

and Mo type oxides are similar. Hence cobalt oxide have NaCl type crystal structure. But very few reports are available on the optical, thermal properties of the cobalt oxide thin films.

CHAPTER III

STUDIES ON COBALT OXIDE COATINGS AS SOLAR ABSORBER

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3.1 INTRODUCTION

In the previous chapter the deposition of cobalt oxide on various substrates is discussed. The optimized parameters were used for the deposition. The deposited films were tested for the solar thermal absorption. For this, small solar thermal absorber cells were designed and fabricated. Temperatures were measured. So here in this chapter the theoretical background of solar thermal conversion is discussed in section 3.2, the experimental setup is given in section 3.3 and the results are discussed in 3.4.

3.2 THEORETICAL BACKGROUND [3,4]

The conversion of thermal energy from solar radiation mainly depends upon the absorptance, emittance and reflectance of opaque, diffuse or specular surface. Solar absorptance and thermal emittance are two basic parameters for characterising the selective nature of various coatings.

3.2.1 Absorptance and Emittance

The absorptance ' α ' of a plane surface is the fraction of incident radiation which is absorbed by the surface. If the surface is opaque to the radiation then absorptance and reflectance sum is unity. Both absorptance and reflectance are functions of the wavelength of radiation

and the angle of incidence. Therefore monochromatic directional absorptance is defined as the fraction of the incident radiation of wavelength λ from the direction μ, Φ is the azimuthal angle. The expression for absorptance is given by -

$$\alpha_{\lambda} (\mu, \Phi) = \frac{J_{\lambda, a} (\mu, \Phi)}{J_{\lambda, i} (\mu, \Phi)} \quad \dots\dots 3.1$$

where 'a' and 'i' are subscripts used for absorbed and incident radiations and $J_{\lambda} (\mu, \Phi)$ is spectral irradiance of the radiation.

The emittance is described as the ability of a surface to radiate thermal power. It is the ratio of the radiancy of the surface to the radiancy of the black body at the same temperature and under the same conditions. While the spectral emittance is the ratio of the spectral radiance i.e. monochromatic radiancy at a given wavelength, from a surface to that of a black body at the same temperature. It is given by the expression -

$$\epsilon_{\lambda} = \frac{J_{\lambda}}{J_{b\lambda}} \quad \dots\dots 3.2$$

The spectral directional emittance of a surface is defined as the ratio of monochromatic intensity by a surface in a particular direction to the monochromatic intensity

emitted by a black body at the same temperature. It can be expressed as

$$\epsilon_{\lambda}(\mu, \Phi) = \frac{J_{\lambda}(\mu, \Phi)}{J_{b\lambda}(\mu, \Phi)} \quad \dots\dots 3.3$$

Hence the total emittance $\epsilon_t(\mu, \Phi)$ is defined as the ratio of the radiancy of the surface to the radiance of the blackbody at the same temperature and included all wavelengths from zero to infinity.

$$\begin{aligned} \epsilon_t(\mu, \Phi) &= \frac{\int_0^{\infty} \epsilon_{\lambda}(\mu, \Phi) J_{b\lambda} d\lambda}{\int_0^{\infty} J_{b\lambda} d\lambda} \\ &= \frac{1}{J_b} \int_0^{\infty} \epsilon_{\lambda}(\mu, \Phi) J_{b\lambda} d\lambda \quad \dots\dots 3.4 \end{aligned}$$

3.2.2 Reflectance

The problem of specifying the reflectance from a surface is more complex than the emittance and absorptance. The surface may be irradiated by radiations whose spectral intensity varies with the angle of incidence. Sometimes only spectral reflectance at the given angle of incidence may be sufficient, but in some instances the spatial as well as spectral distribution of reflected radiation is required. The ratio of the reflected intensity in the θ_r, Φ_r direction to that which is incident on a surface in the $\theta_i,$

Φ_i direction at wavelength λ is termed the σ "bidirectional spectral reflectivity". The expression for this is

$$\sigma_{\lambda}(\theta_r, \Phi_r; \theta_i, \Phi_i) = \frac{J_{\lambda r}(\theta_r, \Phi_r; \theta_i, \Phi_i)}{J_{\lambda i}(\theta_r, \Phi_r; \theta_i, \Phi_i)} \dots\dots 3.5$$

The bidirectional spectral reflectivity can be summed over the wavelength range to give the total reflectivity.

3.2.3 Relationship between Reflectance, Emittance and Absorptance

In order to avoid violation of second law of thermodynamics, the spectral absorptance must be equal to spectral emittance. For an opaque surface -

$$\alpha_{\lambda}(\mu, \Phi) = \epsilon_{\lambda}(\mu, \Phi) = 1 - \sigma_{\lambda}(\mu, \Phi) \dots\dots 3.6$$

By integration one gets that hemispherical characteristics. It can be expressed in same relation -

$$\alpha_{\lambda} = \epsilon_{\lambda} = 1 - \sigma_{\lambda} \dots\dots 3.7$$

Thus the spectral emittance and spectral absorptance can both be calculated from the knowledge of angular hemispherical reflectance.

3.2.4 Defects In CoO

Perturbed Angular Correlation (PAC) spectroscopy can be used to study defects in CoO. The PAC work on

cobaltous oxide (CoO) to investigate defects at high temperatures, where they exist in thermal equilibrium was studied by Th. Wenzel et al [70]. CoO crystalizes with the rocksalt structure having a lattice constant 4.26 Å.

The PAC method utilizes the hyperfine interaction between the magnetic quadrupole moment of an isomeric state of the probe nucleus and either the magnetic hyperfine field or the Electron Field Gradient (EFG) at the nuclear site.

In air CoO is stable only above 1220 K but it oxidizes to Co_3O_4 at lower temperatures. To stabilize the CoO phase below 1220 K the oxygen activity has to be reduced by many orders of magnitude, which consequently also changes the defect concentration. At 1180 K in air the Co_3O_4 phase boundary is reached. However, even at lower temperatures in the CoO phase could be realised by heating the sample in different gas mixtures.

When measuring temperature (T_m) was slowly lowered without quenching, distinct Electron Field Gradients (EFGs) were observed below 900 K. However, one enters the Co_3O_4 phase region during the experiments.

3.3 EXPERIMENTAL SET-UP

For the testing of cobalt oxide as solar thermal absorber, the substrates of aluminium and stainless steel

with the dimensions 3 cm X 5 cm were sprayed with the cobaltous acetate solution according to the optimized parameters. Here three different quantities of solutions viz. 100 ml, 150 ml, 200 ml mixed with 50 ml, 75 ml, 100 ml iso-propyl alcohol respectively were sprayed. Hence we got six sample substrates. For these six sample substrates the cell was designed.

3.3.1 Fabrication of cell

The schematic diagram of this cell is shown in Fig.3.1. The cell is a small plastic box. Its radius is 2.4 cm while the height is 1.6 cm.

The coated substrates were pasted on the cells with the help of araldite. For this purpose the suitable window for the cell was required. Here a small aluminium sheet of size 4.7 cm X 2.7 cm was taken. It was heated to a high temperature on heater. With the help of this hot small strip the windows in the lids of box were obtained. These lids were then pasted to the box by araldite. Here precaution was taken that the lid is leakproof.

When the lid was tightly fixed to the box. the substrates were then pasted with araldite in the similar manner. They were kept under pressure for the tight and also leakproof pasting of the coated substrates.

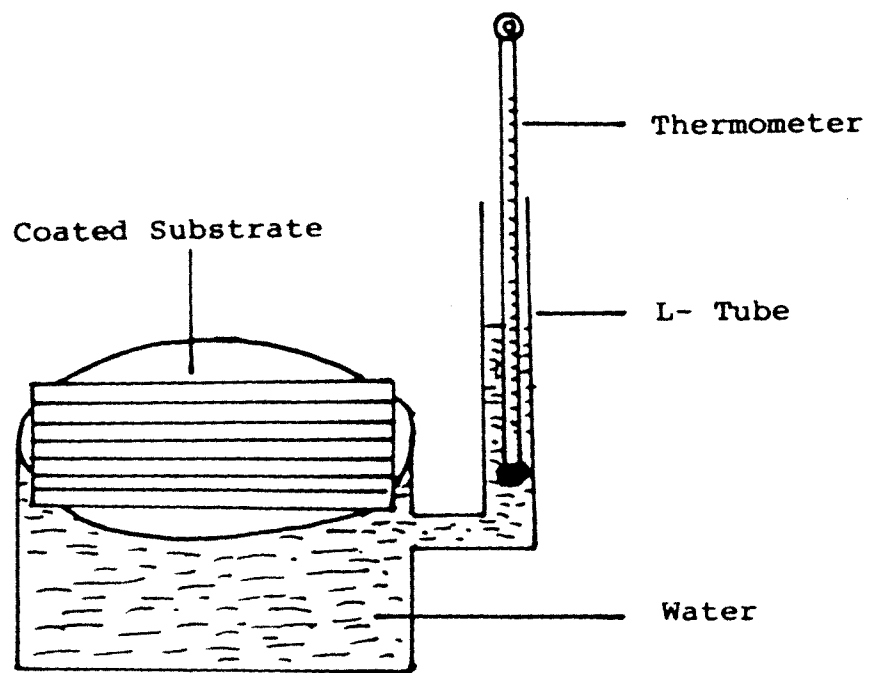


Fig. 3.1- Schematic Diagram of Absorber Cell

Now to measure the temperature of the liquid inside the cell, the cells were attached with L-shaped glass tubes. The tubes are 3 cm wide and 5 cm long. their inner diameter was 0.6 cm. It is suitable to keep the thermometer in it. These tubes were also attached to the cell with the help of araldite adhesive.

All the cells thus formed were again tested for leakage. No leakage was observed in any cell. So now tap water was filled in all cells. Nearly 28 ml of water was filled in each cell. The water level in the L.tube was kept just above the substrate level; so that water remains always in touch with lower surface of the substrate. Thus the cells were made ready for the observations.

3.3.2 Scheme of Observations

The numbers were given to cells with the substrates sprayed by different volumes of solutions. They were A-1, S-1 i.e. aluminium-1, stainless steel-1 respectively for 100 ml solution mixed with 50 ml isopropyl alcohol. Similarly A-2, S-2, A-3, S-3 are numbers for 150 ml, 200 ml solution sprayed respectively.

All these cells were then kept under the sun from 10.00 am to 4.00 pm. The Surya Mapi, to measure intensity of light in mW/cm^2 , was also kept with it. Temperature measurements and intensity readings were noted from 10.00 am to 4.00 pm after each half hour.

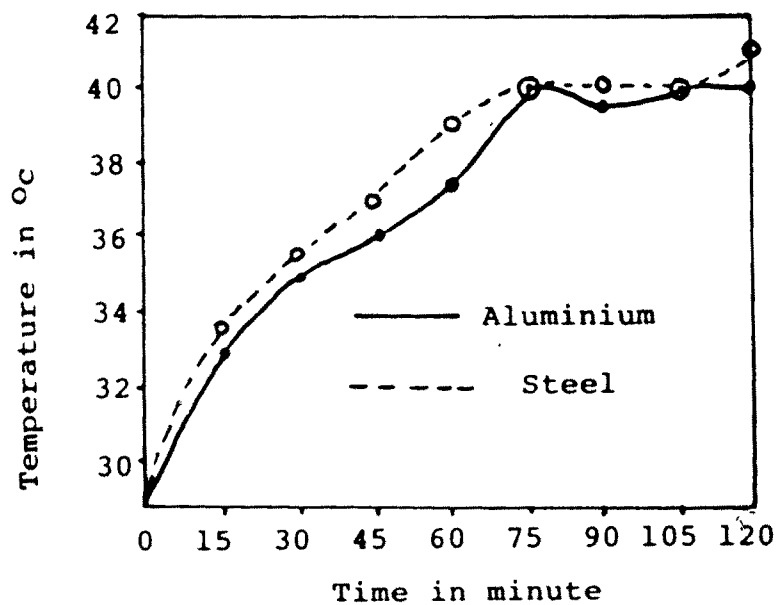


Fig. 3.2- Variation of Temperature with Time for 100 ml solution sprayed.

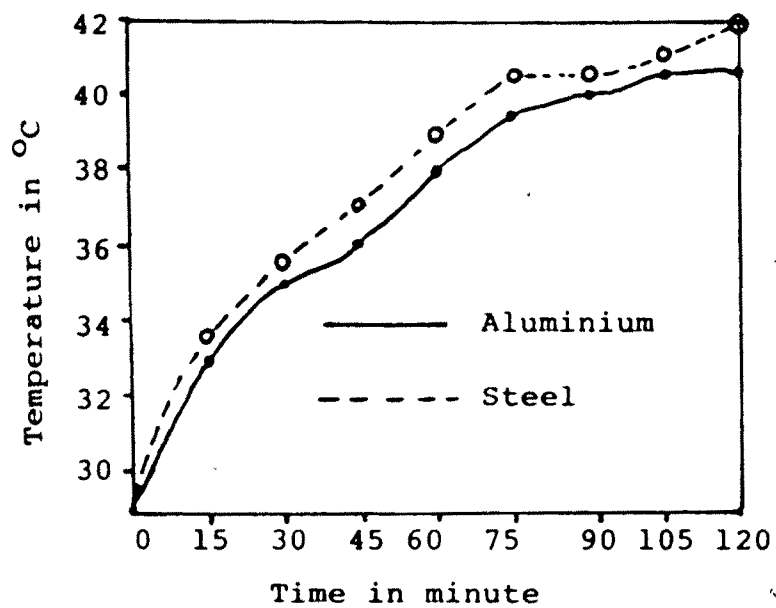


Fig. 3.3- Variation of Temperature with Time for 150 ml. solution sprayed.

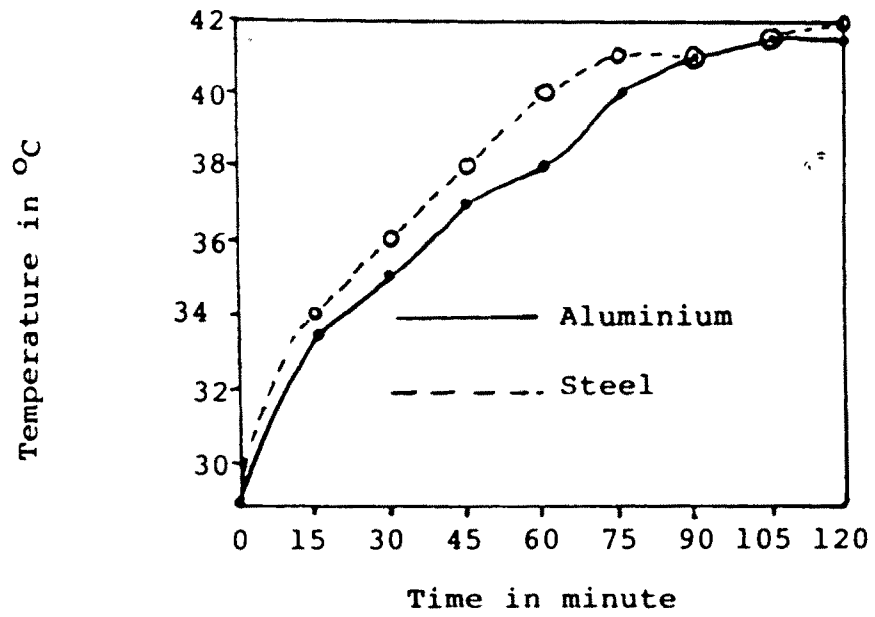


Fig. 3.4 Variation of Temperature with Time for 200 ml Solution sprayed.

Again all these cells with the Surya-Mapi were kept under 500 W flood light lamp (Halogen tube). The temperature measurement and intensity were noted for two hours.

3.4 RESULTS AND DISCUSSION

The films obtained by spray of cobaltous acetate solution with all optimised parameters, were uniform and good natured. They were grayish black in colour.

In all six cells were fabricated. Out of these six cells, three were of aluminium substrate and three of steel substrate. These three different cells were due to different quantities of solutions sprayed on substrate namely 100 ml, 150 ml, 200 ml. These cells were kept under the Sun. The cobalt oxide coating absorbs thermal energy from incident solar radiations. Hence temperature of water in cell rises. But it could not rise much. Though it rises to some extent, it immediately falls because of even a small breeze fo wind. So it was decided to test these cells in a rather controlled atmosphere. Hence a 500 W halogen tube was used as source. The temperature measurements were taken in the laboratory for two hours.

As temperatures were noted under the halogen tube, the intensity of incident light remains constant at 32 mW/cm². It is so because the distance and angle of incidence

both are constant. The variations of temperature against time were plotted. In these graphs the dotted lines show variation of temperature with steel substrate and continuous line shows that with aluminium substrate.

Fig.3.2 shows variation of temperature with time when 100 ml solution of cobaltous acetate was sprayed on the substrates. Here temperature is observed to increase linearly with time in the first 75 minutes. Then there appears saturation for half an hour in case of steel substrate and again rise in temperature is observed. While for aluminium it decreases and again increases. Finally, there appears saturation. At 75th and 105th minute the temperature for both aluminium and steel substrate was same. Here the cell with steel substrate show more rise in temperature than that with aluminium.

From Fig.3.3 it is clear that the rise of temperature is linear with time the rate is more in the beginning. It slows down after 90 minutes. No saturation is observed. Hence, there do not appear any overlapping of plotts. It is for 150 ml solution sprayed. Here also steel shows more rise in temperature.

Similarly Fig.3.4 shows variation of temperature when 200 ml solution of cobaltous acetate was sprayed. Here also temperature rises with time. From 90 to 105 minutes

temperature was same for both cells. But at the end in this case also cobalt oxide on steel substrate shows more rise in temperature as compared to that on aluminium substrate.

3.5 CONCLUSIONS

From the above discussion it is clear that for 150 ml solution of cobaltous acetate mixed with 75 ml of iso-propyl alcohol sprayed on substrates, the rise in temperature for both aluminium and steel is regular. No fall of temperature or saturation is observed during two hours. Also the coated film of cobalt oxide on stainless steel substrate show more rise in temperature as compared to that on aluminium substrate.