heating the surface in air.

Our survey of coating designs that provide selectivity for solar thermal energy conversion is completed by including the class of resonant absorbers (often called Mie scatterers), consisting of small (<200 Å) metal particles embedded in a dielectric film (*28*). The optical

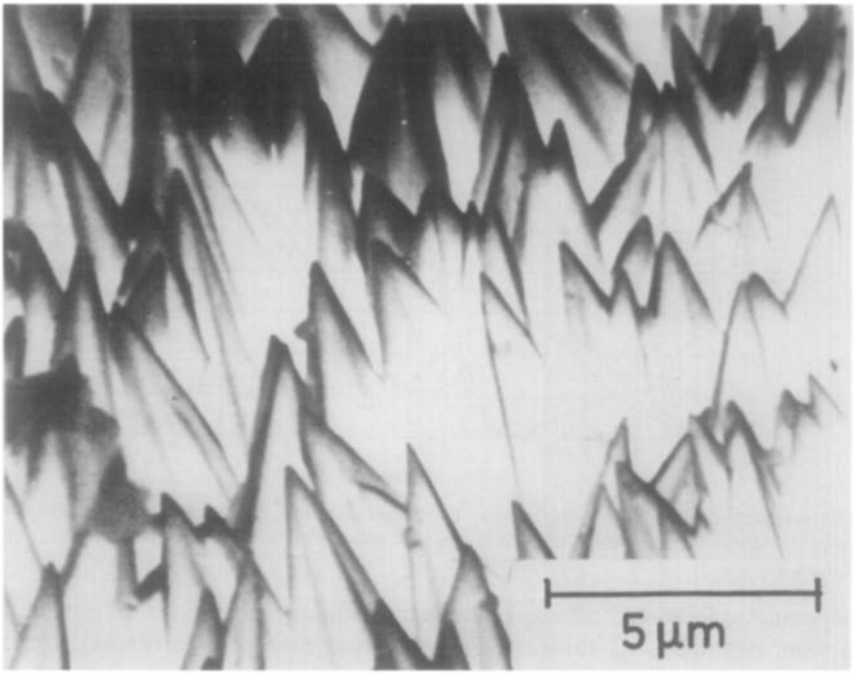

Fig. 8. Scanning electron micrograph of a rhenium whiskers deposited by CVD.

properties can be tailored by controlling the size and shape of the metal particles so that strong absorption over the solar spectrum is obtained. Since the composite appears transparent at longer wavelengths emittance control is provided by an underlying metallic reflector, i.e., absorber–reflector tandem design. The structure can be obtained by a variety of methods including sputtering (*39*) and electrodeposition (*30*). Some of the high absorptance of electroplated black chrome has also been attributed to this effect (*31*). The long-term high-temperature durability of such coatings is not yet well known. Costs would appear to be comparable to those quoted above for other coating designs using similar fabrication methods.

In summary I have identified five basic methods for obtaining surface selectivity. They are

1. single material;
2. bulk absorber–reflector tandem;
3. interference films;
4. controlled surface morphology;
5. resonance absorption of small particles in a dielectric.

Good selective absorbers utilize more than one of these methods. For example, black chrome is an absorber–reflector tandem that relies on free chromium in the Cr_2O_3 matrix, trapping by a roughened surface, and a graded refractive index to obtain high absorptance across wide acceptance angles while maintaining a low emittance.

Many different material systems are potentially useful as selective surfaces and will undoubtedly be studied during the coming years.

The costs for coating solar–thermal absorbers with selective surfaces can be expected to run from less than \$1/m^2 to as high as a few dollars per square meter. Even the upper end of this price range seems relatively inexpensive when compared to the present total system costs of \$200/m^2. By using a selective surface the gain in system efficiency would seem to more than compensate for their additional costs and lead to lower energy costs for all three collector designs considered.

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