NASA TM X-1379

DEPOSITION OF ALUMINUM AND SILICON OXIDE ON EPOXY-COATED SUBSTRATES

By Ferdinand L. Acampora and Adolph E. Spakowski

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – CFSTI price $3.00

DEPOSITION OF ALUMINUM AND SILICON OXIDE ON EPOXY COATED SUBSTRATES

by Ferdinand L. Acampora and Adolph E. Spakowski

Lewis Research Center

SUMMARY

A method was developed for preparing highly reflective surfaces suitable for concentrating solar energy. Aluminum films 0.06-micron thick were deposited on epoxy-coated magnesium substrates in a glass-enclosed metallizing system. The soft reflective material was covered with a protective layer of silicon oxide. The following factors were considered of prime importance to produce coatings of high optical quality: (1) complete curing of the epoxy resin, (2) careful cleaning and handling of the substrates, (3) cooling of the substrates during the deposition of aluminum and silicon oxide, and (4) depositing silicon oxide at a decreasing rate. Spectral measurements made from 2.5 to 35 microns show that silicon oxide coatings increased the emittance of aluminum films from 0.06 to 0.43 while the normal absorptance remained virtually unchanged. Calculations showed that the increased emittance would decrease the equilibrium temperature of a mirror in space only if the emittance of the back surface of the mirror was less than 0.45.

INTRODUCTION

Solar energy must be focused by large reflectors for practical utilization of solar-powered heat engines for electric power conversion in space. Present methods of forming and polishing large metal reflectors produce light-scattering losses because of surface irregularities. These losses can be reduced considerably by applying a thin coating of epoxy resin to the metal surface. Metallizing the smooth resin surface produces a highly reflective surface suitable for concentrating solar energy. Aluminum is the most suitable metal for metallizing the resin, since aluminum has high reflectance from the ultraviolet far into the infrared region. However, its low emittance in the infrared region results in overheating the mirror. One method commonly used to minimize the reflector temperature is to use a coating with high emissivity in the infrared region,

such as partly oxidized silicon monoxide hereinafter referred to as silicon oxide.

This form of silicon oxide can be deposited to form a coating with higher emissivity than aluminum in the infrared region. The coating does not absorb appreciably in the spectral region from 0.3 to 3 microns where 97 percent of the solar flux is contained. In effect, the silicon oxide increases the thermal emission from the aluminum film while the solar absorptance remains fairly constant. In addition, the mechanically hard, strongly adherent silicon oxide protects the soft reflective material from abrasion and from chemical attack while in the earth's environment.

In this report, a method is described for preparing silicon oxide aluminized mirrors in a glass-enclosed metallizing system. Highly reflective aluminum films were deposited reproducibly on epoxy-coated magnesium substrates. The problem of preserving the integrity of the epoxy base material from the destructive stresses applied during the silicon oxide deposition was solved by substrate cooling and film growth-rate regulation. Spectral data were obtained for the coatings.

APPARATUS

The aluminum and silicon oxide depositions were carried out sequentially without breaking the vacuum in the metallizing system, which was enclosed in a 76-centimeter glass bell jar (fig. 1). The glow discharge cathode was a 23.5-centimeter loop of 1.3-centimeter steel rod located 28 centimeters below the substrate. An optical thin-film monitoring system was used to regulate all depositions. A 550-millimicron narrow band-pass interference filter was used on the lead sulfide photodetector, which enabled monochromatic wavelength monitoring.

The two magnesium substrate sizes studied were 2.5 by 2.5 by 0.2 centimeter and 12.7 by 15.2 by 0.2 centimeter. The substrates were coated on one side with 0.003-centimeter-thick thermosetting epoxy (type EP-3, Emerson and Cumings, Inc.) which is a two-component unfilled epoxy using an aliphatic amine hardener. The epoxy was cured to a hard, smooth coating with few surface defects. Surface blemishes in the subsequent films were kept to a minimum by careful cleaning and handling of the substrates. A 17.8- by 17.8- by 0.3-centimeter-steel plate was used to support the substrates 56 centimeters above the evaporation sources (fig. 2). To cool the holder, an M-shaped pattern of steel tubing (0.32 cm diam) was soldered to one side and connected to the water supply.

The aluminum and silicon monoxide evaporation sources are shown in figure 3. Four braided tungsten-wire filaments mounted in parallel afforded high aluminization rates. The silicon oxide source was separated from the aluminum source by a stainless-steel vapor deflector (not shown in fig. 3). The silicon monoxide source box was 2.5 by

3.5 by 6.4 centimeters and was fabricated from 0.051-centimeter-thick tantalum. It was supported in a rectangular heat baffle also made from 0.051-centimeter tantalum. The capacity of the source box was about 50 grams of pea-sized material. The evaporation heater was a braided tungsten-wire filament which was insulated from the box by Vycor sleeves wedged in the notches on the sides (see fig. 3). Two Chromel-Alumel thermocouples were attached to the inside bottom of the box. The power consumption during the silicon oxide evaporation was 70 watts.

Reflectance measurements of selected samples were obtained with the 521 Perkin-Elmer Spectrophotometer in the wavelength range from 2.5 to 35 microns. Comparative emittance data were taken by a steady-state heat-balance method with a carbon-arc solar simulator (ref. 1). The hemispherical total emittance and the ratio of normal solar absorptance to hemispherical total emittance were measured at room temperature in vacuum.

PROCEDURE

Careful cleaning and handling of the substrates was essential to produce good coatings. The epoxy-coated substrates were cleaned with cotton that was soaked with 25-percent OT aerosol, rinsed with distilled water, and dried in vacuum. Before coating, they were dusted with clean, dry inert gas.

The samples were mounted on the water-cooled plate directly over the sources. A rotating shutter was located so that the film-monitor reflector disk would not be obstructed when the substrate was masked (see fig. 2). The silicon monoxide charge was heated to 800° C in a vacuum of 10^{-5} torr for 15 minutes to eliminate impurities. A cylindrical, steel heat shield, 61 centimeters high by 41 centimeters in diameter and open at the top, was used to protect the glass bell jar. The sample surface was then cleaned for 30 minutes by ionic bombardment in a 5×10^{-3} torr partial pressure of oxygen. The glow discharge potential was 1000 volts. At the end of the discharge process, the system was evacuated to approximately 1.5×10^{-6} torr.

For each run, 4 grams of 99.999-percent aluminum wire segments were distributed uniformly on the filaments. The filament temperature for the aluminization was established by slowly increasing the power setting to prevent premature charge vaporization. At a power level of 510 watts, deposition rates of approximately 300 Å per second were achieved (samples 11 to 13, table I). Synchronous motions of the shutter plate and film monitor reflecting disk were required in order to deposit only one opacity thickness of aluminum that was estimated at 500 Å from data by Vasicek (ref. 2) and 600 to 700 Å by Hass (ref. 3, p. 338). Interferometric measurements of aluminum films, which were simultaneously deposited on glass surfaces, yielded film thicknesses in this range. The

bell jar pressure increased to about 8×10^{-6} torr during the aluminum vaporization but subsequently decreased to 1.5×10^{-6} torr. At this time, water flow was started through the substrate holder.

For the silicon monoxide evaporation, 50 grams of silicon monoxide (Kemet select grade, 10 mesh) was further pulverized before use. Filament power for the silicon monoxide evaporation was established at 70 watts. At this power level, the initial oxide deposition rate was 2 Å per second. The aluminized sample remained masked. Dry oxygen was admitted to the bell jar, and the pressure was regulated at 1.2×10^{-4} torr with a needle valve. Several quarter wavelengths of partly oxidized silicon monoxide were deposited on the optical monitor before the aluminized substrate was unmasked. The film thickness, as a function of time, is shown for two samples in figure 4. Substrated temperatures were maintained at about 50° C during depositions. The time required to deposit 1.1 microns of silicon oxide was generally 3.5 hours. After the deposition was completed, special care was taken to maintain the sample at 50° C or lower.

Reflectance and emittance measurements were taken as soon as possible after the sample was removed from the system in order to detect subsequent changes in the coatings.

RESULTS AND DISCUSSION

The formation of satisfactory mirror films is dependent not only on evaporation conditions during the deposition of the reflecting surfaces but also on the condition of the substrate surface. The epoxy was sprayed onto polished magnesium plates, and the polymer film was then cured. The coatings were clear; blemishes and defects could be observed only with considerable difficulty. However, after the aluminum film was deposited, hazing, pits, and glove marks were readily apparent. A representative sampling of the evaporations performed is given in table I.

The first five samples in table I were films of poor quality exhibiting crinkles, fissures, and pits. In the first set of runs, the substrates were not cooled; they reached temperatures over 130° C because of thermal radiation from the source. In many of these runs, crinkling of the aluminum films occurred. Figure 5 shows an example of crinkling and fissuring (sample 1). This type of deformation of the aluminum (and overcoating of silicon oxide) resulted when the sample was rapidly cooled from the high temperature experienced during the deposition of the silicon oxide. The high temperature was characteristic of the uncooled substrate and the constant rate of silicon oxide deposition. Under the latter condition, the silicon monoxide charge nearest the filament heater was converted in part to silica residues with the result that additional heat was required to maintain a constant deposition rate. Water cooling the substrate holder and using the

constant rate of silicon oxide deposition prevented the aluminum films from crinkling but did not eliminate the tendency of the films to fissure (e.g., samples 4 and 5, table I).

An example of fissuring is shown in the photograph of sample 2 in figure 6 at a magnification of 75. The fissuring resulted from the unequal expansion of the magnesium and epoxy due to the high temperatures during the silicon oxide deposition. When the stresses exceeded the tensile strength, permanent deformation by fissuring occurred. To relieve a portion of the stress built up during the deposition of silicon oxide at a constant rate, a decreasing deposition rate was tried. The appropriate power was applied to the silicon monoxide source to establish the initial deposition rate, and the evaporation proceeded without any change in the power setting. The net result was a decreasing rate of deposition and a lower epoxy surface temperature. Another beneficial effect of the slower growth rate was to provide additional time for the inherent stresses to anneal. The resulting mirror film shown in figure 7 was excellent except for the pits. The pits are very shallow depressions resulting from inadequate epoxy curing.

The use of more extensively cured epoxy substrates with the decreasing deposition rate of silicon oxide produced excellent mirrored surfaces (samples 8 to 10, table I). Samples 8 and 10 are shown in figures 8 and 9, respectively. It should be noted, however, that sample 5, which was made with a well-cured epoxy substrate but with a constant silicon oxide deposition rate, has a fissured mirror surface.

Optical Measurements

The spectral emissivity for a typical uncoated aluminum film and a silicon oxide coated mirror are shown in figure 10. The curves were calculated from the spectral reflectivity measurements by Kirchoff's relation for an opaque specimen: spectral normal emissivity is equal to one minus the spectral normal reflectivity. For these samples, the spectral reflectivity was obtained on a Perkin-Elmer Model 521 Spectrophotometer between 2.5 and 35 microns.

The values of total hemispherical emittance $\epsilon_{T,h}$ for these samples are shown in table II. They were calculated in the following manner. First, the spectral emissivity data were extrapolated from 35 to 50 microns (see fig. 10). The total normal emittance was then calculated by the method indicated in reference 4. These values were converted to total hemispherical emittance by the relations given in reference 5. The calculated emittance data compare favorably with those experimentally obtained for the same sample by the steady-state heat-balance method of Curtis and Nyland (ref. 1).

Data on similar samples obtained by other investigators are contained in table II. The extremely low $\epsilon_{T,h}$ value of 0.011 reported by Drummeter and Hass (ref. 3, p. 338) is for a freshly prepared aluminum surface under optimum conditions.

Equilibrium Temperatures of Mirror in Space

The equilibrium temperature of the solar collector will depend on the thermal properties of both the front and back surfaces. A sample calculation was made to illustrate this point. The position of the mirror in the space environment is shown in figure 11. The following assumptions were made to simplify the calculations:

(1) The mirror is oriented with respect to the sun, and the back side is exposed to the temperature of outer space, 0° K.

(2) The areas of the front and back are equal, $A_1 = A_2$.

(3) $T_1 = T_2$.

A heat-balance equation can then be written for the mirror:

$$\underset{\text{Heat absorbed}}{Q_s \alpha_1 A_1} = \underset{\text{Heat rejected (front)}}{\epsilon_1 A_1 \sigma T_1^4} + \underset{\text{Heat rejected (back)}}{\epsilon_2 A_2 \sigma T_2^4} \tag{1}$$

$$Q_s \alpha_1 = \epsilon_1 \sigma T_1^4 + \epsilon_2 \sigma T_2^4 \tag{2}$$

$$Q_s \alpha_1 = \sigma T^4 (\epsilon_1 + \epsilon_2) \tag{3}$$

and finally, solving for the temperature,

$$T = \left[\left(\frac{0.135}{5.67 \times 10^{-12}} \right) \left(\frac{\alpha_1}{\epsilon_1 + \epsilon_2} \right) \right]^{1/4} \tag{4}$$

where

A	area
Q_s	heat received from Sun
T	temperature
α	absorptance
ϵ	emittance
σ	Stefan-Boltzmann constant

and the subscripts 1 and 2 refer to the front and back surfaces of the mirror, respectively.

In equation (4), the relation between the thermal properties of the surfaces and the temperature of the collector is shown. Thus, the temperature not only will depend on the properties of the sun-side surface but will be controlled to a marked degree by the dark-side emittance. In table III, the overcoating of aluminum with silicon oxide increases α_1 to 0.14 and ϵ_1 to 0.43 to produce an interesting relation. Although the thermal properties of the front surface have been improved greatly, the temperature of the mirror is controlled to a larger extent by the emittance of the back side. Thus, for all values of $\epsilon_2 > 0.45$, the temperature of the mirror will increase when silicon oxide covers the aluminum surface. It is only for the cases where the back side is reflective, $\epsilon_2 < 0.45$, that the temperature will be decreased by a front coating of silicon oxide. Therefore, from a temperature standpoint, the higher emittance attainable on the back side will yield the lowest equilibrium temperatures. These high emittances can be obtained by painting the back side with almost any thermal-control paint.

If equilibrium temperatures for the actual solar collector in space are required, the flat-plate model must be replaced by the actual paraboloid collector. Also a correction must be introduced to account for the blocking of solar energy by the receiver of the heat engine and for any reradiation to the collector.

CONCLUSIONS

A method was developed to deposit aluminum and silicon oxide films sequentially on epoxy-coated magnesium substrates for use as solar collectors. The following factors were considered to be of prime importance to produce coatings of high optical quality:

1. Completely cured epoxy resin
2. Careful cleaning and handling of substrates
3. Substrates cooled during the deposition of aluminum and silicon oxide
4. Silicon oxide deposited by a decreasing rate of deposition

Optically, the silicon oxide film increased the aluminum-mirror emittance from 0.06 to 0.43 while the normal absorptance remained nearly unchanged.

Calculations showed that the increased emittance would lower the equilibrium temperature of a mirror in space only if the emittance of the back surface was less than 0.45.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 19, 1966,
120-33-06-04-22.

REFERENCES

1. Curtis, Henry B.; and Nyland, Ted W.: Apparatus for Measuring Emittance and Absorptance and Results for Selected Materials. NASA TN D-2583, 1965.

2. Vašíček, Antonín (Mrs. H. Watney-Kaczér, trans.): Optics of Thin Films. Interscience Publishers, 1960, figure 87.

3. Drummeter, Louis F., Jr.; and Hass, Georg: Solar Absorptance and Thermal Emittance of Evaporated Coatings. Physics of Thin Films. Vol. 2 of Advances in Research and Development. Georg Hass and R. E. Thun, eds., Academic Press, 1964, pp. 305-361.

4. Liebert, Curt H.: Spectral Emittance of Aluminum Oxide and Zinc Oxide on Opaque Substrates. NASA TN D-3115, 1965.

5. Dunkle, R. V.: Emissivity and Inter-reflection Relationships for Infinite Parallel Specular Surfaces. Symposium on Thermal Radiation of Solids. NASA SP-55, 1965, pp. 39-44.

6. Curtis, Henry B.: Measurement of Emittance and Absorptance of Selected Materials Between 280° and 600° K. J. Spacecraft Rockets, vol. 3, no. 3, Mar. 1966, pp. 383-387.

TABLE I. - DEPOSITION PARAMETERS

Sample	Epoxy-film quality	Temperature, °C		Deposition rates, Å/sec				Film thickness, μ		Film quality
		Silicon monoxide charge	Substrate holder	Aluminum	Silicon oxide			Aluminum	Silicon oxide	
					Constant	Decreasing				
						Initial	Average			
1	Pitted	817	~130	88	1.5	---	----	0.06	0.55	Pitted, fissured, crinkled
2		821	~130	55	3.1	---	----		.39	Pitted, fissured
3		833	~130	82	1.9	---	----		.55	Pitted, fissured, crinkled
4		904	50	114	2.0	---	----		1.1	Pitted, fissured
5	Smooth	859	50	95	2.1	---	----		1.1	Fissured
6	Pitted	834	42	114	---	1.9	0.81		1.1	Pitted
7	Pitted	842	49	111	---	2.1	.83		1.1	Pitted
8	Smooth	822	54	122	---	2.0	1.4		1.1	Smooth
9		789	49	119	---	1.7	1.0		1.1	
10		805	41	120	---	1.7	1.0		1.1	
11		---	----	330	---	---	----		----	
12		---	----	280	---	---	----		----	
13		---	----	240	---	---	---		----	

TABLE II. - EMITTANCE AND ABSORPTANCE FOR MIRROR SURFACES

Source	Sample (from table I)	Composition, μ		Total normal absorption, α_s	Total hemi-spherical emittance, $\epsilon_{T,h}$	Temperature, T, ^{o}C	Absorptance to emittance ratio, α/ϵ
		Aluminum	Silicon oxide				
(a)	----	0.06	---	0.08	----	----	----
Ref. 6	----	1.0	---	----	0.06	25	----
(a)	8	.06	1.1	.18	.43	35	0.42
(a)	10		1.1	.14	.43	35	.32
(a)	10		1.1	.14	.43	44	.33
(a)	10		1.1	.14	.44	54	.31
Fig. 10	----		---	----	.04	25	----
Fig. 10	8	----	1.1	----	.40	25	----
Ref. 6	----	.10	1.1	.13	.26	27	.50
Ref. 3, p. 338	----	.06	---	.082	.011	27	7.5
Ref. 3, p. 351	----	(b)	1.1	.12	.25	27	.48

[a]Method of ref. 1.
[b]Film.

TABLE III. - CALCULATED MIRROR TEMPERATURES

Absorptance of the front surface, α_1	Emittance		Temperature T, ^{o}K
	Front surface, ϵ_1	Back surface, ϵ_2	
Uncoated aluminum			
0.08	0.05	0.05	372
		.20	296
		.45	248
		.70	224
		.93	210
Silicon oxide coated aluminum			
0.14	0.43	0.05	289
		.20	270
		.45	248
		.70	234
		.93	222

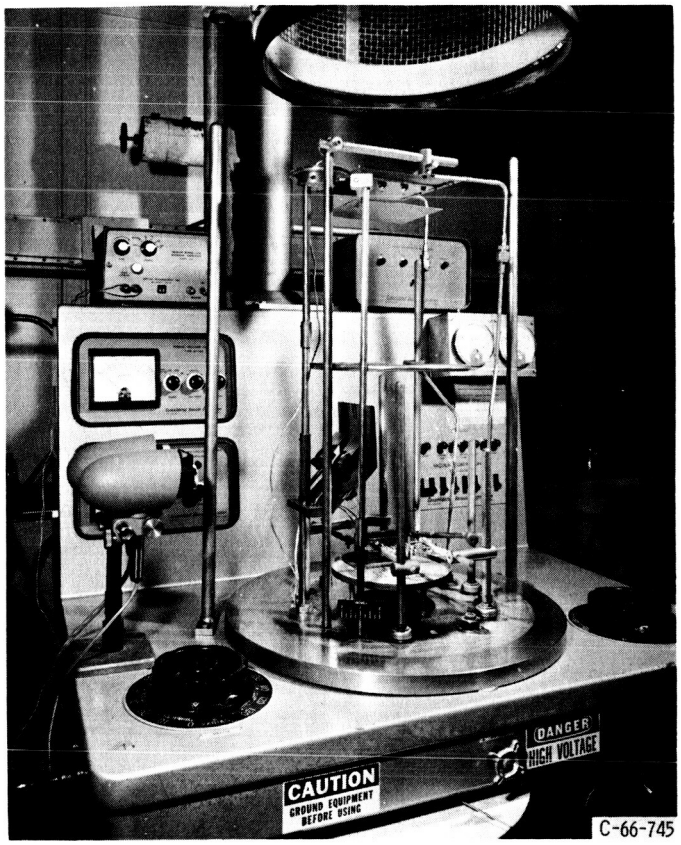

Figure 1. - Glass-enclosed vacuum metallizing system.

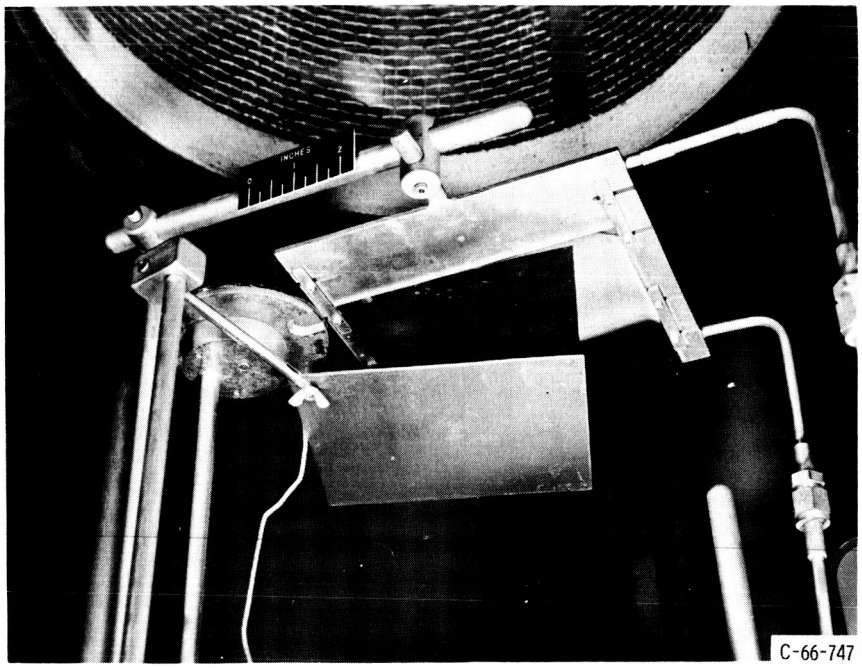

Figure 2. - Substrate holder, optical film monitor, and shutter assembly.

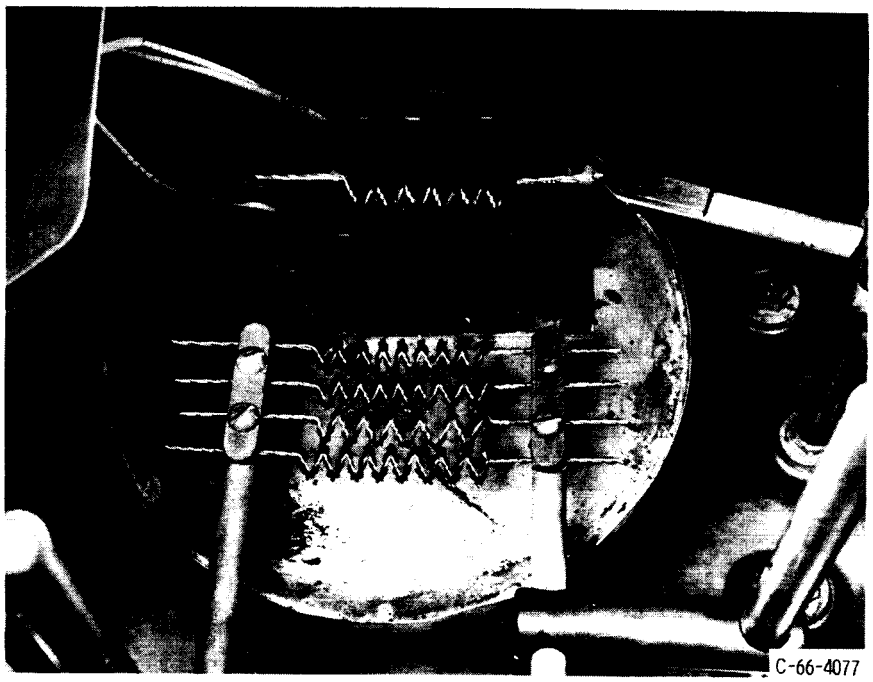

Figure 3. - Aluminum and silicon monoxide evaporation sources.

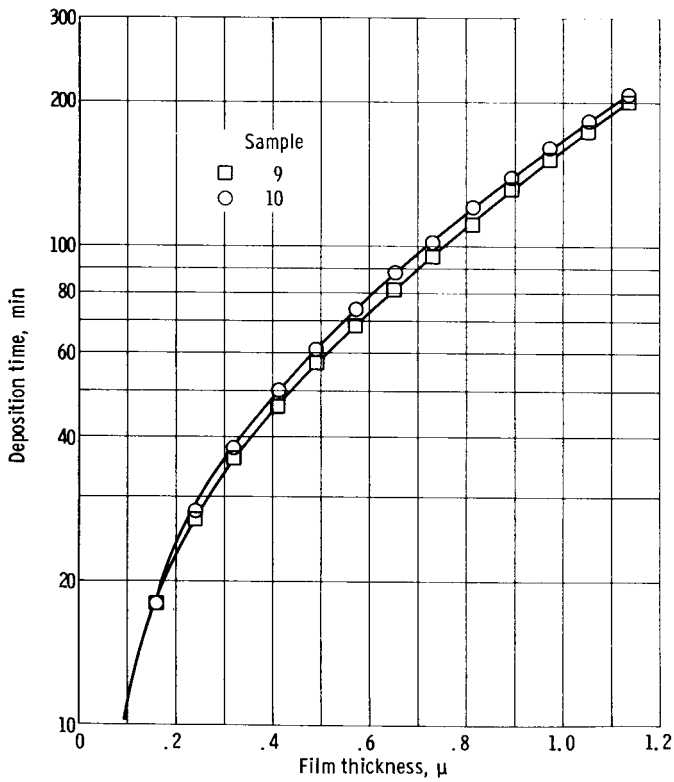

Figure 4. - Deposition rate of silicon oxide.

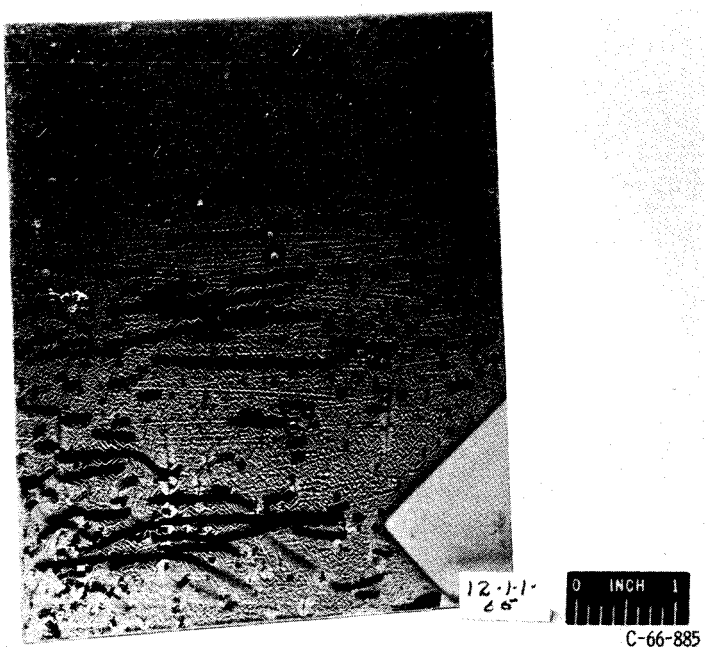

Figure 5. - Crinkles and fissures in reflective surface. Sample 1.

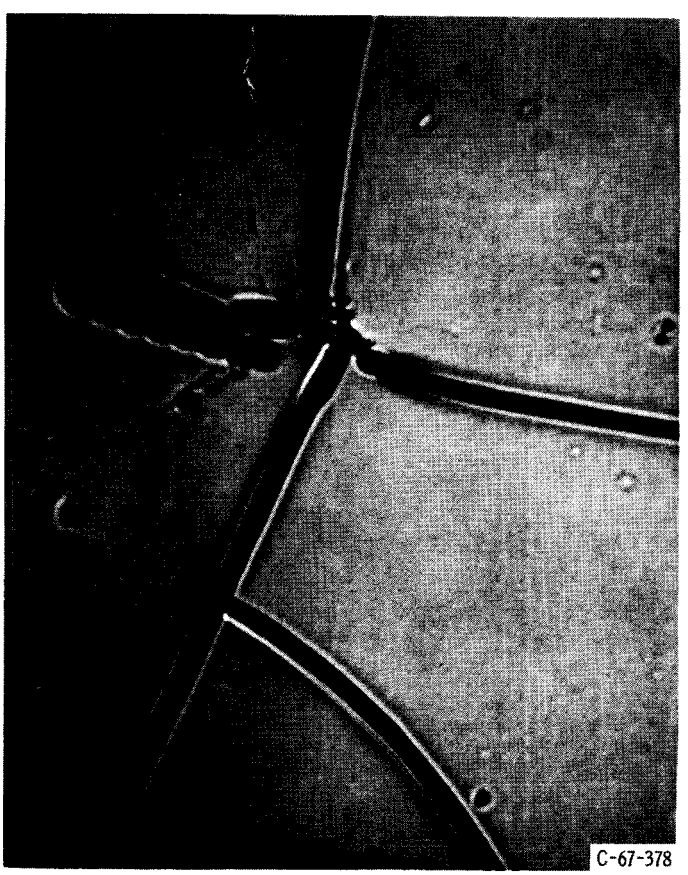

Figure 6. - Extensive fissuring of reflective surface. Sample 2. X75.

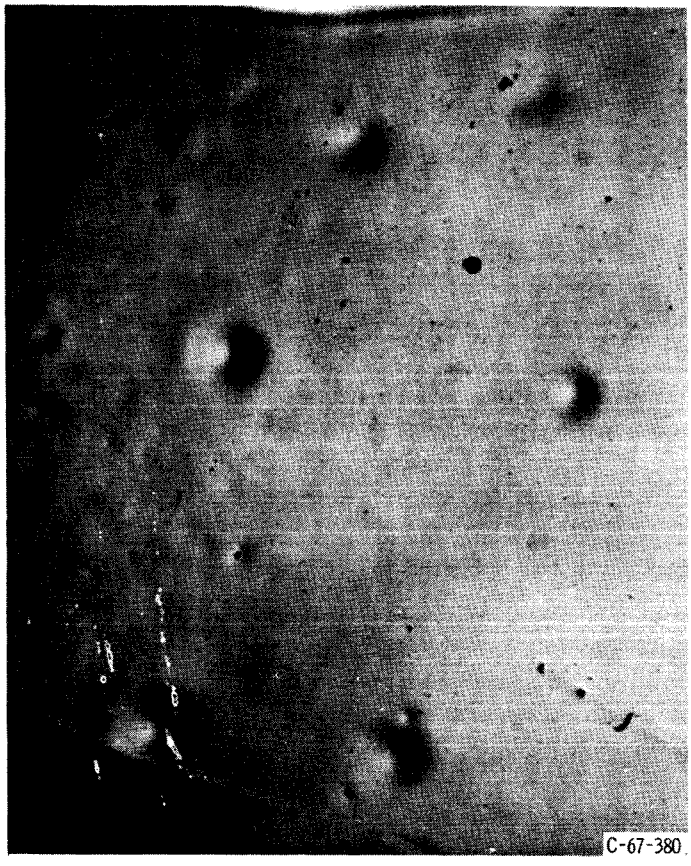

Figure 7. - Pitting in reflective surface. Sample 7. X75.

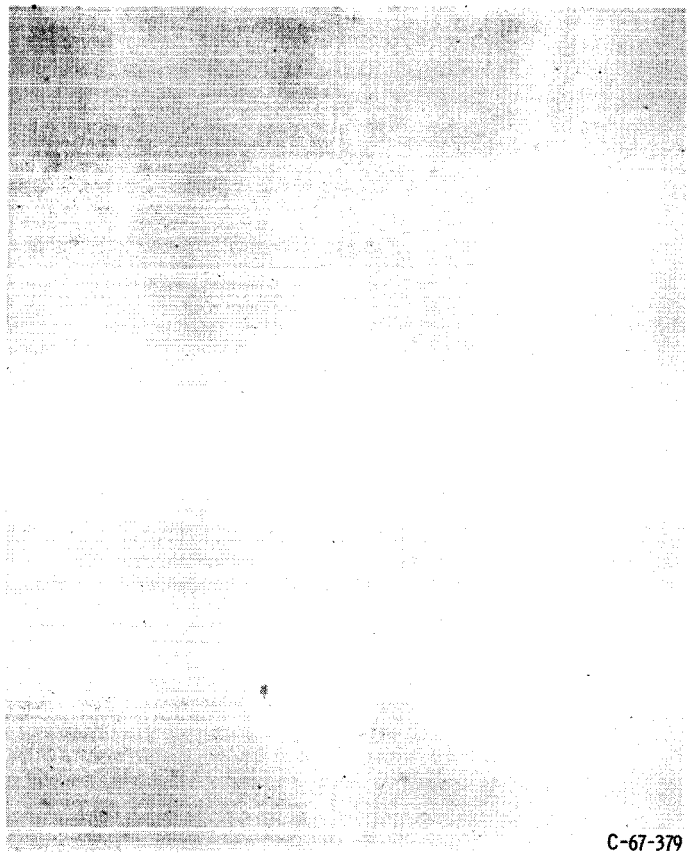

Figure 8. - Excellent reflective surface. Sample 8. X75.

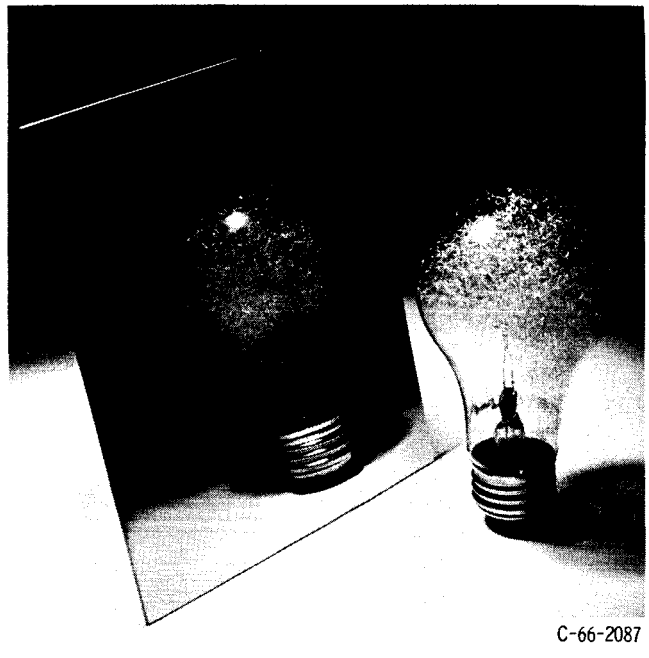

Figure 9. - Uniform reflective surface. Sample 10.

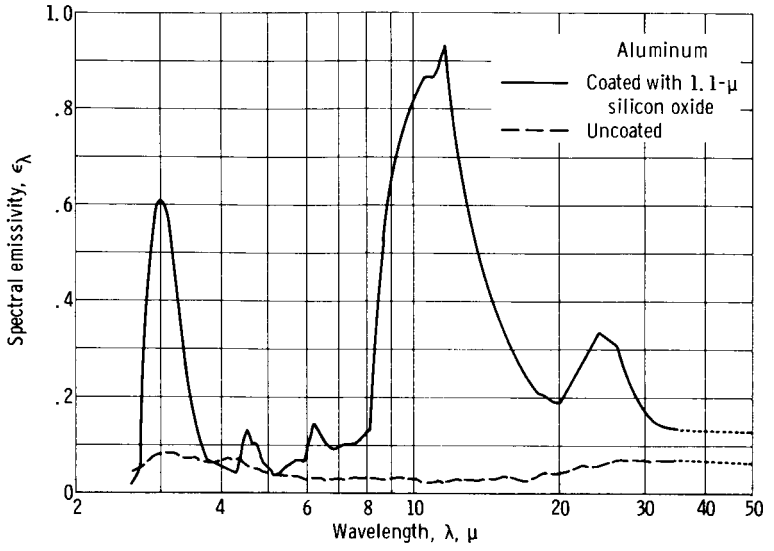

Figure 10. - Spectral emissivity of reflector surfaces.

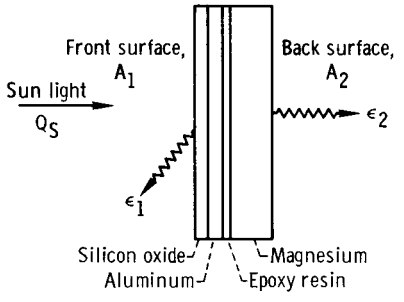

Figure 11. - Solar collector model.

NASA-Langley, 1967 —— 3 E-3729