OXIDIZED COPPER FOR PHOTOTHERMAL CONVERSION
OF SOLAR ENERGY

BY

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Abstract:

A high absorptance (>0.90) is an essential factor in the efficient use of a solar collector. However, equally important is the need to keep the emittance as low as possible (<0.20). Both the absorptance and emittance depend on the optical properties of the coating and the substrate. The solar optical properties of copper oxide coatings on copper substrate have been investigated. The coatings were formed by three different methods, namely, dry thermal oxidation, sodium chlorite oxidation and the Ebanol C treatment. Temperature and time have been the most fundamental parameters. Specular reflectance profiles are presented in the wavelength range 0.35 – 15 μm and the total reflectance profiles in the interval 0.35 – 2.0 μm for some representative samples, of those that have shown a remarkably low reflectance in the wavelength region 0.3 – 2.0 μm.

Scanning electron microscope analysis of the sample surfaces has provided evidence of how changes in the topographical structure of the coatings could alter their reflectance characteristics and hence absorptance and emittance. The surface structure is in turn related to the treatment temperature and time. X-ray diffraction analysis has also revealed some interesting results. Whereas the thermal and sodium chlorite treatments tended to give Cu₂O coating at least up to the temperatures and treatment durations investigated, the Ebanol C method tended to form both oxide types with the CuO phase being the most dominant.

Evaluation of the reflectance data shows that it is possible by proper choice of treatment parameters to form coatings with \( q_s = 0.90, e_T < 0.20, q_s = 0.96, e_T < 0.20 \) and \( q_s = 0.96, e_T = 0.10 \) for the thermal, Ebanol C and chlorite treatments respectively.
All heated bodies emit thermal infrared radiation whose wavelengths and intensities depend on the absolute temperature of the body and the emittance of the surface. Reflectance data is often used to evaluate selective coatings because it is easy to measure. However, the values of emittance derived from reflectance data would not necessarily represent the actual values at the operating temperature of the collector. It is therefore necessary to know the emittance of coatings is related to the increase in the temperature. This is because the collector must not be allowed to operate at temperatures that might result in the degradation of its optically- and thermally-functional properties.

A vacuum calorimeter for measurement of the emittance of the coatings has been designed, constructed, tested, and calibrated. The emittance, as a function of temperature, of some of the representative samples have been measured and the result are presented.

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CONTENTS

Abstract

Acknowledgements

List of important figures

List of important tables

1 INTRODUCTION .................
   1.1 General
   1.2 Summary of research problem...
   1.3 Physics of spectral selectivity....
   1.4 Ideal absorber ..................

2. REVIEW OF THE MATERIALS AND METHODS
   2.1 General
   2.2 Single surface systems ..............
   2.3 Composite surface systems ............

3 THE THEORIES OF OPTICAL ABSORPTION IN SOLIDS
   3.2 General
   3.2 The Lorentz Theory ................
   3.3 Teh Drude Theory .................

4 THE OPTICS OF THIN FILMS
   4.1 General
   4.1.1 Fresnels coefficients ..............
   4.1.2 Boundary conditions ..............
   4.1.3 Notation and phase-matching conditions
   4.1.4 Energy reflection (R) and transmission (T)
            coefficients
   4.2 Reflection and transmission of a single film

5 EXPERIMENTAL
   5.1 Sample Preparation .................
   5.2 Sample Treatment .................
   5.3 Reflectance Measurement ...........
   5.4 Evaluation of solar absorptance, a_s, and
      thermal emittance, e_T
   5.4.2 Thermal emittance, e_T
6 RESULTS
6.1 General ...................... 44
6.2 Dry Thermal Oxidation....... 45
6.3 Sodium Chlorite Oxidation 48
6.4 Ebanol C treatment ........ 48

7 EMITTANCE MEASUREMENT
7.1 General ...................... 67
7.1.1 Radiative heat transfer .. 67
7.1.2 Vacuum technique 68
7.1.3 Design requirements 69
7.2 Survey of existing methods 71
7.2.1 Comparing temperature drops along coated fins 71
7.2.2 Butler Method .............. 73
7.2.3 Vacuum Calorimetric Method 73
7.3 Experimental Method 74
7.3.1 Apparatus .................. 74
7.3.2 Testing apparatus ........ 79
7.3.3 Data Collection .......... 81
7.3.4 Results .................... 83
7.4 Sources of error ............ 83

8 DISCUSSION
8.1 General ...................... 86
8.2 Comparison with Theory ..... 87
8.2.1 Dry Thermal Oxidation .... 87
8.2.2 Sodium chlorite and Ebanol C treated surfaces 90
8.2.3 Total emittance .......... 95
8.3 Limitations ................. 98

9 FUTURE

10 SUMMARY AND CONCLUSION

BIBLIOGRAPHY
List of important figures

Figure:

1.1 Blackbody at about 6000K and the extraterrestrial splar spectral flux 4
1.3 Spectral radiance distributions of the Sun and blackbody at 373K 9
1.4 Generalized spectral transmittance of a semiconductor 11
1.5 Solar absorptance of an ideal absorber 11
2.1 Spectral transmittances of thin films of PbS and silicon 15
2.2 Spectral reflectance of copper(l) oxide 15
3.2 Reflectivity of a Drude metal and the measured reflectivity of copper 22
5.3 Principle of the Beckman DK-2A spectrophotometer 40
6.1-4.4 Reflectances of thermally oxidized polished copper 46
6.5-6.7 Reflectance of sodium chlorite oxidized polished copper 49
6.8-6.10 Reflectances of Ebanol-C oxidized polished copper 52
6.11 Diffraction amplitude as a function of scattering angle 58
6.12 Intensity as a function of scattering angle for oxide film at 600°C for a duration of 4 min 58
6.13-6.15 Variation of $a_s$ and $e_T$ with the duration of oxidation 59
6.16-6.18 Variation of $\Delta a_s/\Delta t$ and $\Delta e_T/\Delta t$ with the duration of oxidation 62
6.19 Variation of $a_s$ with $e_T$ for the thermally-, chlorite and Ebanol C treated samples 64
7.2 Schematic representation of vacuum system for the measurement of total hemispherical emittance 75
7.3 Chamber with sample

7.4 Sample-heater assembly

8.1 Comparison of theoretical reflectance and experimental measured reflectance of copper oxide film thermally produced at 250°C for 25 min

8.2 Comparison of theoretical reflectance of a rough surface with experimentally measured reflectances of the chlorite- and Ebanol C oxidized surfaces

8.3 Theoretical specular reflectance of a rough surface taking into account plasma resonance
List of important tables

Table

6.1 Solar absorptances and thermal emittances of thermally oxidized copper at different temperatures and durations of oxidation 54

6.2 Solar absorptances and thermal emittances of chlorite oxidized copper at different temperatures and duration of oxidation 55

6.3 Solar absorptances and thermal emittances of Ebanol C oxidized copper at different temperatures and duration of oxidation 56

6.4 Estimate of proportion of CuO to Cu₂O for the films 57

7.3 Temperature dependence of thermal emittance 84
1. INTRODUCTION

1.1 General:

Efficient photothermal conversion of solar energy can be achieved by maximizing the absorption of the solar spectral flux and minimizing the emission of the thermal infrared radiation form the absorber surface. This means that the absorber surface must be 'black' to incident radiation in the solar spectral region (< 2μm) and be transparent to radiation longer than 2μm. This is called selective absorption. It can be achieved by several techniques. Multilayer absorber surfaces can be designed to provide selective absorption by interference effects, but such absorbers are usually very expensive in terms of materials and the fabrication techniques currently in use are far too sophisticated for the technologies of most developing countries. Another problem is that multilayer systems may suffer stability problems at elevated temperatures. An alternative method is to form a surface layer by coating which will absorb the solar spectral flux but be transmitting in the infrared. Such a coating may be formed on a surface with a low infrared emittance such as a polished metal.

An ideal system would make use of a semiconductor coating with an energy gap $E_g$ lying between 0.5eV($\lambda=2.5\mu m$) and 1.2eV($\lambda=1\mu m$) where $\lambda(\mu m) = 1.24/E_g(eV)$. Such materials include silicon (Si): $E_g = 1.1eV$ and germanium (Ge): $E_g = 0.7eV$. Unfortunately most semiconductor materials have high refractive indices which result in high reflectivities at the air-semiconductor interface. For instance polished lead sulphide (Pbs): $E_g = 0.5eV$ and a refractive index $n = 4.1$ in vacuum would have a normal reflectance of about 40% (reflectance, $R = (n-1)^2/(n+1)^2$).
However the reflectance can be lowered by proper thickness control and optimal surface roughness to give destructive interference. Copper(I) oxide (Cu₂O) with \(E_g = 2.17\text{eV}\) would appear to be unsuitable because of the rather high energy gap \(E_g\). But proper choice of control parameters would result in the desired selective absorption even for this semiconductor.

It is important to evaluate the optically- and thermally-functional properties of the solar absorber at temperatures at which it will operate. Such evaluation must include stability at operating temperatures long term durability and degradation in the spectral selective properties. In particular, it must be established that the thermal emittance \(e_T\) remains tolerable as the surface temperature of the absorber increases. Since radiation losses from any surfaces are proportional to the difference in the forth powers of the temperature of the surface and that of the surroundings, it is imperative that the emittance maintains its stability even at operating temperatures.

1.2 Summary of the Research Problem

1.2.1 Principle of photothermal solar energy conversion

Photothermal conversion is based on the well known phenomenon that material bodies heat up when exposed to the Sun's radiation. For the highest efficiency, as much of the Sun's energy must be absorbed as possible by the collector surface. The equilibrium temperature of an absorbing surface depends however, on at least two factors. These are,

(a) the quantity of solar energy absorbed which depends on the solar absorptance, \(a_s\); and

(b) the quantity of energy emitted by the surface, which depends on the thermal emittance, \(e_T\).
The solar absorptance, $a_s$, is the fraction of the radiant solar flux absorbed by a surface. The thermal emittance, $e_T$, is the fraction of radiant energy emitted by a surface compared to the radiant energy emitted by a blackbody at the same temperature.

To know the condition that must be satisfied by an ideal solar collecting surface, it is necessary to compare the solar input flux relative to the energy reradiated by the collector surface. The reradiated energy will be in the thermal infrared region. Hence the starting point is to compare the wavelength distribution of the solar flux to the spectral emission of a blackbody in the thermal infrared.

1.2.2 Insolation

It is important to have well documented data of some of the spectral characteristics of the solar energy to be collected if the design of a solar collector is to yield the desired results. Considerable knowledge of extraterrestrial solar irradiation has been made available largely through the space research program. The quantity of energy incident per unit area normal to a surface at the mean distance of the sun from the earth is called the solar constant. Many measurements have been made of this quantity by the use by the use of balloons, high altitude aircraft and spacecraft. The currently accepted value is 1353 W/m² [8]. Variations of about 3% occur due to the ellipticity of the earth's orbit. The extraterrestrial radiation peak occurs at about 0.48 µm so that by applying Wien's Displacement Law (see next section) the spectral radiation can be approximated by a blackbody at about 6000K (shown dotted in figure 1.1 together with the spectral distribution after passage through the atmosphere). The alteration in the total solar flux and its spectral distribution is due to absorption and scattering caused by ozone, oxygen, water vapour and carbon dioxide.
Fig. 1.1 Black-body at about 6000 K and the extraterrestrial solar spectral flux distribution and after passage through one \( (m=1) \) and two \( (m=2) \) airmasses.
The implication of the decrease in the radiation of the Sun in the infrared region combined with water vapour absorption bands below 20 \( \mu m \) is that on a **clear day** approximately 99\% of the solar energy is found at wavelengths below 3 \( \mu m \). This terrestrial spectral flux will of course depend on location and atmospheric conditions. For this reason the terrestrial insolation is defined in terms of a standard solar flux. Such a standard is based on a combination of theoretical models for atmospheric attenuation and scattering, together with actual spectral insolation measurements at different geographic locations. The standard solar flux is favourable because it provides a common basis for the comparison of solar absorbers and photothermal systems with regard to the efficiency of absorption of flux and the overall conversion of the flux to useful energy. The most widely used standard solar flux is based on the work by Moon [8]. The solar flux also depends on the length of the atmosphere traversed by the solar radiation. Such a pathlength of atmosphere is called an **air mass** and is usually denoted by the symbol \( m \). For example, air mass \( m = 1 \) refers to the vertical path at sea level. The solar flux generally has two components, consisting of the direct flux which arrives at the collector surface and the diffuse or scattered component. The former is undeviated from the Sun-collector direction whereas the latter is incident at all angles because of various scattering mechanisms. The diffuse component may be quite an appreciable fraction of the total incident flux even on a clear day. The typical range is about 8 - 20\% [8].

1.2.3 Blackbody Radiation

The solar flux incident on a solar collector is converted into heat. This makes the absorber the hottest component in the solar collector system. Hence it becomes necessary to minimize thermal losses in the absorber itself.
Fig. 1.2. Dependence of the peak of emission on the absolute temperature: Wien's law.
Conduction and convection can be reduced to tolerable levels by proper choice of materials and careful design. As the temperature of the absorber surfaces increases above ambient, the reradiated energy rapidly increases. The ability of a surface to radiate thermal energy is measured in terms of an ideal blackbody which absorbs all radiation incident on its surface. The spectral radiance distribution of a blackbody is defined to be the energy reradiated per unit projected area per unit time per unit wavelength interval. This distribution is governed by Planck's radiation formula,

\[ q_B = \frac{C_1}{\lambda^5} \left( \exp\left(\frac{C_2}{\lambda T}\right) - 1 \right) \]  \[ 1.1 \]

where:  
- \( \lambda \) is the wavelength in meters,
- \( T \) is the absolute temperature
- \( C_1 = 1.19 \times 10^{-16} \text{ W/m}^2 \)
- \( C_2 = 1.4388 \times 10^{-16} \text{ m-K} \)

the subscript B refers to blackbody.

The spectral emissive power increases with temperature at all wavelengths. The peak of emission shifts to shorter wavelengths with increasing temperature according to Wien's Law,

\[ T_\lambda_{\text{max}} = 2898 \mu\text{m-K} \]  \[ 1.2 \]

where \( \lambda_{\text{max}} \) is the wavelength of maximum emission in microns. This behaviour is illustrated in figure 1.2. The total energy emitted by a blackbody depends on the forth power of the absolute temperature:

\[ q_r = \sigma T^4 \]  \[ 1.3 \]

where \( \sigma = 5.67 \times 10^{-8} \text{ W/m K} \) is the Stefan-Boltzmann constant. Most real surfaces radiate only a fraction of this value. The ratio of the energy radiated by a real body to that for a blackbody is called the thermal emissivity or emittance. Thus for real surfaces (1.3) is modified to,

\[ q_r = e_T \sigma T^4 \]  \[ 1.4 \]
where \( e_T \) is the thermal emissivity or emittance and is less than unity. Figure 1.3 compares the spectral radiance distribution of the Sun for air mass, \( m = 2 \) and the spectral radiance distribution of a blackbody at 373K (100°C). It can be seen that the solar and blackbody spectral radiance distributions lie in well separated wavelength regions. This is the basic consideration of the idea of spectral selectivity. Another important consideration is based on Kirchhoff's Law which simply states that for a given surface the monochromatic emittance and the monochromatic absorptance are equal for radiation of any given wavelength. Thus,

\[
\varepsilon_\lambda = a_\lambda
\]

where \( \varepsilon_\lambda \) is the monochromatic emittance and \( a_\lambda \) is the monochromatic absorptance at wavelength \( \lambda \). From consideration of conservation of flux, the sum of the absorptance \( a_\lambda \), transmittance \( \tau_\lambda \) and reflectance \( r_\lambda \) must be equal to unity for any given medium. This may be expressed as,

\[
a_\lambda + \tau_\lambda + r_\lambda = 1
\]

If the material is not transparent, i.e., the result is,

\[
a_\lambda + r_\lambda = 1
\]

In expressions (1.6) and (1.7) \( r_\lambda \) is the monochromatic reflectance at wavelength \( \lambda \). Kirchhoff's Law enables one to re-write equation (1.5) for an opaque medium as,

\[
\varepsilon_\lambda = a_\lambda = 1 - r_\lambda
\]

Expression (1.5)' is useful because it allows \( \lambda \) or \( a_\lambda \) to be determined from a reflection measurement.
Sea level sunlight air mass, $m=2$
Total incident flux is $900 \text{ w/m}^2$

Spectral radiation distribution of blackbody at 373K.
Total hemispherical flux $1100 \text{ w/m}^2$

Wavelength, $\mu \text{m}$

Fig. 1.3. Spectral radiance distribution of the Sun for airmass two ($m=2$) and the spectral radiance distribution of a blackbody at 373K.
1.3 The Physics of Spectral Selectivity

The physics of spectral selectivity is determined by the laws outlined in the previous section and the fact that the solar spectrum and the spectra of black bodies heated to moderate temperatures do not overlap by any appreciable amount. However, the optical properties of the metals to be used as a substrate also play a very important role. Solar absorbers have been made by coating metals with black paint. Black paint is a very good absorber with a solar absorptance $q_S = 0.95$. But the argument against its widespread use in the solar collectors is that it has a high thermal emittance, with for instance, $e_{373K} = 0.90\{13\}$. In energy balance terms, this means that the loss to re-radiation alone, would balance an incident solar energy input of approximately 660W at a collector surface temperature of about 100°C and a sky temperature of 17°C (net loss, $Q = e_T (T^4 - T_s^4)$, where $T$ is the collector temperature and $T_s$ is the sky temperature).

For a surface to be spectrally selective there must be a thin coating of a semiconductor on a well polished metal substrate which is highly reflecting to radiation longer than 2μm. The generalized spectral transmittance curve of a semiconductor is shown in figure 1.4. Maximum absorption occurs in region A where the photon of incident light has sufficient energy to excite electrons from the valence band across the energy band gap $E_g$, to the conduction band. The excitation can occur through a direct or indirect transition. A direct transition is one involving only an optical photon, producing negligible change in the wave vector of the electron. The transition of the electron to the ground state occurs in most cases by the interaction with the vibrational modes by which the energy of the electron is transformed into lattice heat. The second most important region is B. This is the region where the semiconductor becomes transparent to infrared radiation.
Fig. 1.4. Generalized spectral transmittance of a semiconductor.

Fig. 1.5. Solar absorptance of an ideal absorber.
Metals are characterized by their high reflectivity and opacity except in very thin films. These optical properties are associated mainly with the absorption of electromagnetic radiation involving indirect optical transition by the free electrons in the metal.

Coating a semiconductor on a well polished metal, permits the latter to 'see through' the semiconductor layer through the former being transparent to radiation in the infrared. In this way the emittance of the semiconductor is suppressed through the high reflectance of the metal substrate.

1.4 The Ideal Absorber

An ideal absorber which would absorb all incident solar flux and not emit the thermal infrared radiation should have an absorptance/emittance which depends on the wavelength as shown in figure 1.5. No such intrinsic material exists. A combination of materials can be used to achieve only an approximate ideal spectral absorptance profile. Some of the techniques involved are reviewed in the next chapter.
2 REVIEW OF THE METHODS AND MATERIALS FOR PRODUCING SELECTIVE SURFACES

2.1 General

Several techniques exist for producing selective surfaces. This chapter reviews two types of surface systems. These are single surface systems and composite surface systems.

2.2 Single Surface System

2.2.1 Isotropic Plane Slab of Solid

The most elementary system which may be considered is the isotropic plane slab of solid. As described by the Lorentz and Drude theories (see chapter 3), spectral selectivity arises from the dependence of n and k on the wavelength of the incident radiation. Typically metals have the proper variation of n and k with wavelength to make them selective absorbers. Unfortunately, the cut-off frequency of metals lies in the ultraviolet region. This precludes the use of plane metallic slabs as solar absorbers.

2.2.2 Uniform Rough Slab

Controlled surface roughness may be used to boost the spectral selectivity of metallic surfaces. The degree of surface roughness must be large compared to the wavelength of the visible region of the solar spectrum. The cavities in the surface would result in multiple reflections and consequently an increase in the absorptivity. The problem is that whilst surface roughness would enhance the absorptibility of metallic surfaces, it would also inevitably result in considerably higher reradiation loss because of the larger effective area of the absorber.
2.3 Composite Surfaces Systems

Selective surfaces may also be produced by coating well polished metal surfaces with paints or thin semiconductor layers. The most common methods of preparing semiconductor coatings are by painting, spraying electroplating, chemical treatment, vacuum evaporation and chemical vapour deposition.

2.3.1 Painting

High absorptance is obtained when polished metals are coated with paints and maximum absorptance results if black paint is used. But the efficiency of collection is lowered by the rather high thermal emittances of such coatings. Lead sulphide and silicon paints have been produced [11], which show good reflectivity except for a strong absorption band around 8-10μm. This is illustrated in figure 2.1 in the transmission mode. Production techniques involve precipitation from lead acetate solution by bubbling hydrogen sulphide. The precipitate is then washed, freeze-dried and mixed with activated silicon resin. Finally it is heat-treated at 200°C for approximately sixteen hours. Coatings with solar absorptances of about 0.94 have been obtained in this way.

2.3.2 Spraying

It has been reported [11] that good selective coatings can be formed by spraying aqueous solutions onto polished metals. The metal surface must be heated in a precise manner to obtain the best results. Details of the method have not, so far, been widely published, neither are typical values of absorptance obtainable.

2.3.3 Electroplating

In the electroplating technique metallic ions from solution are deposited onto a polished or etched cathode
by passage of an electric current. Solar collectors of this configuration are reported to have been designed by Gillet and his co-workers [11]

2.3.4 Chemical Treatment

Chemical reagents can be used to make selective coatings on polished metals. In one method polished copper is dipped into a solution containing a mixture of sodium chlorite and sodium hydroxide in water [13, 16]. The mainly copper (I) oxide films formed in this way have $q_s$ values of between 0.90 and 0.96.

The Ebanol C (trade name: Ethone Inc; New Haven, Connecticut, USA) process for chemically blackening copper and copper alloys and the Ebanol S process for steel and steel alloys are capable of producing good selective coatings with the proper choice of treatment parameters. Typical solar absorptance values as calculated from near-normal reflectance data [11] are, Ebanol C: $q_s = 0.91$ and Ebanol S: $q_s = 0.85$.

Copper can also be coated with copper sulphide (CuS) by treating in ammonium sulphide solution to produce surface with $q_s = 0.80$ or better. The reflectance curve of a thin of CuS is shown in figure 2.2.

2.3.5 Vacuum Evaporation

Materials can be deposited in vacuum onto an appropriate substrate by resistive heating, electron bombardment or radiofrequency sputtering. These types of thin films usually make use of antireflective, absorptive and interference effects to achieve spectral selectivity. Vacuum evaporated silicon with an overlayer of silicon dioxide antireflection coating of thickness 8.33Å has typical $q_s$ values 0.60 - 0.65.
Fig. 2.1 Spectral transmittance of thin films of PbS (full curve) and silicon (broken curve).

Fig. 2.2 Spectral reflectance of copper(I) sulphide film on a copper substrate.
2.3.6 Chemical Vapour Deposition

Chemical vapour deposition (CVD), a technique adapted from the semiconductor industry, has been used for the deposition of multilayer stacks for high temperature (> 500°C) photothermal conversion of solar energy. Selective absorbers with solar absorptances $a_s = 0.80$ and $a_s/e_T = 12$ have been obtained in this method [8]. Of greater significance is the fact that both $a_s$ and $e_T$ have been measured at 500°C.

Basically the stainless steel substrate to be coated with silicon is placed in a hot zone (> 100°C) of a furnace and exposed to a silane/carrier gas mixture. The silane (SiH$_4$) breaks up through the transfer of thermal energy at the surface of the hot substrate, leaving behind a thin layer of silicon absorber. Successive layers can be deposited if the process is repeated through different reaction zones.
3 THE THEORIES OF OPTICAL ABSORPTION IN SOLIDS

3.1 General

A study of spectral selectivity necessitates mention of the now largely ad hoc classical theories of Lorentz and Drude. The classical theory of absorption and dispersion of electromagnetic radiation in solids is due mainly to these two workers. The Lorentz model, whose quantum mechanical analog includes all direct interband transitions applies to insulators and semiconductors. Interband transitions are those for which the final state of an electron lies in a different band but with no change in the wave vector, in the reduced zone scheme. On the other hand, the Drude model which applies to free electron metals has a quantum mechanical analog which includes all intraband transitions. These are transitions to an empty band within the same state.

3.2 The Lorentz Theory

In general classical dispersion theory begins with an equation of motion of an electron of charge, e and mass m. The model considers an atom with electrons bound to the nucleus in a manner similar to a small mass bound to a big mass by a spring. The motion of the electron in the presence of an electromagnetic field is then described by the following expression,

\[ m \dddot{\vec{r}} + m\gamma \ddot{\vec{r}} + m\omega^2 \dot{\vec{r}} = -e(\vec{E} + \vec{V} \times \vec{B}) \] 3.1

where the second term on the left hand side represents viscous damping and accounts for energy losses, and the term, \( m\omega^2 \dot{\vec{r}} \) is the restoring force; it represents the binding of the electron. \( \vec{E} \) and \( \vec{B} \) are respectively the electric and magnetic field vectors associated with the incident electromagnetic radiation and \( \vec{V} \) is the velocity of the electron.
On the right hand side of the equation, the term arising from the interaction with the magnetic field is negligibly small compared to that of the electric field and can be neglected. If further it is assumed that $\mathbf{E}$ varies as $\exp(-i\omega t)$ where $\omega$ is the angular frequency of the incident radiation and $i = \sqrt{-1}$, then the solution to equation 3.1 leads to the following result for the dielectric constant,

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = 1 + \frac{(Ne^2/\varepsilon_0 m)}{(w_0^2 - w^2 + i\gamma w)}$$  

3.2

where $\varepsilon_1$ and $\varepsilon_2$ are respectively the real and imaginary parts of the complex dielectric constant $\varepsilon$, $N$ is the number of electrons per unit volume and $\varepsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$ is the vacuum permittivity and all underlined quantities are complex. Rationalizing equation 3.2 gives,

$$\varepsilon_1 = 1 + \frac{(Ne^2/\varepsilon_0 m)}{(w_0^2 - w^2)/(w_0^2 - w^2) + \gamma^2 w^2}$$  

3.3

$$\varepsilon_2 = \frac{(Ne^2/\varepsilon_0 m)}{(\gamma w/(w_0^2 - w^2))^2 + \gamma^2 w^2}.$$  

3.4

Solution of Maxwell's equations for the boundary between two media, one a vacuum, leads to the following expression for the complex refractive index

$$n = (\varepsilon_1/\varepsilon_0 + i\sigma/\varepsilon_0 w)^{1/2}$$  

3.5

provided that the second medium is nonmagnetic. In equation (3.5) $\varepsilon_1$ is the real part of the dielectric constant given by (3.3), $\sigma$ is the electrical conductivity of the second medium. $n$ can also be expressed in terms of the real and imaginary parts,

$$n = n - ik$$  

3.6

where $n$ is the real refractive index and accounts for the dispersion of the incident radiation and $k$, the extinction
coefficient expresses the fact that energy is dissipated in the medium. One can express \( n \) and \( k \) in terms of \( \varepsilon_1 \) and \( \varepsilon_2 \),

\[
    n = \left[ \frac{1}{2} \left( (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_2 \right) \right]^{1/2} \quad 3.7
\]
\[
    k = \left[ \frac{1}{2} \left( (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1 \right) \right]^{1/2} \quad 3.8
\]

The reflectance of solids at normal incidence can then be shown to be,

\[
    R = \frac{\left[ (n - 1)^2 + k^2 \right]/\left[ (n + 1)^2 + k^2 \right]}{\left[ (n - 1)^2 + k^2 \right]/\left[ (n + 1)^2 + k^2 \right]} \quad 3.9
\]

If expressions (3.3) and (3.4) and (3.7)-(3.9) are used to analyse the refrequency dependence of a solid in terms of whether it is reflecting, absorbing or transparent a typical result obtained is shown in figure 3.1. The main drawback with applying these classical expressions to real materials is that they tend to treat the electrons as if they all had one resonance frequency \( \omega_0 \). Real materials however, could be thought of as consisting of a collection of Lorentz oscillators with different frequencies spread over a band. However, the Lorentz oscillator frequency should prove helpful if it is considered to be the transition frequency across the band gap of a semiconductor.

3.3 The Drude Theory for Metals

For free electrons \( \omega_0 = 0 \) because the electrons are not bound. Then the expressions for \( \varepsilon_1 \) and \( \varepsilon_2 \) become,

\[
    \varepsilon_1 = 1 - \frac{Ne^2}{\varepsilon_0 m} (\omega^2 + \gamma^2)^{-1} \quad 3.10
\]
\[
    \varepsilon_2 = \frac{Ne^2}{\varepsilon_0 m} \left( (\gamma/\omega)/(\omega^2 + \gamma^2) \right) \quad 3.11
\]

where \( \gamma \) takes account of the damping mechanism due to the scattering of electrons arising from electrical resistivity. In a quantum mechanical derivation can be shown [2] to be
Fig. 3.1 Variation of the reflectivity $R$, $n$, $k$, with the energy $\hbar \omega$ of the incident photon as given by expressions 3.7–3.9
Fig. 3.2 Reflectivity of a Drude metal and measured reflectivity of polished copper (---)
traditional to the reciprocal of the mean free time between collisions. For each value of \( w \), \( \varepsilon_1 \) and \( \varepsilon_2 \) can be calculated and from these, \( n \) and \( k \) and hence \( R \), the reflectance. Typical result of such a calculation for the reflectivity of a Drude metal is shown in figure 3.2. The dashed curve is the spectral reflectance of polished copper as measured in this study. It is more realistic to analyse the reflectivity of a metal in terms of its electrical conductivity. This can be done by equating the squares of (3.5) and (3.6) hence their real and imaginary parts. This results in a relation of \( n \) and \( k \) given by,

\[
\begin{align*}
n &= \left[ \frac{\varepsilon_1}{2\varepsilon_0} + \frac{1}{2}\varepsilon_0\left(\varepsilon_1^2 + \sigma^2w^2\right)^{1/2} \right]^{1/2} \\
k &= \sigma/2\varepsilon_0w[\varepsilon_1/2\varepsilon_0 + 1/2\varepsilon_0(\varepsilon_1^2 + \sigma^2w^2)^{1/2}]^{1/2}
\end{align*}
\]  

For a metal \( \varepsilon_1 \approx 0 \), which means that \( n \approx (\sigma/2\varepsilon_0w)^{1/2} \). Using this fact in (3.9) gives the reflectivity of a metal

\[
R \approx 1 - 2(\sigma/2\varepsilon_0w)^{1/2}
\]

As predicted that for light in the visible part of the spectrum, a metal such as copper with \( \sigma \approx 10 \, (\Omega m)^{-1} \) must have a reflection coefficient \( R \approx 0.96 \). In general \( \sigma \) is frequency dependent, and can be obtained by use of equation (3.5) with \( \varepsilon_0 = 0 \). The results give the real and imaginary parts of the complex conductivity, \( \sigma \) respectively as,

\[
\sigma = \sigma_1 = (N\varepsilon_0^2\hbar/\tau)(1 + w^2\tau^2)^{-1}, \quad \sigma_2 = (N\varepsilon_0^2\hbar/\tau^2)w^2(1 + w^2\tau^2)^{-1}
\]

where \( \tau = 1/\gamma \) is the scattering relaxation time. In terms of the dc or low frequency value of the real conductivity \( \sigma_1 \) can be written as,

\[
\sigma_1 = \sigma_0 \langle \tau (1 + w^2\tau^2)^{-1} \rangle / \langle \tau \rangle
\]
where the angle brackets denote averages. The optical behaviour observed will depend upon the magnitudes of \( w \) and \( \sigma_0 \). A number of frequency ranges can be identified,

(i) Low frequency, low conductivity range \((w\gamma<1, n=(\varepsilon_1/\varepsilon_0)^{1/2})\).

The term \((w\gamma)^2\) can be neglected compared to unity and \(\sigma_1 = \sigma_0\). The absorption coefficient is given by [3],

\[
\alpha = 2w k/c = 4\pi\sigma_0/c (\varepsilon_1/\varepsilon_0)^{1/2}
\]

(ii) Low-frequency, high conductivity range

\((w\gamma<1, n=(\varepsilon_1/\varepsilon_0)^{1/2})\)

This means that the penetration of the material is proportional to \(w^{-3/2}\).

(iii) High frequency range.

This corresponds to the ultraviolet region and will not be dealt with since it does not relate to studies on solar absorber surfaces.

The behaviour of selective absorbers can be qualitatively analysed in terms of the behaviour of the thin film semiconductor and the metallic substrate when irradiated by electromagnetic radiation. Since, according to equation (3.14) the metallic substrate has a high reflectance throughout the spectral region of interest, the spectral selectivity of the absorber surface is expected to depend entirely on the extent to which the semiconductor layer can absorb the solar spectral flux and at the same time be transparent to infrared radiation. The former condition would be met by a semiconductor with a low value of \( n \) for low reflectivity at the air-semiconductor interface and low values of \( k \) for increased absorption.
(the absorption $e^{-\alpha d}$, where $d$ is the distance moved by the radiation in the material). For most semiconductors $k$ is sufficiently small, but $n$ has values in the range 3 - 5 which means that reflectivity at the semiconductor - air interface will lie in the range 20 - 40% approximately.
4 THE OPTICS OF THIN FILMS

4.1 General

The reflective and transmissive properties of thin films can be calculated from electromagnetic theory in terms of the refractive index and thickness of the thin film material. In the case of absorbing films, the refractive index is a complex quantity. This makes the expressions for the transmittance and the reflectance quite cumbersome. The derivation of the transmittance and reflectance requires knowledge of the Fresnel coefficients which express the ratio reflected/incident (r) and transmitted/incident (t) amplitudes of the incident electromagnetic radiation.

4.1.1 Fresnel Coefficients

The Fresnel coefficients can be determined by considering the reflection and transmission of light at an interface between two isotropic and homogeneous optical media which have different optical properties. The four relevant Maxwell's equations are,

\[ \nabla \cdot \vec{D} = 0 \]
\[ \nabla \cdot \vec{B} = 0 \]
\[ \nabla \times \vec{E} = -\partial \vec{B} / \partial t \]
\[ \nabla \times \vec{H} = \partial \vec{D} / \partial t + \vec{j} / \varepsilon \]

where \( \vec{E} \) and \( \vec{H} \) are the electric and magnetic field intensities and the operator \( \nabla \) is given in cartesian coordinates by,

\[ \nabla = \vec{i} \partial / \partial x + \vec{j} \partial / \partial y + \vec{k} \partial / \partial z \]

where \( \vec{i} \), \( \vec{j} \) and \( \vec{k} \) are unit vectors in the x, y and z directions respectively.
In general the electric displacement \( \vec{D} \) and the magnetic flux density \( \vec{B} \) will have components given by

\[
D_i = \sum_{j=1}^{3} \varepsilon_{ij} E_j
\]

\[
B_i = \sum_{j=1}^{3} \mu_{ij} H_j
\]

where \( \{ \varepsilon_{ij} \} \) are the elements of a dielectric tensor \( \hat{\varepsilon} \) and \( \{ \mu_{ij} \} \) are the elements of the permeability tensor \( \hat{\mu} \). The components of \( \vec{D} \) and \( \vec{B} \) given in (4.3) are applicable to linear isotropic media. The word 'linear' is used to describe the fact the \( D_i \)'s and \( B_i \)'s have a simple linear relationship with the \( \{ \varepsilon_{ij} \} \) and the \( \{ \mu_{ij} \} \)-respectively. Often there is also a linear relationship between the current density and the electric field,

\[
J_i = \sum_{j=1}^{3} \sigma_{ij} E_j
\]

If the linear medium is isotropic the three tensors become multiples of the unit tensor \( \hat{1} \), thus,

\[
\hat{\varepsilon} = \varepsilon \hat{1}, \quad \hat{\mu} = \mu \hat{1}, \quad \hat{\sigma} = \sigma \hat{1}
\]

Thus for instance one can write \( \varepsilon_{ij} = \varepsilon \delta_{ij} \) etc where \( \delta_{ij} = 1 \) if \( i=j \) and \( \delta_{ij} = 0 \) if \( i \neq j \). The quantities \( \varepsilon \), \( \mu \) and \( \sigma \) are then called the dielectric constant, the permeability and conductivity respectively. In this case the expressions for \( \vec{D}, \vec{B} \) and \( \vec{J} \) simply become

\[
\vec{D} = \varepsilon \vec{E}
\]

\[
\vec{B} = \mu \vec{H}
\]

\[
\vec{J} = \sigma \vec{E}
\]
Fig. 4.1 Reflection and refraction of light at an interface between two transparent media: (i) \(E \perp\) and (ii) \(E \parallel\) plane of incidence.

Fig. 4.2 Reflected intensity of a transparent layer of a substance of refractive index \(n_1\) on a substrate of refractive index \(n_2\).
4.1.2 Boundary Conditions

The continuity conditions for the components of the electric and magnetic field vectors of the incident electromagnetic radiation are derived in many books on electromagnetic theory [eg.30]. These state that:

(a) the normal components of $\vec{D}$ and $\vec{B}$ must be continuous across an interface between two media,

$$D_{n2} = D_{n1}, \quad B_{n2} = B_{n1} \quad 4.7$$

where the subscript $n$ denotes normal and 1 and 2 refer to the media.

(b) the tangential components of $\vec{E}$ and $\vec{H}$ must be continuous across the interface,

$$E_{t2} = E_{t1}, \quad H_{t2} = H_{t1} \quad 4.8$$

The required continuity for the tangential components of $\vec{E}$ and $\vec{H}$ can be used to derive the reflection and transmission coefficients.

4.1.3 Notation and Phase-matching conditions

By letting the interface coincide with the $x$-$y$ plane and the plane of incidence lie in the $y$-$z$ plane as shown in fig. 4.1, the $\vec{E}$ and $\vec{H}$ fields may be resolved into their components in the plane of incidence. Only the case where $\vec{E}$ is perpendicular to the plane of incidence and $\vec{H}$ lying in the plane of incidence will be considered. A notation is adopted (fig. 4.1) in which the superscripts will denote incident(i) reflected (r) and transmitted (t) whilst the subscript refers to the components, e.g. $E_x^i$ refers to the incident $x$ component of $\vec{E}$. Both $\vec{E}$ and $\vec{H}$ have a time dependence $\exp(iwt)$ and a spatial dependence $\exp(-ik \cdot \vec{r})$ for the incident wave $\exp(-ik \cdot \vec{r})$ for the reflected wave and
\[ \exp(-jk^t \cdot \hat{r}) \] for the transmitted wave, and \( i = \sqrt{-1} \) is underlined to differentiate it from an ordinary letter. The wave vectors will have components \([31]\),

\[
\hat{k}^i = (0, k_y^i, k_z^i) = (\eta_1w/c)(0, \sin \theta_i, \cos \theta_i)
\]

\[
\hat{k}^r = (k_x^r, k_y^r, k_z^r), \text{ where } (k_x^r)^2 + (k_y^r)^2 + (k_z^r)^2 = (\eta_1w/c)^2
\]

\[
\hat{k}^t = (k_x^t, k_y^t, k_z^t), \text{ where } (k_x^t)^2 + (k_y^t)^2 + (k_z^t)^2 = (\eta_2w/c)^2
\]

where \( \eta_1 \) and \( \eta_2 \) are the refractive indices of the two media. The continuity conditions on \( E^r_{\text{tan}} \) and \( H^r_{\text{tan}} \) cross the interface at \( z=0 \), then takes the form,

\[
E^i_{\text{tan}} \exp(-iyk_y^i) + F^r_{\text{tan}} \exp(-ik_k^r + yk_y^r) = F^t_{\text{tan}} \exp(-iyk_y^t) \]  \hspace{1cm} 4.10

where \( F \) denotes \( \vec{E} \) or \( \vec{H} \). Equation (4.10) must hold for all \( x \) and \( y \) and will be valid only if the phases are everywhere the same. One consequence of this is the condition \([31]\),

\[
k_x^r = k_y^t = 0 \]  \hspace{1cm} 4.11

which implies that the reflected and transmitted waves must lie in the plane of incidence. Other requirements are,

\[
k_x^r = k_x^i, \quad k_y^t = k_y^i \]  \hspace{1cm} 4.12

Using the notation of Fig. 4.1 one can write the reflected wave vector as,

\[
\hat{k}^r = \eta_1(w/c)(0, \sin \theta_i, -\cos \theta_i) \]  \hspace{1cm} 4.13
and the transmitted wave vector as,

\[ \mathbf{k}^t = n_z(w/c)(0, \sin \theta_r \cos \theta_r) = (w/c)(0, n_z \sin \theta_r, n_z \cos \theta_r) \]  

Now that phase-matching has been properly established the boundary conditions become conditions on the amplitudes of the waves \( \mathbf{E} \exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \) and \( \mathbf{H} \exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \)

\[ E_x^i + E_x^r = E_x^t \]  \[ H_y^i + H_y^r = H_y^t \]  

From the third of Maxwell's equations (4.1) one finds,

\[ \mathbf{E} = w(\varepsilon \mu)^{1/2} \mathbf{u} \times \mathbf{E} = w(\varepsilon \mu)^{1/2} k / |k| \times \mathbf{E} \]  

where \( \mathbf{u} \) is a unit vector in the direction of propagation, i.e. perpendicular to \( \mathbf{E} \). If both media are nonmagnetic then \( \mu_1 = \mu_2 = \mu_o \) and the continuity of the tangential component of \( \mathbf{H} \) implies the continuity of \( \mathbf{k} \times \mathbf{E} \),

\[ (\mathbf{k}^i \times \mathbf{E}_x^i)_y + (\mathbf{k}^r \times \mathbf{E}_x^r)_y = (\mathbf{k}^t \times \mathbf{E}_x^t)_y \]  

Now the \( \mathbf{E} \)'s have only x components and hence

\[ E_x^i = E_x^i, \quad E_x^r = E_x^r, \quad E_x^t = E_x^t \]  

The \( \mathbf{k} \)'s have only y- and z-components. Thus,

\[ (\mathbf{k} \times \mathbf{E}_x^t)_y = k_z E_x^t \]  

By using equations (4.15) and (4.17) one obtains,

\[ E_x^i + E_x^r = E_x^t \]  

\[ k_z^i E_x^i + k_z^r E_x^r = k_z^t E_x^t \]
Since \( k_z^r = -k_z^i \) (using the first of equations (4.9) and equation (4.13) ) it follows that

\[
E^i - E^r = (k_z^r/k_z^i) E^t \tag{4.22}
\]

When (4.20) and (4.22) are solved one obtains

\[
E^t = 2E^i / (1 + k_z^r/k_z^i) \tag{4.23}
\]

\[
E^r = (1 - k_z^r/k_z^i)(1 + k_z^r/k_z^i)^{-1} E^i \tag{4.24}
\]

4.1.4 Energy reflection (R) and Transmission (T) coefficients

The average Poynting vector \( \langle \vec{S} \rangle \) gives the time-average power per unit area. For a plane wave this is maximum for a plane perpendicular to the plane of propagation and is given by [30],

\[
\langle \vec{S} \rangle = 1/2(\varepsilon/\mu)^{1/2} |E|^2 \vec{u} \tag{4.25}
\]

where \( \vec{u} = \vec{k}/|\vec{k}| \) is a unit vector in the direction of propagation. The average power crossing unit area of a plane surface parallel to the interface is given by the magnitude of the z-component of \( \vec{S} \) which is \( S_z = S \cos \theta \)

Thus for the three waves,

incident: \( S_z^i = 1/2(c \eta_1/\mu_1) |E|^2 \cos \theta_i \)

reflected: \( S_z^r = 1/2(c \eta_1/\mu_1) |E|^2 \cos \theta_i \)

transmitted: \( S_z^t = 1/2(c \eta_2/\mu_2) |E|^2 \cos \theta_t \)

The energy reflection and transmission coefficients are defined by the ratios,
\[ R = \frac{S^r_z}{S^i_z} = \frac{|E^r|}{|E^i|}^2 = r r^* \]

\[ T = \frac{S^t_z}{S^i_z} = \frac{|E^t|}{|E^i|}^2 \left( \frac{n_2 \cos \theta_i}{n_1 \cos \theta_i} \right) \]

By using the z-components of the \( k' \)'s in equations (4.9), (4.13) - (4.15) in expressions (4.23) and 4.24) it can be shown that the reflection \( (r_s) \) and transmission \( (t_s) \) for the s-polarized light are given by

\[ r_s = \frac{(n_1 \cos \theta_i - n_2 \cos \theta_t)}{(n_1 \cos \theta_i + n_2 \cos \theta_t)} \]

\[ t_s = \frac{2n_1 \cos \theta_i}{(n_1 \cos \theta_i + n_2 \cos \theta_t)} \]

For the case in which \( \vec{E} \) lies parallel to the plane of incidence (i.e. the p-polarized light) the coefficients are,

\[ r_p = \frac{(n_2 \cos \theta_i - n_1 \cos \theta_t)}{(n_1 \cos \theta_i + n_2 \cos \theta_t)} \]

\[ t_p = \frac{2n_1 \cos \theta_i}{(n_2 \cos \theta_i + n_1 \cos \theta_t)} \]

4.2 Reflection and Transmission of a Single Film

Consider the general case of light incident at an angle \( \phi_i \) on a film of index \( n_1 \) and thickness \( t \) (fig. 4.2) coated on a substrate of index \( n_2 \). The reflectance and transmittance are determined by summation of the multiple reflected and transmitted beams taking into considering the phase difference \( \delta_i = \left( \frac{2\pi}{\lambda} \right) n_1 t \cos \phi_i \) between the reflected amplitudes. One sums the amplitudes of the successive rays either in air \( (n_0) \) or in the film material \( (n_1) \). The electric field has the same value on either side of the \( S_1 \) interface.

\[ \text{medium of index } n_0 \quad \text{medium of index } n_1 \]

\[ E = E^i + E^r \]

\[ = E^t \]

The reflection coefficient \( r \) being less than unit amplitude
one has $r^N = 0$ as $N$, the number of reflections becomes very large. The value of the resulting field in air ($n_0$) is an expression of the form,

$$E = X + Y + YZ + YZ^2 + YZ^3 + \ldots$$

$$= X + Y(1 + Z + Z^2 + Z^3 + \ldots)$$

$$= X + Y(1 - Z)^{-1}$$

where $X = 1 + r_1$, $Y = t_1 t'_1 r_2 \exp(-i\delta_1)$, $Z = r'_1 r_2 \exp(-i\delta_1)$

This gives the value of the field in air as,

$$E = 1 + r_1 + t'_1 \exp(-i\delta_1)[1 - r'_1 r_2 \exp(-i\delta_1)]^{-1}$$  \hspace{1cm} \text{(4.31)}$$

In a similar manner the value of the field in the film material may be obtained as,

$$E = t'_1[1 + r_2 \exp(-i\delta_1)][1 - r'_1 r_2 \exp(-i\delta_1)]^{-1}$$  \hspace{1cm} \text{(4.32)}$$

Further it can be shown that [31] $r = -r'$ and that the continuity of the electric field satisfies the condition $tt' = 1 - r^2$ so that the last two expressions can be seen to be identical and the reflected amplitude $r$ is,

$$r = r_1 + [(1 - r_1^2) r_2 \exp(-i\delta_1)][1 + r'_1 r_2 \exp(-i\delta_1)]^{-1}$$  \hspace{1cm} \text{(4.33)}$$

The value of the reflectivity $R = |r|^2$ is then given by,

$$R = [r_1^2 + r_2^2 + r_1 r_2 \cos 2\delta_1][1 + r'_1 r_2 + 2r'_1 r_2 \cos 2\delta_1]^{-1}$$  \hspace{1cm} \text{(4.34)}$$

The transmitted energy value is,

$$T = (n_2/n_1)(t_1 t'_2)^2[1 + r_1^2 + 2r_1 r_2 \cos 2\delta_1]^{-1}$$  \hspace{1cm} \text{(4.35)}$$
It is seen from equation (4.34) that the reflectivity will have minima where \( \cos 2 \gamma_1 = -1 \). If the film is sufficiently thick for two or more maxima/minima to be obtained in a spectrophotometric curve for normal or near normal incidence (\( \leq 10^\circ \)) then the optical thickness \( n_1 t \) may be determined. If successive maxima/minima are at \( \lambda_m \) and \( \lambda_{m+1} \), then

\[
 n_1 t = \frac{1}{2} \lambda_m \lambda_{m+1} (\lambda_{m+1} - \lambda_m)^{-1}
\]

where \( m = 1, 3, 5 \) etc at the minima and \( m = 2, 4, 6 \) etc at the maxima. The reflectance maxima and minima are given by [32],

\[
 R_{\text{max}} = \left[ \frac{(n_2 - n_0)/(n_2 + n_0)}{\sqrt{n_1^2}} \right]^2
\]

\[
 R_{\text{min}} = \left[ \frac{(n_1^2 - n_0 n_2)/(n_1^2 + n_0 n_2)}{\sqrt{n_1^2}} \right]^2, \quad n_0 \geq n_1 \geq n_2
\]

Later in chapter 6, equation (4.36) is used to determine the thickness of the thermally oxidized countings and equation (4.34) is used qualitatively in comparison with the experimental measurements on the thermally oxidized samples.
5 EXPERIMENTAL METHOD AND EQUIPMENT

5.1 Sample Preparation

Samples were sawn off an oxygen-free high conductivity (OFHC) copper sheet, 3mm in thickness to typical dimensions of 45x25mm. This copper sheet is processed by Granges Metalverken of Vestaras in Sweden. Polishing of samples was necessary because specular reflectence in the wavelength interval 0.35 – 15μm had to be measured. Mechanical polishing was performed in six stages using progressively finer abrasives, with the aid of equipment manufactured by A.P. Struers of Denmark. The last two stages of the polishing using aluminium oxide (Al₂O₃) paste of particle sizes of 1μm and 0.3, were very critical. Before each of these last two stages, the samples were thoroughly cleaned in alcohol, rinsed in distilled water and then dried. This was repeated after the last polishing. From this point onward care was taken not to touch the polished surfaces with fingers as the presence of any grease could affect the final result.

5.2 Sample Treatment

Three oxidation processes were performed as follows, (i) dry thermal oxidation at atmospheric pressure, (ii) sodium chlorite oxidation and (iii) the Ebanol C treatment developed by Ethone Inc. of New Haven, Connecticut, U.S.A

5.2.1 Dry Thermal Oxidation

The samples were oxidized in an oven of the type manufactured by AB Fabrics of Uppsala in Sweden. The wiring of the oven, including the thermostat and power supply switch unit is illustrated schematically in figure 5.1. It was necessary to calibrate the oven for the temperature at a chosen location inside. For this purpose a single junction alumel-chromel thermocouple was used. The measurements obtained were then corrected to zero degree reference by adding room temperature (≈ 20°C) thermal emf to give the
Fig. 5.1 Schematic representation of the wiring of the oven:
- SU - Switch unit, TU - Thermostat unit.
- TC - Thermocouple, switch S is closed when oven is closed.

Fig. 5.2 Graph showing temperature regulation characteristics of the thermostat.
actual temperature that would obtain if there had been a reference junction held at zero degree Celsius (0°C). Temperature gradients were checked and found not to vary by more than 15°C from the back to the front of the oven chamber. A check was also made on the temperature control characteristics of the thermostat unit. A typical temperature versus time cooling and heating curve obtained with the thermostat dial set at approximately 300°C is shown in Figure 5.2. Because of the rather pronounced fluctuations in the oven temperature due to the control characteristics of the thermostat, it became necessary to continually monitor the temperature with the thermocouple and the control dial adjusted when necessary so that the temperature could not vary by more than 10°C.

The effect of opening the oven in order to place the sample was also checked. It was established that the temperature would not be seriously affected provided the time of opening was less than about 20 seconds.

Oxide coatings were formed at 200°C, 250°C, 300°C and 450°C. The oxidation temperature was measured about 1 cm above the surface of the sample.

5.2.2 Sodium Chlorite Treatment

This oxidation process was accomplished in a chemical bath consisting of 100 g of sodium (NaOH) to 50 g of sodium chlorite (NaClO₂) per cubic decimeter (dm³) of distilled water; a recipe recommended by Close [13] and also recently used by Karlsson and Westastrand[16]. The more than a dozen samples used were divided into three groups of four treated at 55°C, 60°C and 65°C for increasing treatment times. As the formation of the oxide was found to be quite sensitive to temperature gradients it was necessary to preheat the sample in a distilled water bath maintained at the same temperature as the chemical treatment bath. The samples were then quickly transferred to the chemical bath which was stirred with a magnetic stirrer to minimize the effects of
temperature gradients due to convection currents.

6.2.3 Ebanol C Special Treatment

To obtain evenly oxidized coatings the procedure recommended by Ethone Inc. was performed. Degreasing and cleaning of the surfaces was followed by an activation by means of a dip in 10% by volume of sulphuric acid at room temperature. As in the sodium chlorite method the samples were prewarmed in a water bath maintained at the same temperature as the treatment bath which consisted of 180g of Ebanol C Special per cubic decimeter (dm³) of distilled water. The surfaces were treated at 102°C, 75°C and 50°C for increasing treatment times whilst the solution was continuously stirred.

6.3 Reflectance Measurement

Determination of the near normal (= 10° off normal) reflectance profiles of the samples at room temperature was accomplished in two stages. The first stage consisted in measuring specular reflectance in the wavelength interval 0.35 - 3.0μm. For this purpose, a double beam ratio recording Beckman DK-2A spectrophotometer was used. Its principal mode of operation is illustrated in figure 5.3. Depending on the spectral region of interest, the tungsten and hydrogen lamps provide the light sources. The mirrors A condense the light from the source into a parallel beam, which is chopped and mirror E and prism F provide a folding mechanism for changing the beam direction by 180°. Mirror I is a beam splitter whilst N is a beam selector. J and M are reference and sample beams respectively. The use of the Detectors P and Q, just like that of the lamp sources, depends on the spectral region being investigated. This is because their sensitivities are different for the different spectral regions. In this work the tungsten lamp and lead sulphide detector were used.

The Perkin Elmer 157 sodium chloride spectrophotometer was used for specular reflectance measurements in the infrared wavelength region, 2.5 - 15μm.
Fig. 5.3 Principle of the Beckman DK-2A spectrophotometer:

A - source condensing mirror  
B - entrance mirror  
C - entrance beam chopper  
D - entrance slit  
E - collimating mirror  
F - quartz prism  
G - exit slit  
H - exit beam condensing lens  
I - rotating mirror  
J - reference beam  
K - reference stationary mirror  
L - sample stationary mirror  
M - sample beam  
N - rotating mirror  
O - detector selector mirror  
P - lead sulphide cell  
Q - photomultiplier tube  
R - mirror coupling shaft
As some of the samples showed a remarkably low reflectivity in the spectral region 0.35 - 3\(\mu\)m it became necessary to determine the extent to which this was due to diffuse scattering of the incident radiation. The total hemispherical reflectance was measured for each representative sample with the aid of a Perkin Elmer 350 spectrophotometer in the wavelength interval 0.35 - 2.0\(\mu\)m. The special feature of this measuring instrument is that the detector is located inside an integrating sphere coated with a high reflectivity substance such as magnesium oxide (MgO). The sample and detector are arranged such that all radiation originating at the sample must eventually reach the detector through multiple reflections within the integrating sphere.

5.4 Evaluation of Solar Absorptance and Thermal Emittance

The basic method in evaluating selective surfaces for photothermal conversion of solar energy is to determine the solar absorptance, \(a_s\), and the thermal emittance, \(e_t\), of each surface.

5.4.1 Solar Absorptance

To evaluate the solar absorptance, \(a_s\), use is made of the spectral reflectance data in the wavelength interval 0.3 - 2.5\(\mu\)m. The usual practice is to choose a centre wavelength of a band containing the same fractional energy division of the solar spectrum for a given air mass. This provides a simple method for integrating the results to give solar reflectance and hence solar absorptance. For example, if it is desired to make use of a centre wavelength of a band containing 2\% energy division of the solar spectrum, then there should be fifty such divisions between 0.3 and 2.5\(\mu\)m.

However in this study, a slightly different approach was adopted. The average reflectance for every 0.1\(\mu\)m wavelength interval was computed and the value obtained multiplied by the fractional energy of the solar spectrum of air mass, \(m = 2\) found in the appropriate wavelength interval.
This was done for every 0.1\( \mu \text{m} \) wavelength interval from 0.3-2.5\( \mu \text{m} \). The products obtained were then summed up to give the solar reflectance and hence solar absorptance.

The starting point is the equation (1.7),

\[
\alpha_\lambda = 1 - r_\lambda \quad (1.7)
\]

This means that a knowledge of the monochromatic reflectance \( r_\lambda \) implies the monochromatic absorptance \( \alpha_\lambda \). The absorptance of any surface is then given by

\[
a = \left( \int_0^\infty (1 - r_\lambda) H_\lambda d\lambda \right) / \int_0^\infty H_\lambda d\lambda \quad 5.1
\]

The quantity \( H_\lambda d\lambda \) is any radiative flux incident hemispherically on a surface per unit time and area in a wavelength interval \( d\lambda \). The solar absorptance, results if the solar spectral flux \( S_\lambda,^m d\lambda \) is substituted for \( H_\lambda d\lambda \). The second subscript, \( m \) in \( S_\lambda,^m \) denotes the air mass. In practice the limits of integration are 0.3\( \mu \text{m} \) and 3\( \mu \text{m} \) and the integrals are changed into summations,

\[
a_s = \sum_{\lambda_1}^{\lambda_2} (1 - r_\lambda) S_\lambda^m \Delta \lambda / \sum_{\lambda_1}^{\lambda_2} S_\lambda^m \Delta \lambda \quad 5.2
\]

The denominator is simply the total incident solar flux at air mass \( m \), which for \( m = 2 \), is equivalent to 900W/m\(^2\). The wavelength limits are \( \lambda_1 = 0.3\mu \text{m} \) and \( \lambda_2 = 3\mu \text{m} \).

5.4.2 Thermal emittance

Specular reflectance data of the samples in the infrared spectral region were used to evaluate the thermal emittance, \( e_T \). The expression used is given by,

\[
e_T = \sum_{\lambda_1}^{\lambda_2} (1 - r_\lambda) q_\lambda B \Delta \lambda / q_r \quad 5.3
\]
where $\lambda_1'$ is the lower wavelength limit of the spectral flux distribution of a black body at any temperature $T$, $\lambda_2'$ is the upper limit, $r_\lambda$, is the monochromatic reflectance in the infrared wavelength region, $Q_{\lambda',B}^{\Delta \lambda'}$ is the spectral flux found in the wavelength interval $\Delta \lambda'$ and $T$ is the total radiative power of a black body at any temperature $T$. For $T = 373K$, $Q_T = 1100W/m^2$. As with the calculation of solar absorptance, the spectral radiance distribution of a black body at 373K, obtained with the aid of expression (1.1) was subdivided into divisions of 0.5µm between 3µm and 15µm. For a black body at 373K approximately 31% of the total power emitted has wavelengths greater than 15µm. This fact is illustrated in figure 1.3. In most cases encountered in this work the spectral reflectances of the samples attained a maximum value at at least 15µm. For ease of computation it was assumed that the spectral reflectance remained constant for wavelengths longer than 15µm. Thus the spectral reflectance was simply multiplied by the percentage spectral flux found at more than 15µm. Taking these factors into consideration the expression for the thermal emittance can be rewritten,

$$e_T = \sum_{3 \mu}^{15 \mu} (1 - r_\lambda) Q_{\lambda,B}^{\Delta \lambda} q_r + f$$

where $f$ is the product of the spectral reflectance and the percentage spectral flux of a black body at 373K found at wavelengths longer than 15µm.
6 RESULTS

6.1 General

The results of the near informal incidence reflectivity measurements and the derived values of solar absorptances and thermal emittances are presented. The tables of results also include total hemispherical absorptances calculated using data of the diffuse reflectivity measurements in the spectral region 0.35μm - 2.0μm, and extrapolated to 3μm. Such measurements were performed for the representative cases whereby the low reflectivities of the coatings in the solar spectral region appeared too good to arise from intrinsic absorptive properties of the oxide films. As the measurements have conformed such remarkably low reflectivity was a result of a significant component of the incident radiation being diffusely reflected and consequently not reaching the detector. The reason for this was revealed by scanning electron microscopy of the surfaces which show an apparently rough morphology. All the scanning electron microscope photographs were taken with the aid of a Philips 501 at a primary beam voltage of 20kV and at an angle of 45°. The results of characterization of the samples by X-ray diffraction are also presented. An attempt has been made to relate the solar absorptances and thermal emittances of the coatings to the treatment times. The results, presented in figures 6.13 - 6.15 and figures 6.16 - 6.18, show that in general, during the early stages of the oxidation process, the rate of increase of the solar absorptance is much higher than for the thermal emittance. But then a time is reached when the rate of increase of the solar absorptance with time becomes less than for the thermal emittance. Figures 6.16 - 6.18 show plots of Δa_s/Δt and Δe_τ/Δt as functions of time t. Such plots would be helpful in determining when to stop the treatment. A helpful approach would be to stop treatment in the neighbourhood of Δa_s/Δt 0 and Δe_τ/Δt constant.
Finally a comparison of the three methods of producing solar absorber surfaces is made and a presentation is made in the form of figure 6.19. For the cases considered, the thermal oxidation method has tended to produce poorer coatings than the other two methods. That is for the same thermal emittances, the thermal oxidation process has produced coatings of lower solar absorptance than its counterparts.

6.2 Dry Thermal Oxidation

The films formed at temperatures in the range 200°C - 450°C have a variety of interesting colours ranging from yellow, orange, light brown to bluish black. Their reflectance curves show oscillatory behaviour due to interference effects. This is probably due to the smoothness and homogeneity of the coatings. The interference maxima/minima can be used to estimate the thicknesses of the films (the thickness, $t = \{2n(1/\lambda_m - 1/\lambda_{m+1})\}^{-1}$ where $n$ is the refractive index of the film material, and $\lambda_m$, $\lambda_{m+1}$ are the wavelengths of the successive maxima in reflectance) [32]. Thus using the bulk refractive index, $n = 2$ for Cu$_2$O: at 250°C the thicknesses are estimated to be in the range 0.3 - 1.0μm and about 1.8 - 2.5μm at 450°C.

Of significance, however, is that the surfaces have reasonable figures-of-merit ($q_s/e_T > 3$) and because of their smoothness, their spectral selectivity might be linked entirely to the intrinsic absorptive or antireflective properties of the oxide layer. The results of X-ray diffraction analysis of the surfaces have shown that copper(I) oxide (Cu$_2$O) is probably the only constituent formed at temperatures up to 450°C (see figure 6.11). As the oxidation temperature is increased copper (II) oxide (CuO) is also found to be present in proportions depending on the temperature and time. In particular, at 600°C, the two oxides have been estimated to be in a ratio of about seven parts of Cu$_2$O to one part of CuO (figure 6.12 and Table 6.4).
Fig. 6.1 Reflectances of samples thermally oxidized at 200°C

Fig. 6.2 Reflectances of samples thermally oxidized at 250°C
Fig. 6.3 Reflectances of samples thermally oxidized at 300°C

Fig. 6.4 Reflectances of samples thermally oxidized at 450°C
But these oxide layers, which tend to be comparatively thick, have a tendency to be brittle. Their brittleness is probably due to the increased proportion of CuO. The rupturing of the surfaces at elevated oxidation temperatures (> 500°C) could be caused by differences in the mechanical properties of the oxide and the substrate. Oxidation of the surface could result in increased lateral dimensions of the surface layer compared to the metallic substrate. This could result in surface stresses which would subsequently be relieved by rupturing.

6.3 Sodium Chloride Oxidation

This method of treatment of polished copper produced shiny bluish grey oxide films. Their reflectivity curves have a characteristic maximum between 0.5μm and 0.6μm and a minimum somewhere between 0.85μm and 1.15μm as reported elsewhere [16]. A method of estimating the thickness of these coatings has not been worked out since they produce no interference patterns.

Solar absorptances, α, of between 0.85 and 0.90 and thermal emittances of approximately 0.20 have resulted from this process. The best results were obtained at the treatment temperature of 60°C and times between 3 and 8 minutes. The films formed probably consist mainly of Cu₂O (see figure 6.11). Their rather superior solar optical properties could be attributed to the roughness of the surfaces, which have a boulder like appearance with numerous cavities (Plate 2B). The cavities in the surface could result in interreflections with consequent increase in absorptance.

6.4 Ebanol C Treatment

At treatment temperatures well below (but not less than 55°C) the standard temperature of 102°C for chemically blackening copper, the Ebanol C process produces blue black coatings. These have desirable selective absorber optical
Fig. 6.5 Reflectance of the sodium chlorite oxidized samples at a treatment temperature of 55°C.

Fig. 6.6 Reflectance of the sodium chlorite oxidized samples at a treatment temperature of 60°C.
Fig. 6.7 Reflectance of sodium chlorite oxidized samples at a treatment temperature of 65°C.
properties. However, the standard procedure recommended by Ethone Inc. results in a matte black appearance which is due to its dendritic structure (Plate 4B). These surfaces have a very low solar reflectivity (<2%) and a poor thermal emittance of about 50% at 100°C. Their reflectivities are almost zero in the visible and have an absorption band at around 9 μm (figure 6.10).

The surfaces are composed mainly of CuO with some Cu₂O. The results are shown in figure 6.12 for a typical case. Scanning electron microscopy has revealed a dendritic structure for those surfaces prepared by the standard procedure and a spongy surface topography for the lower temperature surfaces (Plates 4A, 4B). The tiny cavities evident as dark areas on the surface could be responsible for the low reflectivity in the solar region by trapping the radiation through multiple reflections. However, surfaces prepared by the standard procedure are capable of producing good selective absorbers with Q₅ = 0.90 and e₃₇₃ₓ = 0.10 provided treatment times are restricted to 10 - 15 seconds. But the reaction proved to be too fast for effective control resulting in unevenly coated surfaces.
Fig. 6.8 Reflectance of Ebanol-c oxidized samples at a treatment temperature of 50°C.

Fig. 6.9 Reflectance of Ebanol-c oxidized samples at a treatment temperature of 75°C.
Fig. 6.10 Reflectance of Ebanol C oxidized samples for treatment temperature of 102°C. The curves below 2μm were derived from total reflectivity data & extrapolated (---) to 4 μm.
Table 6.1 Solar absorptances and thermal emittances of thermally oxidized Copper at different temperatures and duration of oxidation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Oxidation time, min.</th>
<th>Solar absorptance ( \alpha_S )</th>
<th>hemsp. ( \alpha_h )</th>
<th>emittance ( e_{373K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>200</td>
<td>25</td>
<td>0.42</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>75</td>
<td>0.58</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>150</td>
<td>0.76</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>300</td>
<td>0.79</td>
<td>-</td>
<td>0.04</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>25</td>
<td>0.75</td>
<td>0.54</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
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<td>0.62</td>
<td>0.05</td>
</tr>
<tr>
<td>15</td>
<td>&quot;</td>
<td>75</td>
<td>0.90</td>
<td>0.62</td>
<td>0.09</td>
</tr>
<tr>
<td>20</td>
<td>&quot;</td>
<td>150</td>
<td>0.88</td>
<td>0.67</td>
<td>0.20</td>
</tr>
<tr>
<td>21</td>
<td>300</td>
<td>5</td>
<td>0.5</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>22</td>
<td>&quot;</td>
<td>10</td>
<td>0.71</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>19</td>
<td>&quot;</td>
<td>15</td>
<td>0.81</td>
<td>-</td>
<td>0.06</td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>26</td>
<td>0.88</td>
<td>-</td>
<td>0.13</td>
</tr>
<tr>
<td>29</td>
<td>450</td>
<td>3 ( \frac{3}{4} )</td>
<td>0.36</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>30</td>
<td>&quot;</td>
<td>7 ( \frac{1}{2} )</td>
<td>0.79</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>31</td>
<td>&quot;</td>
<td>9 + 11</td>
<td>0.87</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>32</td>
<td>&quot;</td>
<td>11(\frac{1}{2})+28(\frac{1}{4})</td>
<td>0.91</td>
<td>0.63</td>
<td>0.02</td>
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Table 6.2  Solar absorptances and thermal emittances of Sodium Chlorite oxidized Copper at different temperatures and duration of oxidation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature °C</th>
<th>Duration of Oxidation, min.</th>
<th>Solar absorptance Specular, $a_s$</th>
<th>Solar absorptance hemisp., $a_h$</th>
<th>$e_{373K}$ emittance</th>
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<tr>
<td>56</td>
<td>65</td>
<td>2.5</td>
<td>0.85</td>
<td>-</td>
<td>0.04</td>
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<tr>
<td>57</td>
<td>&quot;</td>
<td>5.0</td>
<td>0.92</td>
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</tr>
<tr>
<td>58</td>
<td>&quot;</td>
<td>7.5</td>
<td>0.97</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>59</td>
<td>&quot;</td>
<td>10.0</td>
<td>0.98</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>52</td>
<td>60</td>
<td>3.75</td>
<td>0.87</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>53</td>
<td>&quot;</td>
<td>7.5</td>
<td>0.93</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>54</td>
<td>&quot;</td>
<td>11.25</td>
<td>0.96</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>55</td>
<td>&quot;</td>
<td>15.00</td>
<td>0.91</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>48</td>
<td>55</td>
<td>5</td>
<td>0.85</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>49</td>
<td>&quot;</td>
<td>10</td>
<td>0.94</td>
<td>-</td>
<td>0.09</td>
</tr>
<tr>
<td>50</td>
<td>&quot;</td>
<td>15</td>
<td>0.96</td>
<td>-</td>
<td>0.14</td>
</tr>
<tr>
<td>51</td>
<td>&quot;</td>
<td>20</td>
<td>0.96</td>
<td>0.90</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Table 6.3 Solar absorptances and thermal emittance of Ebanol C oxidized copper at different temperatures and duration of oxidation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature °C</th>
<th>Duration of Oxidation, min.</th>
<th>Solar absorptance Specular, $a_s$</th>
<th>Hemisph. $a_h$</th>
<th>Emittance $e_{373K}$</th>
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<tr>
<td>34</td>
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<td>0.50</td>
<td>0.98</td>
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<td>0.13</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td>1.50</td>
<td>-</td>
<td>0.92</td>
<td>0.20</td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>2.50</td>
<td>-</td>
<td>0.92</td>
<td>0.47</td>
</tr>
<tr>
<td>39</td>
<td></td>
<td>3.75</td>
<td>-</td>
<td>0.96</td>
<td>0.50</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td>5.00</td>
<td>-</td>
<td>0.95</td>
<td>≈ 0.50</td>
</tr>
<tr>
<td>44</td>
<td>75</td>
<td>1.25</td>
<td>0.83</td>
<td></td>
<td>0.07</td>
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<tr>
<td>902</td>
<td></td>
<td>1.67</td>
<td>0.92</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>2.50</td>
<td>0.94</td>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td>46</td>
<td></td>
<td>3.75</td>
<td>0.93</td>
<td>0.90</td>
<td>0.12</td>
</tr>
<tr>
<td>47</td>
<td></td>
<td>5.00</td>
<td>0.94</td>
<td>≈ 0.90</td>
<td>0.16</td>
</tr>
<tr>
<td>-</td>
<td>50</td>
<td>1.25</td>
<td>0.23</td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>41</td>
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<td>3.75</td>
<td>0.64</td>
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<td>40</td>
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<td>0.83</td>
<td></td>
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<tr>
<td>903</td>
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<td>10.0</td>
<td>0.94</td>
<td>0.87</td>
<td>0.11</td>
</tr>
<tr>
<td>TREATMENT</td>
<td>TEMPERATURE</td>
<td>Estimated COMPOSITION CuO: Cu&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Reflecting plane of dominant Component</td>
<td>TREATMENT Time</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
<td>------------------------------------------</td>
<td>----------------------------------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>Ebano C</td>
<td>102°C</td>
<td>5:2</td>
<td>(111) + (002)</td>
<td>300 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>102°C</td>
<td>~4:1</td>
<td>(111) + (002)</td>
<td>150 s</td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>65°C</td>
<td>0:1</td>
<td>(111)</td>
<td>600 s</td>
<td></td>
</tr>
<tr>
<td>Thermal</td>
<td>200°C</td>
<td>~0:1</td>
<td>(111)</td>
<td>300 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300°C</td>
<td></td>
<td></td>
<td>600 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450°C</td>
<td>0:1</td>
<td></td>
<td>450 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>1:16</td>
<td></td>
<td>540 + 660 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600°C</td>
<td>1:7</td>
<td></td>
<td>300 s</td>
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Fig. 6.11 Diffraction amplitude as a function of scattering angle for thin films of the Ebanol C-, thermally- and sodium chlorite treated polished copper surfaces.

Fig. 6.12 Intensity as a function of scattering angle for the oxide film formed at 600°C for a duration of 4 min.
Fig 6.13 Plot of $\sigma_s$ and $e_T$ against duration of oxidation for the samples thermally oxidized at 300°C.
Fig. 6.14 Variation of $q_s$, $e_T$ with the duration of treatment for the chlorite oxidized samples
Fig. 6.15 Variation of \( \alpha_s, e_T \) with the duration of treatment for the Ebanol C oxidized samples.
Fig. 6.16 Plot of $\Delta q_s/\Delta t$ (— — —) & $\Delta e_i/\Delta t$ (– – –) against the duration of treatment for the thermally oxidized samples.

Fig. 6.17 Plot of $\Delta q_s/\Delta t$ (× × ×) & $\Delta e_i/\Delta t$ (○ ○ ○) against duration of treatment for the chlorite oxidized samples.
Fig 6.18 Plot of $\Delta q_s/\Delta t$ (× ×) & $\Delta e_r/\Delta t$ (○ ○) against duration of treatment for the Ebanol C oxidized samples.
Fig 6.19

- a - Ebanol C: 75°C
- b - Chlorite: 60°C
- c - Thermal: 300°C
PLATE 1: Thermally oxidized at 450°C - 540 + 660 s
The large zig-zag crack (1B) is an edge of one of the raptured blisters clearly visible in A. Bright areas were caused by charging of film by the incident electron beam.

PLATE 2: Sodium Chlorite oxidized at 65°C for 10 minutes. The tiny (black) cavities which would tend capture the radiation can be seen (2B)
PLATE 3: Ebanol C - oxidized at 75°C - 150 seconds.

PLATE 4: Ebanol C - oxidized at 102°C - 150 seconds.

Notice the dendritic structure in 4B most likely responsible for the large diffuse scattering of the incident radiation (see reflectance curve C in fig 6.10)
EMITTANCE MEASUREMENT

7.1 General

Any instrument designed to measure the thermal emittance of any surface must be able to register the rate of heat loss from the surface. This entails the determination of the true temperature of the surface. Measurements in which the sample is heated from one side will result in temperature gradients and significant heat losses due to conduction through electrical leads. Ideally the measurements have to be carried out with the sample in thermal isolation. But this is difficult to achieve in practice because the sample must be supported in addition to the problem of delivering electrical power to the sample. Conduction and convection heat losses are minimized by placing the sample in an evacuated (<10⁻⁵ torr) chamber.

7.1.1 Radiative Heat Transfer

The basic principles of radiative heat transfer have already been dealt with in section 1.2.3. This section summarizes those factors relevant to the measurement of the total thermal emittance. That all heated bodies emit thermal infrared radiation whose intensities and wavelength spectra depend on the absolute temperature and the optical characteristics of the emitting surface is expressed mathematically by equations (1.1) - (1.4). The total emittance \( e_T \), can be expressed in integral form as,

\[
  e_T = \frac{1}{q_f(T)} \int_{\lambda_B}^{\infty} \varepsilon(\lambda, T) q_B(\lambda, T) d\lambda \quad 7.1
\]

where \( q_f(T) \) is given by (1.4) and \( q_B(\lambda, T) \) is given by (1.1). The spectral emittance, \( \varepsilon(\lambda, T) \) in the integrand of (7.1) is written in the form which expresses dependence on the absolute temperature and the wavelength. Thus it is expected that the total thermal \( e_T \), will vary with temperature. It should be noted that the equation (1.4) assumes that the body does not receive any radiation from its surroundings.
A realistic expression for a body at temperature $T$ in an environment at temperature $T_0$ is,

$$ q_r(T) = e_T \sigma (T^4 - T_0^4) \quad 7.2 $$

If $T$ is at least $5T_0$, then the heat gained by the body from its surroundings is less than one part in six hundred of that radiated by the body to the surroundings. Thus the contribution due to $T_0$ can be neglected.

7.1.2 Vacuum Techniques

Principles of design and Construction of the Chamber

It was necessary to predetermine the pressures that would have to be attained in order to make conduction losses due to the remnant gas in the chamber minimal. The thermal conductivity of a gas, $k$, depends on the number of molecules $n$ and their mean free path $l$ and its dependence is expressed by [17],

$$ k \propto n l $$

$$ l = \frac{1}{\sqrt{2} n \pi d^2} \quad 7.3 $$

$$ P \propto n (\propto 1/l) $$

where $d$ is the diameter of a molecule, and $P$ is the gas pressure. The product $n l$ is independent of $P$ as long as $l$ does not exceed the dimensions of the chamber. When $n$ is reduced (hence $P$) so that $l >$ dimensions of chamber $k$ becomes proportional to $n(\propto P)$ so that $k$ decreases with pressure. The last result is important because one needs to reduce the chamber pressure by roughly two orders of magnitude below the pressure at which $k$ begins to decrease with pressure, in order to make thermal conduction losses due to the remnant gas negligible. This result is utilized later in section 7.3.1 to determine the low pressure limit for which the thermal conductivity is independent of pressure.
Speed Requirements for Pumps in Series

The basic equations governing the operation of a symple vacuum system are given by the effective pumping speeds of the pumps. For the diffusion and rotary pumps these speeds are [18],

\[
\text{Diffusion pump: } S_1 = \frac{C_1 R}{(C_1 P_c - R)} \quad 7.4
\]

\[
\text{Rotary pump: } S_2 = \frac{C_2 R}{(C_2 P_b - R)} \quad 7.5
\]

where \(C_1\) and \(C_2\) are the conductances of the lines connecting the diffusion and rotary pumps to the chamber respectively, \(P_b\) is the pressure maintained by the rotary pump at the diffusion pump outlet, \(P_c\) is the ultimate chamber pressure, \(R\) is the leak rate in litre-torr/sec. The conductance \(C\) of the tubes is given by,

\[
C = \frac{(65D^3/M)(L + 4D/3)^{-1}}{} \quad 7.6
\]

where \(M\) is the gram molecular mass of the gas \(L\) and \(D\) are the length and internal diameter in centimeters of the tube respectively. For air at 20°C, \(C = 12.1 D^3 (L+4D/3)^{-1}\).

Pump Down Time

The pump down time is given by,

\[
t = \frac{2.3 V/S \log_{10}(R/R_c)}{} \quad 7.7
\]

where \(P_o\) is the pressure at which a pump begins to evacuate, \(P_c\) is the final pressure in the chamber, \(V\) is the volume of the chamber in litres and \(S\) is the effective pumping speed.

7.1.3 Design Requirements

The basic requirements that should be met by a simple calorimeter for total emittance measurement are,

1. The chamber must be sufficiently evacuated to minimize the effects of convection and conduction
(ii) The sample must be thermally isolated

(iii) Inside walls of chamber must be blackened to maximize radiative heat transfer

(iv) True surface temperature of the sample must be known

(v) Walls of the chamber 'seen' by the sample must be isothermal

(vi) Apparatus must be calibrated against a sample of known emittance

(vii) A simple technique must be worked out to ensure that steady state in the sample temperature is attained in the shortest time possible, otherwise data would take a very long time to accumulate.
7.2 Survey of Existing Methods

7.2.1 Method of Comparing Temperature Drops Along Coated Fins

This method has been used for thermal control in space and extraterrestrial technology [21] where the only means of heat rejection is by thermal radiation. A modification [22] makes use of the principle that if identical fins of a material differing only in emittance are heated at their bases to the same temperature, then the temperature drop along the fin becomes a function of emittance only. A simplified fin configuration is illustrated in figure 7.1. The derivation of an analytical expression for the heat radiated by the fin is obtained if one considers a radiating fin of known geometry maintained a known base temperature. The solution for such a situation is given elsewhere [21, 23]. The temperature gradient $\Delta T$ along the fin length $l_0$ is related to the other parameters by,

$$\Delta T \propto \left( \frac{\epsilon \sigma l_0^3}{\lambda} \right) / k$$  \hspace{1cm} 7.8

where $\epsilon$ is the emittance, $\sigma$ is the Stefan-Boltzmann Constant, $T_0$ is the base temperature and $k$ is the thermal conductivity of the fin material. A plot of $\epsilon$ versus $\Delta T$ is made for the known emittance samples. The graph is subsequently used to determine unknown emittances of other samples from measured values of $\Delta T$. 
Fig. 7.1 Simplified fin configuration
7.2.2 Butler Method

The underlying principle of this method [27] is to heat a small sample enclosed in an isothermal evacuated chamber. The sample is heated to a suitable temperature $T_1$ greater than the temperature of the chamber walls $T_2$. The power is then turned off so that the sample cools down by thermal radiation. Since the chamber is evacuated, cooling by molecular conduction and convection are assumed to be negligible. A cooling curve is then plotted. With their inner walls of the chamber blackened, $\varepsilon_2 \approx 1$. The slope of the cooling curve at sample temperature $T_1$ is then found, which determines the emittance of the sample, i.e.

$$\varepsilon_1 = -\frac{m_1 c_1 (\Delta T/\Delta t)}{A_1 \sigma (T_1^4 - T_2^4)}$$ 7.9

The subscripts 1 and 2 refer to the sample and chamber respectively, $A_1$ is the area of the sample, $m_1$ is the mass and $c_1$ the specific heat capacity of the sample material.

7.2.3 Calorimetric Method

This method is similar to the Butler method, but instead power is continuously supplied by electrical means until the sample reaches a steady state temperature. Assuming negligible losses due to conduction through electrical leads and remnant gas molecules, then at steady state the power supplied equals the power radiated by the sample. The net radiative exchange between the sample and the chamber walls is given by [21],

$$q = \varepsilon^* \sigma A_1 (T_1^4 - T_2^4)$$ 7.10

where $\varepsilon^*$ is the effective total emittance of the sample given by,

$$\varepsilon^* = \left[ \frac{1}{\varepsilon_1} + \frac{A_1}{A_2} \left( \frac{1}{\varepsilon_2} - 1 \right) \right]^{-1}$$ 7.11
A_1 is the emitting surface area of the sample A_2 is the area of the inside walls of the chamber \( \varepsilon_1 \) and \( \varepsilon_2 \) are the emittances of the sample and inside walls of the chamber respectively. The expression (7.10) can be simplified if \( \varepsilon_2 \approx 1 \) and \( A_2 \gg A_1 \) such that \( A_1 / A_2 \approx 0 \). This results in \( \varepsilon_2 = \varepsilon_1 \) in equation (7.11). Equating (7.10) to the electrical power supplied and rearranging gives the emittance of the sample,

\[
\varepsilon_1 = \frac{IV}{\sigma A_1 (T_1^4 - T_2^4)}
\]

7.12

where I and V are the current and voltage supplied to the heater.

7.3 Experimental Method

7.3.1 Apparatus

A schematic diagram of the apparatus is presented in figure 7.2. The primary components of the apparatus are the chamber which encloses the sample and heater, the rotary and diffusion (oil) pumps, the Pirani and Fenning 8 gauges, liquid nitrogen dewar, power supply, voltmeters (2) and ammeter.

Chamber

Fig 7.3 is a drawing of the chamber with the sample in it. The inside walls of the chamber were painted black \( (\varepsilon = 0.96) \). A simple calculation using equations (7.3), with \( I = 0.1 \text{m} \) (diam. of chamber) and \( n = 3 \times 10^{25} \) molecules/m

\(^3\) showed that the thermal conductivity of the air would remain constant down to at least \( 10^{-3} \) torr. This meant that the chamber had to be evacuated to at least \( 10^{-5} \) torr in order to minimize heat losses due to convection and conduction by the air. The chamber walls were maintained at liquid nitrogen temperature (77K). This latter condition was unnecessary but it conveniently made radiative heat transfer from the chamber walls to the sample sufficiently small to be neglected. However, it could equally well have
Fig. 7.2 Schematic representation of vacuum system for the measurement of total hemispherical emittance:

A - Penning gauge  
B - Pirani gauge  
C - High vacuum valve  
D - Roughing valve  
E - Backing valve  
F - Air inlet valve  
G - Diffusion pump  
H - Rotary pump  
I - Sample/heater
Fig. 7.3 Chamber with the sample.
been possible to make the chamber an isothermal enclosure at any convenient temperature such as the melting point of ice. But then the radiative contribution due to the chamber to the sample would have to be taken into account. Later after testing the apparatus it was found necessary to incorporate a radiation shield within the chamber in order for the sample not to 'see' room temperature effects from the top of the chamber.

Sample and Heater

The sample consisted of two identical parts produced by cutting the original sample into two halves. The two halves were used to enclose the heater so that all power supplied would be transferred to the sample. The uncoated sides of the sample were polished at least to 0.3μm particle size so as to have sides of known emittance. The heater was placed between these two sample halves and secured with the help of very small screws (Fig 7.4). A copper wire flattened to slightly larger dimensions than the diameter of the heater wire formed a radiation shield to reduce losses from the heater. The heater was constructed using manganin wire (= 0.2mm diam.) enclosed in a stainless steel sheath and insulated from it with aluminium oxide powder. The sheath external diameter is approximately 0.5mm. This heater wire is manufactured by OMEGA ENGINEERING INC, Stamford, Connecticut, USA.

Power Supply

Power was supplied to the heater by means of a power supply of the constant voltage/constant current type adjusted to operate in the constant current mode. The sample temperature given by [24],

\[ T(t) = T_0 - C e^{-t/\tau} \] 7.13
Fig. 7.4 Sample-heater assembly with the other half of the sample removed.

Fig. 7.5 Regulating the power supplied to the heater in order for the sample to attain steady state as quickly as possible.
shows that the steady state temperature $T_0$, would take a long time to reach. In equation (7.13) $C$ is a constant and $\tau$ is the time constant given by,

$$\tau = \frac{mc}{4\sigma \varepsilon \varepsilon' A T_0^3} \quad \text{7.14}$$

where $m$ and $c$ are the mass and specific heat capacity of the sample respectively, $A$ is the total emitting surface area which included the uncoated sides and $\varepsilon'$ is the effective total emittance of the sample. This is defined as,

$$\varepsilon' = \frac{(A_c \varepsilon_c + A_p \varepsilon_p)}{A} \quad \text{7.15}$$

where the subscripts $c$ and $p$ denote coated and polished surfaces respectively. In order to reach the steady state ($T = T_0$) as quickly as possible, the power supplied initially was set at $P_1$ which was greater than $P_0$ the power required to maintain the sample at temperature $T_0$. When $T$ was about 10°C less than $T_0$, the power was lowered to $P_0$. This is illustrated in Fig 7.5. The temperature often overshot the predetermined $T_0$ mainly due to thermal inertia.

Temperature Measurement

The temperature was measured with a copper-constantan thermocouple soldered to the radiation shield ring (Fig 7.4). This was done because of the difficulty of measuring the true surface temperature of the sample because of poor thermal contact. In order to counter temperature depression effects at the point of attachment of the thermocouple due to conduction, the leads were anchored to the sample before leading away to the voltmeter. The reference of the thermocouple was held at 0°C.

7.3.2 Testing the Apparatus

A summary of the information describing the component parts of the apparatus is given in Table 7.1. The information was used to make a theoretical evaluation of the performance
Table 7.1

<table>
<thead>
<tr>
<th>Test Run</th>
<th>Component part</th>
<th>Function</th>
<th>Dimensions (cm)</th>
<th>Conductance or Speed (1/s)</th>
<th>Effective Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diffusion pump</td>
<td>High Vac.</td>
<td>-</td>
<td>100</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Rotary pump</td>
<td>Rough Vac.</td>
<td>-</td>
<td>10</td>
<td>0.8</td>
</tr>
<tr>
<td>1</td>
<td>Tube 1</td>
<td>rough vac.</td>
<td>2, ≈50</td>
<td>0.83</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(1st. seg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2nd. seg)</td>
<td></td>
<td>3, ≈80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tube 2</td>
<td>by-pass</td>
<td>3, ≈80</td>
<td>0.3</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Run</th>
<th>Component part</th>
<th>Function</th>
<th>Dimensions (cm)</th>
<th>Conductance or Speed (1/s)</th>
<th>Effective Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diffusion pump</td>
<td>High Vac.</td>
<td>-</td>
<td>100</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Rotary pump</td>
<td>Rough Vac.</td>
<td>-</td>
<td>10</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>Tube 1</td>
<td>rough vac.</td>
<td>2, ≈50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1st. seg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(2nd. seg)</td>
<td></td>
<td>2, ≈50</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Tube 2</td>
<td>by-pass</td>
<td>2, ≈50</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7.2

<table>
<thead>
<tr>
<th></th>
<th>Test Run 1</th>
<th>Test Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Actual</td>
<td>Theor.</td>
</tr>
<tr>
<td>Pump down time for:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotary pump</td>
<td>≈65s</td>
<td>45s</td>
</tr>
<tr>
<td>Diffusion pump</td>
<td>Several hours</td>
<td>24s</td>
</tr>
<tr>
<td>Ultimate chamber pressure (torr)</td>
<td>$10^{-3}$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
of the entire facility and compared to the actual result of the testing.

Before blackening the inside of the chamber, the apparatus was evacuated to assess its performance. The pressure against time (in arbitrary units) graph in Fig 7.6 shows qualitatively the results. A leak was detected and following rectification the lowest pressure obtained was about $2 \times 10^{-4}$ torr. This result agrees rather well with the prediction of the pumping speeds of the rotary and diffusion pumps given respectively by equations (7.4) and (7.5), assuming a leak rate $R = 10^{-5}$ torr-litre/sec. Table 7.2 gives a summary of the results obtained before and after changing the faulty tube, under headings Test 1 and Test 2 respectively.

The chamber was then degreased by washing with alcohol and together with the connecting lines (tubes) was degassed by baking in an oven at 150°C for approximately 24 hours. Then the inside of the chamber was blackened and allowed to dry for about three days. Following this pressures of less than $10^{-5}$ torr were easily obtained and on immersing the chamber in liquid nitrogen pressures dropped to less than $10^{-6}$ torr. This drop in pressure was due to the fact that the remnant gases were frozen since the chamber acted as a cold trap.

7.3.3 Data Collection

The apparatus was checked against a polished copper sample of known emittance [25]. Three other samples, one from each of the thermally-, Ebanol-C and chlorite-oxidized categories were selected for measurement. A modified form of equation (7.12) with the effective total emittance of the sample given by equation (7.15) was used to obtain the total emittance of the coated surface as,

$$\varepsilon_c = \frac{I}{\sigma A_c T_1^4} - \varepsilon_p (A_p/A_c)$$  \hspace{1cm} 7.16
Fig. 7.6 Pump down during the first test run of the facility
where $T_1$ is the sample temperature, and $c,p$ refer to the coated and polished surfaces respectively. Both $I$ and $V$ were measured to an accuracy of at least one part per thousand, whereas $T_1$ was only known to an accuracy of $\pm 1^\circ C$.

7.3.4 Results

The results are presented in Table 7.3 together with the values of emittance calculated from reflectance data. The results seem to agree quite well but it seems strange though, that the emittance of sample 9 does not increase with temperature. But it appears likely that this may be due to the comparatively thin coating obtained by thermal oxidation. However, it is rather the big difference between the $\varepsilon$-values at 293K which does not find an easy explanation.

7.4 Sources of Error

The main sources of error were due to thermal conduction through the suspending lead wires. But these were minimized by taking measurements with the sample temperature close to room temperature. Assuming that the other ends of the leads were at room temperature, this would result in very small temperature gradients and hence thermal conduction. The other sources of error were due to radiation losses from the radiation shield ring. These would be reduced by enclosing the heater in a cavity-type sample. But this would greatly increase the complexity of the sample preparation. The most probable error in the experimental $\varepsilon$-values was obtained by the use of equation (7.16) as,

$$
\% (\Delta \varepsilon / \varepsilon) = \left[ \left( d^2 f_1 + f_2^2 + f_3^2 + 16 f_4^2 \right) + b \left( f_5^2 + f_6^2 + f_7^2 \right) ^{1/2} \right] / (a - b) \times 0.01
$$

where,

$$
a = \frac{I}{\sigma A_c}, \quad b = \varepsilon_p (A_p/ A_c), \quad f_1 = \Delta I / I, \quad f = \Delta V / V
$$
Table 7.3  Temperature dependence of thermal emittance

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>TREATMENT</th>
<th>REFLECTANCE MEASUREMENTS</th>
<th>EMITTANCE METER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>273</td>
<td>293</td>
</tr>
<tr>
<td>-</td>
<td>Plain polished</td>
<td>0.030</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>Thermal:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>300°C - 26 min</td>
<td>0.070</td>
<td>0.130</td>
</tr>
<tr>
<td>35</td>
<td>Ebanol - C:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>102°C - 15 sec</td>
<td>0.080</td>
<td>0.120</td>
</tr>
<tr>
<td>53</td>
<td>Chlorite:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60°C - 7.5 min</td>
<td>0.060</td>
<td>0.080</td>
</tr>
</tbody>
</table>

\[
f_3 = \frac{\Delta A}{A}, \quad f_4 = \frac{\Delta T}{T}, \quad f_5 = \frac{\Delta \varepsilon}{\varepsilon}, \quad f_6 = \frac{\Delta A_p}{A_p}
\]

Taking typical values, \(a = 0.1\), \(b = 0.02\), \(f_1 = f_2 = 0.001\), \(f_3 = f_4 = 0.03\), \(f_5 = 0.005\), \(f_6 = 0.01\), this error is about 5%. This is only the error in the determination of the \(\varepsilon\)-value from the other measured quantities. It says nothing about errors arising from conduction through the leads which have been estimated [28] to be as high as 30% for large temperature drops (100°C) along the leads. This is the reason why the measurements were carried out as close to the room temperature as possible in spite of the objective of the study to measure the \(\varepsilon\)-values at the operating temperatures of the absorber surfaces, which is approximately 100°C.
In spite of the these set backs the experimental \( \epsilon \)-values are in reasonable agreement with those reported elsewhere [25].
8 DISCUSSION

8.1 General

The reflectance curves of the chemical reagent oxidized samples have tended to share certain common features. The curves of the sodium chlorite oxidized samples have a characteristic peak between 0.5 μm and 0.6 μm and a minimum in the reflectivity somewhere between 0.85 and 1.15 μm. The same features are present to a lesser extent for the Ebanol C samples with maxima at 0.4 - 0.5 μm and minima at 0.55 - 0.80 μm. Whilst the former case has previously been reported [16] literature on the latter has not been easy to find. One would be tempted to think that these two methods of producing absorber surfaces result in the formation of one oxide type. But the results of X-ray diffraction analysis contradict this view. The chlorite method produced only Cu₂O whereas the Ebanol C treatment appeared to favour the formation of both oxide types with the CuO phase being the more dominant. It would appear that the actual proportion of CuO to Cu₂O depends on the temperature and duration of the treatment. The higher the temperature and longer the duration of treatment the more of CuO that is formed (see Table 6.4 chap. 6)

The surface morphology of the oxide coatings could be responsible for the similarities in the spectral reflectivities of the wet oxidized samples. In particular the surface morphology could account for the superior solar absorber properties of the chemical reagent produced samples compared to the thermally treated surfaces. Nearly all the reflectivity curves of the thermally oxidized samples were characterized by interference patterns whose amplitudes decreased with decreasing wavelength and hence increasing absorption (absorption coefficient α = 4π k/λ), where k is the extinction coefficient). Existence of interference could arise solely from the geometrical properties of the film and substrate linked to the homogeneity, smoothness and thickness of the coatings.
It should be noted that both the chlorite (≤ 65°C) and the thermal treatments (≤ 500°C) tended to form Cu₂O even though the resulting films showed different optical behaviour.

The total hemispherical reflectivity measurements for the thermally treated samples have tended to be higher than the specular reflectivity measurements in the solar spectral region. This is important to note because this region (0.35-2.0 μm) is the one of interest in as far as the fabrication of efficient solar absorber surfaces is concerned. An attempt has been made in the following sections to account for this difference together with the possible explanation for the occurrence of the peaks and minima (mentioned at the beginning of this chapter) in the reflectivities of the wet chemical oxidized samples.

Finally the results of the measurement of the thermal emittance of the representative samples by vacuum calorimetry show a much more evident dependence of the emittance of the wet chemical oxidized samples on the increase in temperature than for the dry thermally oxidized case. Again this could be linked to the difference in the surface topography and thickness between the dry- and wet-oxidation processes.

8.2 Comparison with Theory

8.2.1 Thermally produced films

The optical properties of a thin film of solid material generally differ from those of the bulk. The difference can be attributed to size effects. To evaluate the results of measurement of the optical behaviour of thin films it is necessary to calculate the relevant optical constants from an assumed model of the film. Such a model would arise from consideration of thin film optics (see ch. 4) and the Lorentz-Drude theories (ch. 3). The theories on thin film optics apply to smooth plane homogeneous films. If the film is rough then the model becomes very complicated (see section 8.2.2). However, certain simplifying assumptions can be made which tend to illustrate the expected behaviour.
The optical behaviour of a thin film depends both on the coating and the substrate. The reflectivity of a polished metal as calculated from the simple Drude theory is given in figure 3.2 (section 3.3) together with the curve obtained from experimental measurement for polished copper. The energy reflection coefficient for a parallel sided isotropic film of refractive index $n_1$ on a substrate of index $n_2$ was derived in section 4.2 and was expressed as,

$$ R = \left( r_1^2 + r_2^2 + 2r_1 r_2 \cos 2\delta_1 \right) \left( 1 + r_1^2 r_2^2 + 2r_1 r_2 \cos 2\delta_1 \right)^{-1} $$

where $r_1$ and $r_2$ are the Fresnel coefficients and $\delta_1 = \left( 2\pi / \lambda \right) n_1 \cos \phi$, is the phase thickness of the film. For normal or near normal incidence ($\theta_1 \leq 10^\circ$) $\delta_1$ is approximately equal to $(2\pi / \lambda) n_1 t$, where $t$ is the thickness of the film. The reflectance as given by equation 8.1 predicts an oscillatory behaviour for wavelengths comparable to the thickness of the film because of the presence of the cosine factor. The interference maxima and minima occur for $\cos 2\delta_1 = \pm 1$, that is for wavelengths given by $\lambda = 4n_1 t / m$ for $m = 2, 4, 6$ etc or $m = 1, 3, 5$, etc. The expression for the reflection coefficients at these maxima/minima are given by equations 4.37 - 4.38. Their evaluation requires knowledge of the optical constants of the film and the substrate material. This has been done for copper(I) oxide Cu$_2$O using the Drude equations (3.3) - (3.4) and (3.1) - (3.9) and assuming: a spring frequency $\hbar \omega_0 = E_g - 2.17$ eV which gives $\omega_0 = 3.3 \times 10^{15}$ s$^{-1}$, a damping constant $\gamma = 1$ eV, effective mass of the electron $m = 0.05$ m where $m$ is the free electron mass and electron density $N = 10^{27}$ m$^{-3}$. The equations for the real and imaginary parts of the dielectric constant become,

$$ \epsilon_i = 1 + 47(4.84 - \hbar^2 w^2)(4.84 - \hbar^2 w^2)^2 + \hbar^2 w^2 ]^{-1} \quad 8.2 $$
Fig. 8.1 Comparison of the theoretical reflectance (---o--) as calculated from the simple Lorentz-Drude theory with the experimental spectral reflectance of the copper oxide film thermally produced at 250°C for a duration of 2.5 min.
\[ \varepsilon_2 = 47hW\left[ (4.84 - \frac{hW^2}{2}) + \frac{hW^2}{2} \right]^{-1} \] 8.3

Equations 8.2 and 8.3 were used to compute the optical constants \( n \) and \( k \) from which the reflectances at the maxima and minima of the interference pattern predicted by equation 8.1 were derived. In these calculations only the real indices (\( n_0 = 1 \) for vacuum, \( n_1 \) for the film and \( n_2 \) for the copper substrate) were used as this simplified the computations. The indices for copper were obtained from elsewhere in literature [32]. The optical constants are given in table 8.1. Figure 8.1 shows the result obtained for an assumed film thickness \( t = 0.3 \mu m \) together with the spectral reflectance of copper thermally oxidized at 250°C for 25 minutes. It can be noted that the reflectance maxima/minima obtained from theory are displaced slightly towards shorter wavelengths with respect to those obtained from experimental measurement. In addition to this, the theoretical reflectance is more than 10% higher than the experimental reflectance for wavelengths \( \lambda > 0.5 \mu m \). There is, however, reasonable agreement between theory and experiment on the occurrence of interference.

8.2.2 Sodium Chlorite and Ebanol C treatment surfaces.

Since the optical behaviour of a semiconductor film-metallic substrate combination would depend ultimately on a number of physical factors other than just plane geometry it is necessary to take these factors into account. The most important amongst these factors to be considered is the effect due to surface roughness. The chemical composition of the film would also play an important role but this is in general more difficult to account for.

A rough surface reflects light in a more complicated way than a plane homogeneous surface [6]. That the chemical
Fig. 8.2 Spectral reflectance of a rough surface (curve a) as calculated using the simple given by expression 8.4 for an rms value of surface roughness $\sigma = 0.1 \mu m$. The curves for the Ebanol C (b: 75°C - 75 s) and the sodium chlorite (c: 55°C - 5 min) are also shown for comparison.
Reagent treated surfaces produced films with a rough morphology is evident from scanning electron microscopy (see chap. 6 plate 2-4). Such roughness must inevitably influence the spectral reflectance of the films e.g. absence of interference. Diffraction theory has been applied [5] to a rough reflecting surface with a gaussian distribution from a mean surface. An rms value of surface roughness $\varphi < \lambda$ was assumed for which the specular reflectance was assumed to vary as,

$$R \propto \exp\left[-\left(\frac{4\pi\varphi}{\lambda}\right)^2\right]$$  

The specular reflectance, Rs, decreases for short wavelengths and vice versa as shown in figure 8.2 for $= 0.1 \mu m$. The experimental curves for copper oxidized by the chlorite method (55°C - 5 min) and the Ebanol C treatment (75°C - 75s) are also included for comparison. It should be noted that for wavelengths $\lambda > 1\mu m$ there is reasonable agreement between theory and experiment. But the simple model of reflection by a rough surface given by expression 8.4 fails to account for the occurrence of the minima in the reflectivity of the wet chemical oxidized surfaces (see fig. 8.2 curves b and c) at around $1 \mu m$ and the peaks (0.5 - 0.6 $\mu m$). A possible explanation could be given in terms of plasma oscillations. The sample model [2] of a plasma considers a free electron gas moving in a uniform distribution of positive charge which maintains an average neutrality. Such a model results in the real part of the dielectric constant being expressed as,

$$\epsilon_r(w) = 1 + \epsilon_r^l(w) - \frac{W_p^2}{w^2}$$

where $W_p^2 = \frac{N e^2}{\epsilon_0 m}$, $N$ is the electron density, $e$ is the electron charge, $\epsilon_0$ is the permittivity of free space and $m$ is the effective mass of the electron. $\epsilon_r^l(w)$ is the lattice contribution to $\epsilon_r(w)$. $\epsilon_1(w)$ is always real; it is negative at low frequencies and positive at high frequencies.
Fig 8.3 Specular reflectance $R_s$ of a rough surface calculated from the bulk reflectance $R_b$ (eq. 3.9) taking into account plasma resonance (eq. 8.5). b & c are the reflectance curves of the Ebano C & chlorite treated surfaces (Fig 8.2)
The frequencies \( \omega_0 \) at which \( \epsilon_1(W) \) changes sign are given by \( \epsilon_1(W) = 0 \), which gives the frequency \( \omega_0 \) as,

\[
\omega_0 = \frac{W_0}{\left[ 1 + \epsilon_1(W) \right]^{1/2}}
\]

8.6

The frequency, \( \omega_0 \) is called the plasma frequency and corresponds to the frequency at which the whole electron gas is set into resonant oscillation with the incident electromagnetic radiation. Equation 8.5 and 8.6 have been evaluated assuming \( N = 10^{27} \, \text{m}^{-3} \), \( m^* = 0.05 \, \text{m} \) (m* is the free electron mass), \( \epsilon_1(W) = 15 \) and frequency range 0.45 - 1.5 \( \mu \text{m} \). Under these assumptions \( \frac{1}{N^2} = 27, \epsilon_1 = 16-27/N^2 \) and by equation (8.6), \( \omega_0 \approx 2 \times 10^{15} \, \text{s}^{-1} \) which corresponds to \( \lambda = 0.95 \, \mu \text{m} \).

The results are given in table 8.2 together with the derived values of \( n, k \) the bulk reflectivity \( R_B \) (equation 3.9 section 3.2) and bulk specular reflectivity \( R_S = R_B \exp[-(4\pi\rho/\lambda)^2] \) arising from consideration of the effect of surface roughness given by equation 8.4. The values of the imaginary part of the dielectric constant, \( \epsilon_2 \), used are those given in table 8.1.

Figure 8.3 shows the theoretical bulk reflectivity \( R_B \), the derived specular reflectance \( R_S (\rho = 0.05 \, \mu \text{m}) \) and the reflectances of the Ebanol C (75°C - 75s) and the sodium chlorite (55°C - 5 min) treated surfaces. The theoretical reflectance minima at \( \lambda = 0.95 \, \mu \text{m} \) is higher than for those obtained from experiment by more than 10%. There is, however, reasonable agreement between theory and experiment. One factor merits clarification: the reason why the bulk reflectivity was used in the theoretical calculations is that the film has been assumed to be thick enough for its optical properties to be approximately those of the bulk in the wavelength range 0.45 - 1.5 \( \mu \text{m} \). We have seen that experiment and theory are in reasonable agreement. What does not find an easy explanation, however, is the fact that the minima in the reflectivity appear to shift to larger wavelengths with increased duration of treatment (see e.g. fig. 6.7 ch. 6).
One could explain this shift in the reflectivity minima in terms of the electron density as it affects the value of the plasma frequency. A large electron density implies a large value for \( \omega_0 \) and in turn implies the location of the plasma edge in the short wavelength region. A shift in \( \omega_0 \) to low frequencies (i.e. long wavelengths) would require a progressive decrease in the electron density as treatment times are increased. It is possible that for short duration of treatment the surfaces are not completely oxidized and hence the copper atoms that would be dispersed throughout the thin film material would tend to contribute electron to make the electron density larger than that of the oxide alone. Stated simply, this implies that the \( N \) that results in reasonable agreement with experiment is an effective electron density. As the treatment durations are increased more of the oxide is formed and a reduction \( N \) results.

The degree of surface roughness should affect the reflective properties of the coatings. Increased surface roughness results in either increased diffuse reflection losses or increased absorption through interreflections in the cavities in the surface layer (see figure 6.9 - 6.10 and plates 3 and 4, ch. 6). For the smooth films increased film thickness also results in the smearing of the interference pattern. This is illustrated by the results from figures 6.1 - 6.4.

8.2.3 Total emittance

The emissivities of oxides are quite high, and for oxidized, copper, \( e_T \approx 0.78 \) at 373K 25. The problem of keeping the emittances of solar absorber surfaces as low as possible is tied to the choice of the proper thickness of the coating that should retain its transparency in the infrared. An analytical expression which shows how the emissivities of oxides depends on the temperature is not known [25]. It is expected that increased thickness and surface roughness could result in increased emissivity. In particular, the increase in thickness of the coating could increase the emittance because the emissivity of the film would approach that of the bulk oxide, which as previously stated, is quite high.
Table 8.1  Optical constants as calculated from theory

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<th>$\lambda$ (μm)</th>
<th>$\hbar \omega$ (eV)</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
<th>$n_1$</th>
<th>$k_1$</th>
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<th>$k_2$</th>
<th>$R_{\text{max}}$</th>
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Table 8.2 Optical constants with the values of $\varepsilon_1$ calculated using equation 8.5

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8.3 Limitations

The thin films formed for use in solar collectors are very thin and are not likely to provide any protection to the substrate material against long term atmospheric corrosion and continuous thermal oxidation. For example it is likely that the predominantly Cu₂O on copper films would eventually form CuO at elevated temperatures by reacting with the oxygen in the air.
Future studies should seek to investigate losses in the optically- and thermally-functional properties of the solar absorber surfaces after long periods of operation. Further improvement of the coatings would appear necessary through the knowledge of optimum treatment parameters such as the chemical reagent concentration, or monitoring of the oxygen partial pressures and controlled surface roughness.

The vacuum calorimeter for the measurement of total emittance must be improved so that measurements at elevated temperatures can be carried out with minimum thermal losses.
The solar optical properties of thin films of oxides of copper have been reported. The spectral reflectances of the thermally oxidized surfaces are characterized by interference patterns which is evidence of the fact that coatings produced in this way are plane, smooth and homogeneous. Those produced by the wet chemical reagent treatments have reflectance curves that are almost featureless except for reflectance peaks at approximately 0.5 - 0.8μm and reflectance minima that appear to shift towards the infrared for longer durations of treatment. The featureless nature of the spectral reflectance profiles could be attributed to the roughness of the coatings and larger thickness, whilst the existence of a minima in reflectivity could be tied to plasma resonance. Of particular interest has been the chemical composition of the films which has apparently played very minimum role, if any, in the spectral reflectivity of the coatings. The chlorite method has produced mainly Cu₂O films whilst the Ebanol C procedure has produced both Cu₂O and CuO with the latter constituent being the more dominant. But as already noted, their solar spectral properties have been very similar, if not, actually identical.

The emittances of the wet chemical reagent oxidized surfaces have tended to be higher than those of the dry thermally oxidized samples. This has been evidence that the former coatings have tended to be thicker than those produced by dry thermal oxidation.
Interaction of radiation with solids

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