THIN FILMS OF GAS-EVAPORATED Co FOR USE IN PHOTOTHERMAL CONVERSION

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Abstract.- Selective surfaces for an efficient solar energy photothermal conversion were obtained by evaporation of Co in a gaseous atmosphere. A bell jar system was used with a Tungsten basket and a gas mixture consisting of oxygen and helium. Using a KBr substrate we performed spectral measurements of the transmittance from 0.38 μm to 20 μm obtaining $\lambda_c \simeq 2.5$ μm. The film observed in a transmission electron microscope revealed a small particles structure for which the filling factor was measured. The results justified the application of the Maxwell Garnett theory.

1. Introduction.- An efficient photothermal solar energy conversion requires a high absorptivity for $\lambda < 2.5$ μm and a low thermal emissivity for $\lambda > 2.5$ μm. Electrodeposition of some transition metals onto reflecting substrates /1-3/, chemical treatments of metals /1/, chemical vapour deposition of interferometric multilayers /4/, sputtering /5/ and evaporation /6/ are some of the known methods to get the desired properties.

In the last years gas-evaporation of some transition metals /7/ has been used as an alternative technique to produce selective films, without the complicating influence of an opaque substrate. Although these systems do not as yet have practical applications, they serve as an excellent basis for studies on the selectivity mechanism.

In this work we show the results of selective surfaces produced by gas-evaporation of Co in an atmosphere consisting of 1 torr of O_2 and 10 torr of He. We describe the film production technique, its spectral transmittance from 0.38 μm to 20 μm, its structure and chemical composition, as well as the influence of a heat treatment on its properties. The data suggest the applicability of the Maxwell Garnett theory and the predictions are compared with the experimental transmittance spectral data.

2.Experimental Procedure.- 2.1. Equipment Description.- The samples were produced in a simple bell jar evaporator with an entry for gas, an outlet for a mechanical pump, three gauges for high (Edwards Penning 8), middle (Varian NRC 802A) and low (Edwards Speedivac C.G. 3) vacuum and

two feedthroughs connected to a variac and a current transformer (60A, maximum). The spectral transmittance (normal incidence) was measured from 0.38 μm to 2.5 μm in a Zeiss DMC 25 single beam spectrophotometer and from 2.5 μm to 20 μm in a Perkin-Elmer 180 double beam spectrophotometer. The structure and chemical composition were determined with a Hitachi HU 12 transmission electron microscope. The mass was measured with an analytical balance (Mettler H20T) and the thickness was evaluated with an optical microscope (Nikon Apophot HM) by focusing successively the top and the bottom of the film.

2.2. Film Preparation.- The Co (purity ⩾ 99 %) was evaporated from a heated tungsten filament. In order to get a gas mixture to produce the intended coatings, several preliminary tests were performed : combinations of oxygen and argon or other partial pressures of O_2 and He were used. The desirable properties were obtained using a gas pressure of 1 torr of O_2 and 10 torr of He. Sootlike deposits were collected 4 cm above the source onto a KBr plate for transmittance measurements, a carbon covered copper grid for transmission electron microscopy and a glass for determination of the mass and the film thickness. No control of the temperature and the evaporation rate was made. The dc measurements of the samples resistivity were larger than $10^4 \Omega m$, which indicates that the Co particles are electrically disconnected.

2.3. Determination of the Optical Parameters, Structure and Chemical Composition of the Films.- In figure 1 we show the transmission spectrum for samples with different mass per unit area values (W/A).

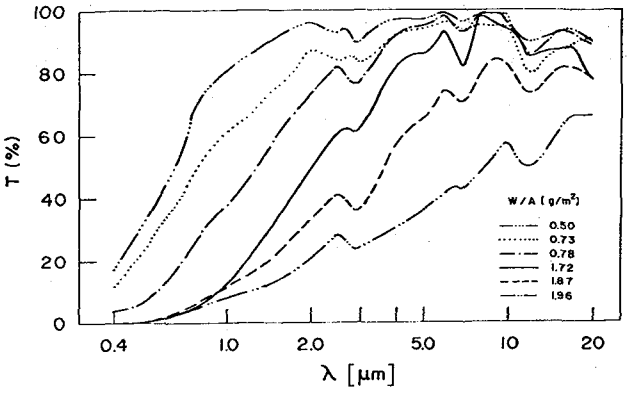


Fig. 1.- Transmittance versus wavelength for Co films produced in the presence of 1 Torr of O_2 and 10 Torr of He with mass density W/A

As can be seen they all exhibit a cut off frequency λ_c which shifts to the infrared as W/A increases. The absorption observed near 3 μm is characteristic of absorbed water and those at around 7 μm and 12 μm are due to the presence of CoO /9,10/. In order to evaluate the solar absorptance (a) and the thermal emittance [e(T)] we considered a coating with mass density W/A on a perfectly specular substrate ; the reflectance of this tandem is equal to the transmittance of a film having mass density 2W/A. For example for the sample with W/A = 1.72 g/m^2 we found a = 0.89 and e(320°C) = 0.15.

The transmission electron microscope pictures (Fig. 2) show that the particles are aggregated into chains and clusters.

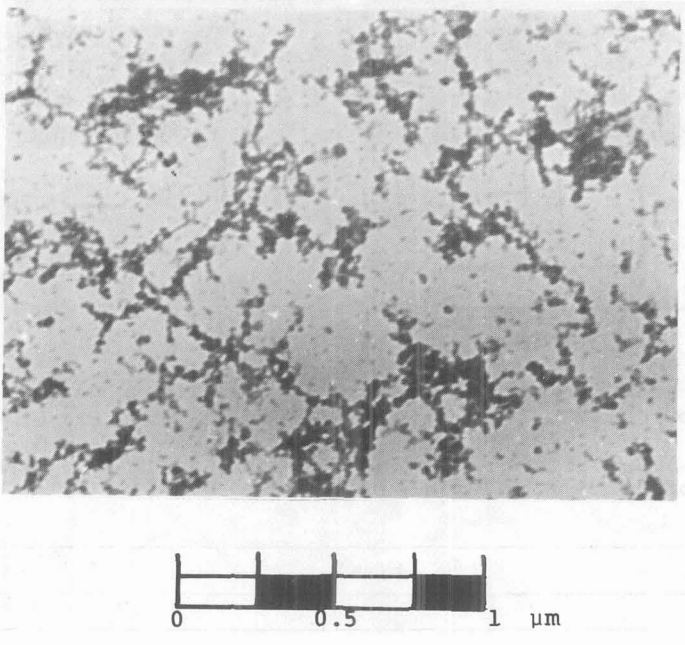


Fig. 2.- Transmission electron micrograph for a Co film produced by gas-evaporation. The voltage of the electron microscope was 75 KV

The electron diffraction pattern, obtained with the same apparatus reveals that the films contain fcc Co and fcc CoO, as can be seen in figure 3. These results were confirmed by an X-ray diffraction pattern.

The volume fraction of metal in the deposit (f) was obtained from $f = (WA)(\rho t)^{-1}$, where $\rho = 8.71$ g/cm^3 /11/ is the Co bulk density and t is the film thickness. We assumed that the amount of CoO is much smaller than Co metal. In Table I we show the values of these quantities for

several samples.

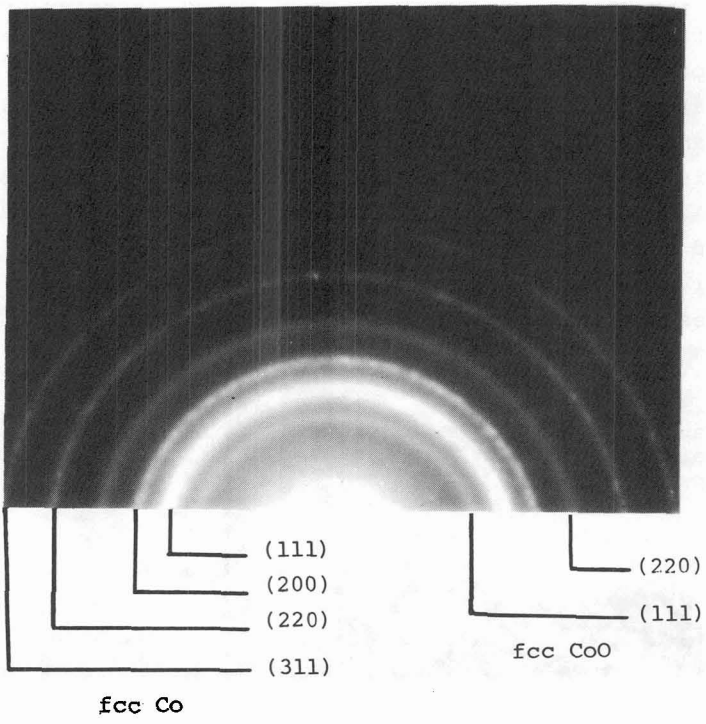


Fig. 3.- Electron diffraction pattern of the film showing lines of fcc Co and fcc CoO

TABLE I : Mass density (W/A), thickness (t) and filling factor (f) for the samples produced with $P(O_2)$ = 1 torr and P(He) = 10 torr

$I/A(g/m^2)$	t(μm)	f ± Δf(%)
0.50	2	2.9 ± 1.5
0.73	4	2.10 ± 0.56
0.78	6	1.49 ± 0.36
1.72	18	1.1 ± 0.1
1.87	29	0.74 ± 0.13
1.96	31	0.726 ± 0.076

2.4. Heat Treatments.- Finally, we put a sample in a furnace containing air which was heated for periods of 8 hours successively at 100°C, 150°C and 200°C. At 200°C breakdown in the selectivity was observed (Fig. 4). At the same time, the structural and chemical properties of the film gradualy changed : bigger clusters were formed (Fig. 5a-d) and all of the Co was transformed into CoO (Fig. 6a-d)

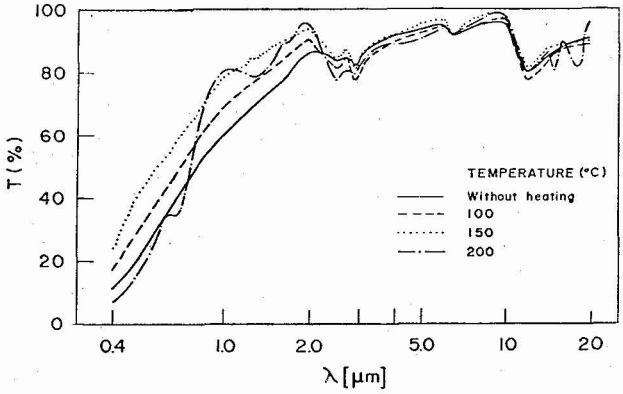
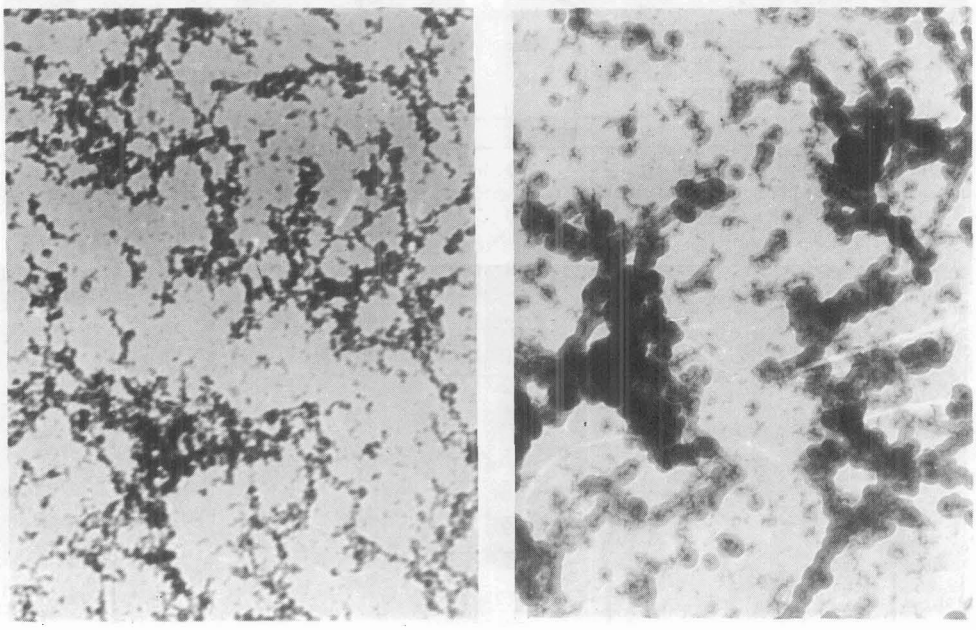


Fig. 4.- Transmittance versus wavelength of a sample with W/A = 0.73 g/m^2 under heat treatments in air at 100, 150 and 200°C during 8 hours at each temperature



a b

Fig. 5.- a- without heating ; b- 100°C

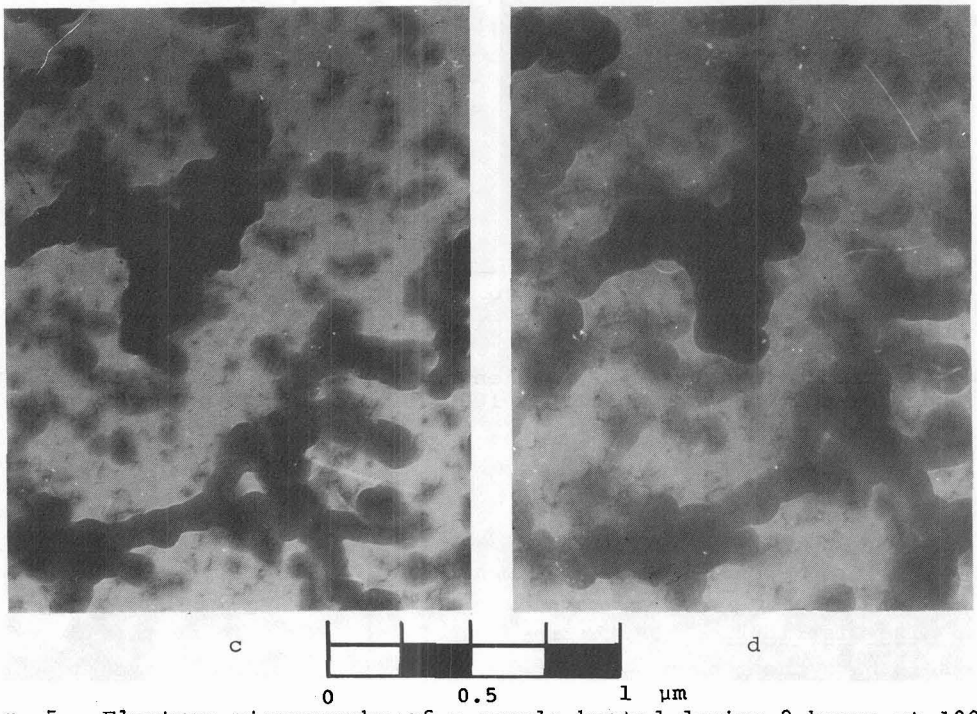


Fig. 5.- Electron micrographs of a sample heated during 8 hours at 100, 150 and 200°C , c - 150°C ; d - 200°C.

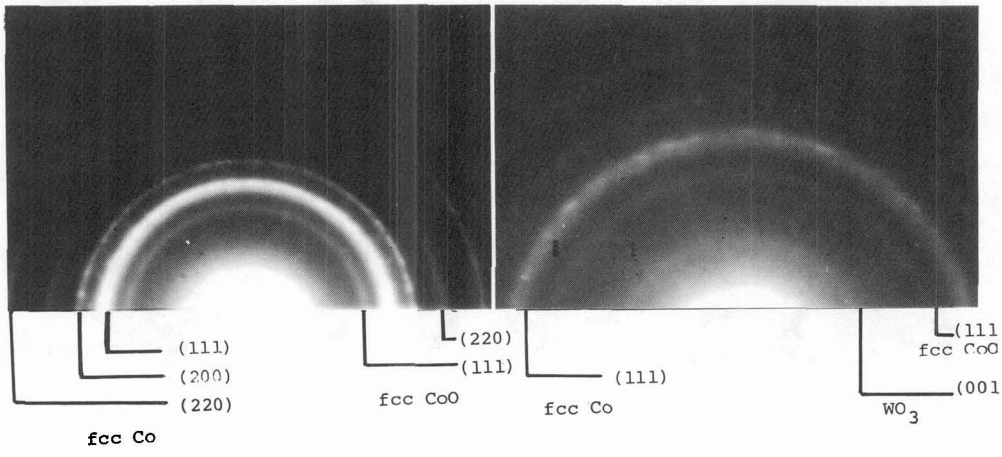
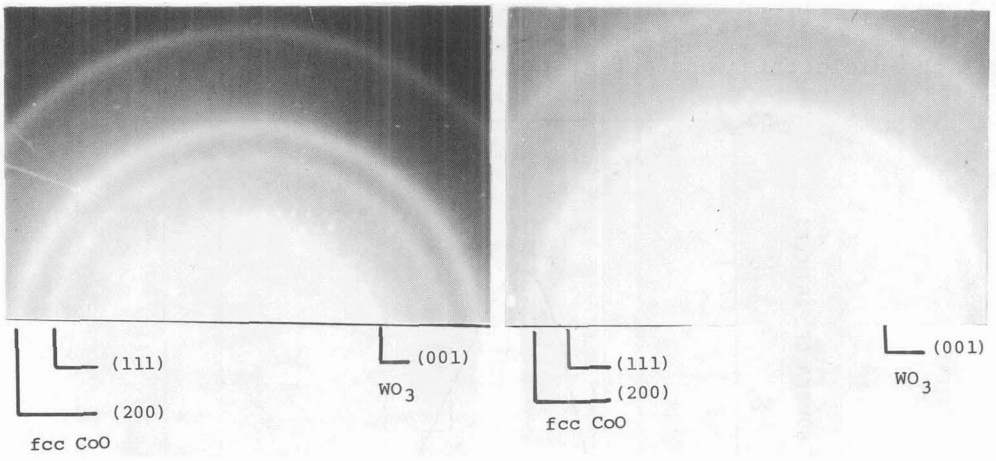


Fig. 6.- a - without heating ; b - 100°C.



c d

Fig. 6.- Electron diffraction patterns of a sample heated during 8 hours at 100, 150 and 200°C. c - 150°C ; d - 200°C.

2.5. Size Distribution.- Particles evaporated from a metal in a gas atmosphere have the tendency to grow by binary collisions accompanied by liquid-like coalescence /12/. As a consequence of this mechanism a log-normal distribution is expected for the particles sizes in the film, as given by the following equation (1)

$$\Delta n = \frac{1}{(2\pi)^{1/2} \ell n\sigma} \exp\left[-\frac{1}{2}\left(\frac{\ell n(x/\bar{x})}{\ell n\sigma}\right)^2\right] \Delta(\ell nx) \qquad (1)$$

where Δn is the fractional number of particles per logarithmic diameter interval $\Delta(\ell nx)$, $\bar{x}$ and σ are respectively the average diameter and the geometrical standard deviation of the particle sizes.

In figure 7 we show that the curve predicted by equation (1) is in a good agreement with the experimental histogram.

3. Application of the Maxwell Garnett theory.- The successful application of the effective medium model of Maxwell Garnett to metal films produced by gas-evaporation is widely known /13/ ; it requires two conditions : the diameter of the particles should be smaller than the wavelength ($\lambda \gg a$) and a small filling factor ($f \ll 1$).

The average complex dielectric constant ($\bar{\varepsilon}$) calculated by the Maxwell Garnett model gives for isolated spheres in air

$$\bar{\varepsilon} = \frac{1 + \frac{2}{3} f\alpha}{1 - \frac{1}{3} f\alpha} \qquad (2)$$

$$\text{with} \quad \alpha = \frac{\varepsilon - 1}{1 + \frac{1}{3}(\varepsilon - 1)} \tag{3}$$

ε is the dielectric constant of the spheres.

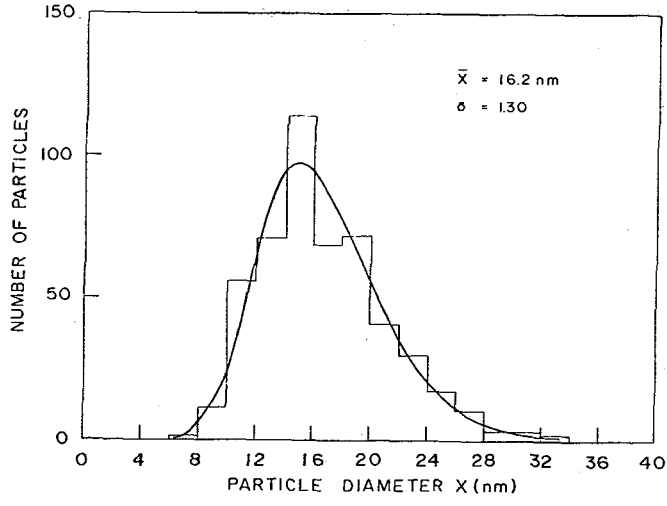


Fig. 7.- Number of particles versus diameter. The histogram was based on a counting of 500 particles. The superposed curve was calculated using the described log-normal distribution for the shown values of $\bar{x}$ and σ. The area under the log-normal plot is equal to the area under the histogram

The electron micrographs show particles isolated or aggregated into chains and clusters. In order to take in account this state of agglomeration equation (3) has to be modified by introducing a new factor α^*, which represents a dipole-dipole interaction /14/ between the particles given by

$$\alpha^* = \frac{1}{3} \sum_{i=1}^{3} \frac{(\varepsilon-1)}{1+L_i^*(\varepsilon-1)}$$

In Table II we give the values of the triplets Li^* for different geometrical configurations of identical spheres.

TABLE II : Effective depolarisation factors Li^* for different geometrical configurations (from Ref. /13/)

Geometrical Configurations	L_1^*	L_2^*	L_3^*
isolated spheres	0.333	0.333	0.333
double spheres	0.250	0.375	0.375
single linear chains	0.133	0.435	0.435
double linear chains	0.139	0.342	0.518
fcc clusters	0.0865	0.0865	0.827

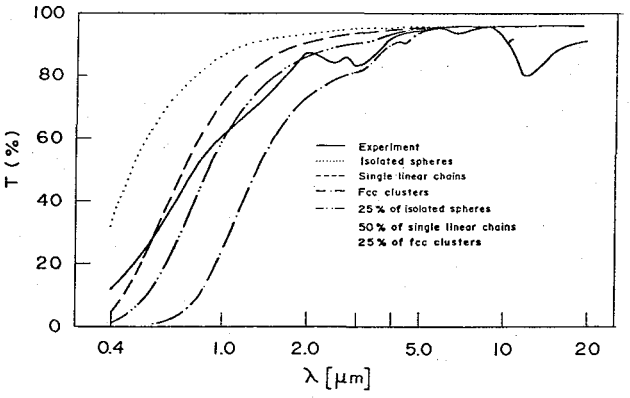


Fig. 8.- Transmittance versus wavelength from calculations based on the Maxwell Garnett theory for a sample with W/A = 0.73 g/m^2 and f = 0.021.

In figure 8 we show the results of the spectral transmittance calculated for a sample with W/A = 0.73 g/m^2 assuming the following configurations : isolated spheres, single linear chains and fcc clusters. Double spheres and double linear chains give, respectively, results very similar to single spheres and single linear chains. A more consistent approach based on the electron micrographs is to consider a combined structure. Assuming 25 % of isolated spheres, 50 % of single linear chains and 25 % of fcc clusters a satisfactory agreement with the experimental results was obtained. Progressively larger discrepancies between the theoretical results and the experimental transmittance data were found for samples with larger values of W/A.

4. Summary and Conclusion.- Selective surfaces for an efficiency solar energy conversion were obtained by evaporation of Co in a gas mixture consisting of 1 torr of O_2 and 10 torr of He. Transmission electron microscopy showed isolated particles, chains and clusters. Electron diffraction patterns determined that the film consisted of Co and CoO. Heat treatments during 8 hours at 100, 150 and 200°C in a sample caused the breakdown in the selectivity at 200°C besides changing its structural and chemical properties. The Maxwell Garnett formalism, including the effect of aggregation of the particles was applied. Considering a combined structure of isolated spheres, single linear chains and fcc clusters we obtained satisfactory agreement between theory and experimental data.

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