Characterization of Selective Solar Absorbers

Experimental and Theoretical Modeling

BY

TUQUABO TESFAMICHAEL
Abstract

This thesis deals with the preparation, optical characterization and analyses of experimental work and theoretical modeling on selective solar absorbers used in solar thermal collectors. The overall goal has been to obtain efficient absorbers by optimizing the optical properties, and to improve their durability using cost-effective techniques.

A Ni-Al₂O₃ absorber was pyrolytically coated with SnO₂ to improve its coating quality. Undesirable increase of solar reflectance obtained as a result of the SnO₂ was reduced by applying a silica antireflection layer produced by a dipping technique from colloidal silica sol. Annealing of Ni particles in an Al₂O₃ matrix was also carried out and compared to particles heated without the matrix. Due to the Al₂O₃ matrix, a much slower oxidation rate was found for the embedded particles. In addition, the optical performance of commercial Ni-Al₂O₃ and Ni-NiOₓ absorbers were experimentally compared at oblique incidence. A better solar-absorptance of the Ni-Al₂O₃ at higher angles of incidence was found. This is due to enhanced optical interference in the double-layer structure of Ni-Al₂O₃, which could not be achieved in the graded index film of Ni-NiOₓ.

The optical properties of Si-Al₂O₃ films of different thicknesses have been investigated by preparing the films using an integral coloration method. The solar-absorptance and thermal-emittance were found to increase with increasing film thickness. Due to high thermal-emittance, the Si-Al₂O₃ coating shows non-selective absorbing properties. Its feasibility for a selective solar absorber was studied by modeling the coating as a function of coating thickness for different particle size and volume fraction using four-flux theory. The results indicated that the Si-Al₂O₃ coating is not a suitable candidate for selective solar absorbers.

Scattering and absorption cross-sections of FeMnCuOₓ and black carbon pigments have been obtained from reflectance and transmittance measurements in the solar wavelength range. The cross-sections were determined by using pellets consisting of low pigment volume fractions dispersed in KBr matrix. The cross-sections exhibit linear dependence of the volume fraction, indicating that single scattering dominates. The cross-sections were used to model the optical properties of solar selective paints using four-flux model resulting in good agreement between calculations and experiments.

Tuquabo Tesfamichael, Department of Materials Science, The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

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For Her Devotion, To My Sister Alem
and
my Family
LIST OF PUBLICATIONS


My contribution in the above papers:

I and II Experiments and part of calculations
III Experiments and calculations
IV Calculations and part of experiments
V and VI Part of experiments
VII and VIII Experiments and calculations
IX and X Calculations and part of experiments

Paper not included in this thesis:

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# GLOSSARY AND CONSTANTS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Quantity</th>
</tr>
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<tbody>
<tr>
<td>Abs</td>
<td>Absorptance</td>
</tr>
<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>$A_c$</td>
<td>Area of a collector</td>
</tr>
<tr>
<td>$B(\lambda, T)$</td>
<td>Blackbody spectrum</td>
</tr>
<tr>
<td>$C_{abs}$</td>
<td>Absorption cross-section</td>
</tr>
<tr>
<td>$C_{ext}$</td>
<td>Extinction cross-section</td>
</tr>
<tr>
<td>$C_{sca}$</td>
<td>Scattering cross-section</td>
</tr>
<tr>
<td>Ext</td>
<td>Extinction</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>EMT</td>
<td>Effective Medium Theory</td>
</tr>
<tr>
<td>$F$</td>
<td>Weight fraction</td>
</tr>
<tr>
<td>$F_R$</td>
<td>Collector heat removal factor</td>
</tr>
<tr>
<td>$F'$</td>
<td>Collector efficiency factor</td>
</tr>
<tr>
<td>$G(\lambda)$</td>
<td>Solar spectral irradiance</td>
</tr>
<tr>
<td>$G_T$</td>
<td>Total solar energy flux</td>
</tr>
<tr>
<td>$G_{sc}$</td>
<td>Solar constant</td>
</tr>
<tr>
<td>$I$</td>
<td>Flux in the forward direction</td>
</tr>
<tr>
<td>$J$</td>
<td>Flux in the backward direction</td>
</tr>
<tr>
<td>$K$</td>
<td>Effective absorption coefficient per unit length</td>
</tr>
<tr>
<td>$K_{\alpha}$</td>
<td>Incident angle modifier</td>
</tr>
<tr>
<td>L</td>
<td>Depolarization factor</td>
</tr>
<tr>
<td>N</td>
<td>Complex refractive index</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared wavelength range</td>
</tr>
<tr>
<td>Q or q</td>
<td>Collector energy output</td>
</tr>
<tr>
<td>R</td>
<td>Reflectance</td>
</tr>
<tr>
<td>RUC</td>
<td>Random unit cell</td>
</tr>
<tr>
<td>$T$ (italic)</td>
<td>Temperature</td>
</tr>
<tr>
<td>T</td>
<td>Transmittance</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>S</td>
<td>Effective scattering coefficient per unit length</td>
</tr>
<tr>
<td>$S(0)$</td>
<td>Forward Scattering amplitude</td>
</tr>
<tr>
<td>$U_L$</td>
<td>Collector heat coefficient</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet wavelength range</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible wavelength range</td>
</tr>
<tr>
<td>$a$</td>
<td>Particle radius</td>
</tr>
<tr>
<td>$d$</td>
<td>Film thickness</td>
</tr>
<tr>
<td>$f$</td>
<td>Particle volume fraction</td>
</tr>
<tr>
<td>k</td>
<td>Wavenumber</td>
</tr>
<tr>
<td>$k$ (italic)</td>
<td>Intrinsic absorption coefficient per unit length</td>
</tr>
<tr>
<td>$(mC)_{eff}$</td>
<td>Effective thermal capacitance</td>
</tr>
</tbody>
</table>

Symbol | Constants | Value
---|---|---
\( n \) | Refractive index | |
\( r \) | Reflection coefficient | |
\( r_0 \) | Sun-earth distance | |
\( r_s \) | Mean radius of the solar disk | |
\( s \) | Intrinsic scattering coefficient per unit length | |
\( t \) | Time | |
\( \chi \) | Scattering size parameter | |
\( \alpha_{\text{sol}} \) | Solar absorptance | |
\( \varepsilon_{\text{therm}} \) | Thermal emittance | |
\( \varepsilon \) | Dielectric function | |
\( \bar{\varepsilon} \) | Average dielectric function | |
\( \theta \) | Angle of incidence | |
\( \theta_D \) | Diffraction angle | |
\( \kappa \) | Extinction coefficient | |
\( \lambda \) | Wavelength | |
\( \rho \) | Mass density | |
\( \eta \) | Collector efficiency | |
\( \tau \) | Angular transmittance of glass | |
\( \tau' \) | Relaxation time | |
\( \omega \) | Frequency | |
\( k_B \) | Boltzmann constant | (8.61739 x 10^{-5}) eV/K |
\( \sigma \) | Steffan-Boltzmann constant | (5.6697 x 10^{-8}) Wm^{-2}K^{-4} |
\( h \) | Planck’s constant | (1.0545 x 10^{-34}) Js |
\( c_1 \) | first Planck’s radiation constant | (3.7405 x 10^{8}) W \mu m^{-2} |
\( c_2 \) | second Planck’s radiation constant | (1.43879 x 10^{4}) \mu m K |
\( G_{\text{sc}} \) | Solar constant | (1367\pm1\%) W/m^2 |
1 INTRODUCTION

The amount of clean air varies with geographical locations, elevation and seasons. These variations are a function of industrial and agricultural activities of the place and its surroundings, the use of fossil fuels for energy and transport, and the general dynamic nature of the atmosphere. This means that, due to human activities the composition of our atmosphere is changing rapidly. Gases such as carbon monoxide, carbon dioxide and ozone are created as a consequence of the above activities. The enhancement of the environmental problems on the one hand and the increasing need of energy from time to time on the other alarm people to look for alternative energy resources. This has stimulated the utilization of solar, wind, geothermal, biomass and other renewable energy technologies. Despite the encouraging signs in developing such alternative energy resources and technologies on a large scale, slowness of effective policy has contributed to a gradual progress. In order to see the prospects of clean energy systems using cost competitive and efficient technologies that satisfy demands, an intensive research on renewable energy must be encouraged.

Solar energy, which is abundantly available in many parts of the world, can play a major role as an alternative energy resource. Using the sun's energy one can produce heat or electricity by capturing the radiation of the sun. Photo-voltaic devices use semiconducting materials to convert sunlight directly into electricity (quantum conversion), while solar thermal devices convert solar radiation into heat (thermal conversion). Solar thermal devices are used to heat water and air inside buildings at lower temperatures ($T<300^\circ$C) and to create steam for electricity generation at high temperatures. Photothermal devices used for heating water and air conditioning are mainly flat plate collectors which are simple and inexpensive. The most important and critical part of the flat plate solar collectors is the absorber surface. In order to maximize the output from the solar collectors, the absorber should be spectrally selective; exhibit high solar absorptance and low thermal emittance. Thermal losses from heated absorbers are due to conduction, convection and radiation. Selective surface coatings play an important role, especially when temperatures are required in the vicinity of boiling temperature of water or when the temperature difference between absorber and ambient is high. High quality of the absorber surfaces is important in order to achieve collector durability. What is needed are coatings which will not optically degrade significantly during the life time of the collector and also withstand stagnation temperature and humidity. Coating life time of the absorber and hence the collector performance can also be influenced by the tribological properties of the absorbing surface.

The possibility of practical selective absorbing surfaces was first shown by Tabor (Israel) and by Gier-Dunkle (USA) at the first international solar energy conference in Tucson, AZ in 1955. Their work was based on coatings of some oxides and sulfides deposited on a metal substrate. A thorough investigation of selective surfaces was, however, not started until the time of the oil crisis in the mid 1970s. A review of several varieties of commercial and research selective absorbers, and an annotated bibliography for such work, can now be found elsewhere. The most common type of selective absorber is the absorber-reflector tandem which is obtained by combining two surfaces, one surface which is highly absorbing in the solar region and another highly reflecting in the infrared. Several techniques can be used to produce this surface, generally divided into wet-chemical, paint and vacuum deposition techniques. In general, the wet chemical approaches have been the most widely used techniques for low temperature solar absorber applications. Some of the well known commercial absorbers developed by wet chemical technique are black chrome (USA), nickel pigmented aluminum...
oxide (Sweden and Japan) and MAXORB (UK). Paints have the potential of being a less expensive coating that can be produced by simpler methods. Various potential pigments that could be developed for selective paint coatings are described elsewhere.\textsuperscript{5,11,12} There are at least two commercialized selective paints on the market under the trademarks Solarect-Z (Slovenia) and SolkoteHI/SORB-II$^\text{TM}$ (USA). Vacuum deposition techniques are nowadays also gaining advantages which allow roll coating processes for large scale production at a relatively low cost. Commercial absorbers such as Sunstrip (Sweden) and Interpane (Germany) produced by reactive dc magnetron sputtering and TiNOX GmbH (Germany) made by activated reactive evaporation are products obtained using the vacuum deposition processes. This thesis discusses results of selective solar absorber surfaces which are of the absorber-reflector tandem types obtained by some several of the above mentioned methods.

Section 2 gives a general theoretical background on thermal and solar electromagnetic radiation. It also discusses the optical properties of inhomogeneous media treated using Lorenz-Mie theory, effective medium theories, two-flux and four-flux radiative transfer theories. A novel approach of determining optical properties of absorbing-scattering medium using reflection-transmission measurements are also explained. Optical characterization of an energy-efficient selective absorbing surface and the most commonly used selective surface designs with emphasis on non-homogeneous composite absorbers are also described in this section. In addition, a commonly used flat plate solar thermal collector is discussed here briefly. Section 3 deals with experimental techniques including sample preparation, optical measurements and characterization of different absorbing surfaces. The absorbers are inhomogeneous, consisted of particles such as metal, semiconductor, or black-pigment embedded in dielectric matrices. Methods used for high temperature accelerating aging to test durability of solar absorbers is also mentioned. Covering absorber surfaces by a transparent coating to protect it from degradation and the use of an antireflection layer to reduce front-surface reflection of the transparent coating is presented in this section. The experimental results are summarized in section 4. Finally, concluding remarks and abstracts of the appended papers are given in sections 5 and 6, respectively.
2 THEORETICAL BACKGROUND

2.1 Electromagnetic Radiation

Electromagnetic phenomena have been recognized as originating from a distribution of electric charge and current which gives rise to the electromagnetic field. J. C. Maxwell was the first who concisely formalized the known results of electricity and magnetism in a theory of classical electromagnetism in 1865. A spectacular immediate result of Maxwell’s electromagnetic theory was the prediction that light itself was a form of electromagnetic radiation. Electromagnetic radiation can be divided into ranges of wavelengths according to the different criteria. Certain wavelength ranges of the electromagnetic spectrum, namely the solar which covers the UV/Vis/NIR (λ=0.3-2.5 µm) and thermal (λ=2.5-50 µm), are the most important for the application of solar energy (see section 2.3 for the spectral distribution).

2.1.1 Thermal Radiation

All heated objects emit thermal electromagnetic radiation whose wavelength and intensity are dependent on the temperature of the body and its optical characteristics. A blackbody is one that absorbs all wavelengths of the incident radiation and emits the maximum amount of energy for a given body temperature, \( T \). It is an ideal surface whose emissive power, given by Planck’s law \( B(\lambda, T) \), is used as a reference to compare with the properties of real surfaces. The spectral blackbody radiation is given by:

\[
B(\lambda, T) = \frac{c_1}{\lambda^5 \left[ e^{c_2/\lambda T} - 1 \right]},
\]

where \( c_1=3.7405 \times 10^8 \) W \( \mu m^4 \) m\(^{-2} \) and \( c_2=1.43879 \times 10^4 \) \( \mu m \) K are the first and second Planck’s radiation constants, respectively. The wavelength \( \lambda \) is given in \( \mu m \) and \( B(\lambda, T) \) in W m\(^{-2} \) \( \mu m^{-1} \). The total emitted energy can be obtained by integrating the Planck’s spectrum over the whole wavelength range. Stephan-Boltzmann law gives the hemispherical total emitted energy for an ideal blackbody as:

\[
B(T) = \sigma T^4,
\]

where \( \sigma=5.6696 \times 10^{-8} \) W m\(^{-2} \) K\(^{-4} \) is the theoretical Stephan-Boltzmann constant which differs from the experimentally determined value by 0.3% (\( \sigma_{\text{exp}}=5.729 \times 10^{-8} \) W m\(^{-2} \) K\(^{-4} \)).

2.1.2 Solar Radiation

The sun which is the center of the solar system is about 1.496\( \times 10^{11} \) m from the earth. With an estimated diameter of 1.39196\( \times 10^9 \) m, it has a total radiated energy of about 3.84451\( \times 10^{23} \) kW. The spectrum of the radiated energy varies from long infrared wavelengths to very short wavelengths of gamma radiation. But most of the radiation is absorbed or scattered far up in the ionosphere, the ozone layer or the atmosphere by nitrogen, oxygen, ozone, water vapor, carbon-dioxide and other atmospheric components. The extraterrestrial solar radiation prior to the atmospheric absorption just above the earth’s atmosphere is almost a constant with the numerical value \( G_{sc}=1367\pm1\% \) W/m\(^2\) throughout the year. \( G_{sc} \) is called as the solar constant. About 8.03% of the radiation in the range UV, 46.41% is visible and the rest 46.40% falls into the NIR. The effective blackbody temperature of the sun can easily be obtained from the solar constant, \( G_{sc} \) as:

\[
T_{\text{eff}} = \left( \frac{2 \sigma G_{sc}}{c_2} \right)^{1/4}
\]

\[ T = \left[ \frac{G_{\text{in}}}{\sigma} \left( \frac{r_0}{r_s} \right)^2 \right]^{1/4}, \quad (2.3) \]

where, \( r_0 \) and \( r_s \) are the sun-earth distance and the mean radius of the solar disk, respectively. Equation (2.3) gives a temperature of 5777 K. However, the blackbody spectrum of the sun doesn’t strictly follow the extraterrestrial spectrum \(^{16}\) and hence can not be used for characterizing solar energy coatings such as solar absorbers.

Absorption and scattering are the major phenomena that occur when incident electromagnetic radiation strikes a particle depending on the size, shape and optical properties of the particle. Scattering can be produced by small or large particles as well as by multiply reflected radiation and is favored at shorter wavelength as confirmed by scattering theory.\(^{16}\) For any sufficiently small particle as compared to the incoming wavelength, regardless of its shape, a strong Rayleigh scattering that is symmetric in the forward and backward directions dominates.\(^{17}\) One example of Rayleigh scattering is the scattering of solar radiation by atmospheric molecules which gives the sky its blue color. The terrestrial solar spectral distribution and intensity can vary with the change of the atmospheric scattering and absorbing components and also the path of the rays that traverse the atmosphere (air mass).\(^{16}\) The irradiation of the solar flux that reaches the surface of the earth, therefore, varies considerably. Theoretical as well as measured spectral distribution of solar irradiance at the surface of the earth for typical atmospheric conditions can be found elsewhere.\(^{15,16,18-20}\)

Unlike the direct and diffuse spectral irradiance, the change of the total intensity with change of the atmospheric components is not large except with the variation of air mass at shorter wavelengths. For a given geographical location of pressure \( P \), air mass is defined as the ratio of optical mass at an oblique path to that of the vertical path and can be approximated mathematically by\(^{21}\):

\[ AM = \frac{P}{P_0} \left[ \cos \theta + 0.15(93.885 - \theta)^{2.55} \right]^{-1}, \quad (2.4) \]

where \( P_0 \) is the atmospheric pressure at sea level and \( \theta \) angle of incidence of light with respect to the zenith. For angles of incidence less than 60° equation (2.4) can be replaced by:

\[ AM = \frac{P}{P_0} \left[ \cos \theta \right]^{-1}. \quad (2.5) \]

At large air mass number, the UV and blue end of the Vis spectrum undergoes much stronger depletion (by absorption and scattering) than the red end Vis spectrum and hence at sunset, most of the short-wavelengths are scattered back which gives a red color to the sun. To characterize the optical properties of solar selective absorbing surfaces, as discussed in the following sections, an air mass of 1.5 (AM1.5) is employed. AM1.5 is commonly used particularly at higher latitudes and a smaller number should be applied for lower latitudes. On the other hand, air mass variation have shown only small differences on the solar weighted optical properties of selective solar absorbers.\(^{22}\)
2.2 Optical Properties of Inhomogeneous Media

Light traversing a medium is scattered only when the medium has inhomogeneities. Many materials used in applications are inhomogeneous or disordered. Their optical properties are derived from optical measurements combined with modeling of the experimental results using appropriate theoretical considerations. In this section, as it gives basis to the main work of this thesis, we present the optical properties of particles embedded in a non-absorbing medium. For particles which have a size much smaller than the wavelength of the incident light effective medium theories can be applied. If the particles are of the order or larger than the incident wavelength, scattering becomes important in addition to absorption and Lorenz-Mie theory provides a solution to the single scattering problem. In case of multiple scattering radiative transfer models are used to handle such effects.

2.2.1 Lorenz-Mie Scattering Theory

Electromagnetic radiation scattered into a particular direction by an isotropic, homogeneous sphere is described by Lorenz-Mie theory. For a particle smaller or larger than the incoming wavelength, the Lorenz-Mie scattering theory can generally be applied for solving the scattering and absorption phenomena. When a single particle is illuminated by an incident electromagnetic radiation, part of the incident energy is absorbed and the rest is scattered out. Mie explicitly solved Maxwell’s electromagnetic equations and investigated scattering by a single particle in a non-absorbing matrix for a wide size range. Due to the proceeding work of Lorenz the complete solution is called Lorenz-Mie theory. The theory is extremely complex and involves the index of refraction and size of the particle, the wavelength of light and the index of refraction of the host medium as parameters in combinations of spherical Bessel functions. Scattering by small and large particles were extensively summarized by Kerker, van de Hulst and Bohren-Huffman. The scattering conditions have been characterized by the application of boundary conditions and the series expansion of the electric and magnetic fields of a scattering amplitude in the forward direction, $S(0)$:

$$S(0) = \frac{1}{\pi} \sum_{n=1}^{\infty} (2n + 1)(b_n + c_n),$$

where $b_n$ and $c_n$ denote scattering coefficients containing Bessel functions and their derivatives. The Lorenz-Mie theory is applicable for a single spherical particle and hence is treated as single scattering event. For particles with complex shapes, an approximate expressions can be obtained elsewhere. The scattering size parameter, $x$ for spherical particle of radius, $a$, complex refractive index, $N_1$, surrounded by a non-absorbing medium of refractive index, $N_2$, is given by:

$$x = k \cdot a, \quad (2.7a)$$

where $k$ is wavenumber in the medium:

$$k = \frac{2\pi}{\lambda} = \frac{2\pi N_2}{\lambda_0}, \quad (2.7b)$$

and $\lambda$, $\lambda_0$ are the wavelengths in the medium and vacuo, respectively. Note that the symbol $k$ (non-italic) used for wavenumber and $k$ (italic) will be used later for absorption coefficient. Using Eq. (2.7) and the forward scattering amplitude, $S(0)$ evaluated from Lorenz-Mie, scattering parameters such
as, cross-sections of scattering and absorption \(^{29}\), the forward scattering ratio, \(\zeta\), the single-particle scattering diagram (phase function) \(^{27,28}\) and other parameters \(^{37}\) can be obtained.

The forward scattering ratio under collimated illumination, \(\zeta_c\), gives the fraction of the total energy scattered into the forward hemisphere and is used in the four flux calculations discussed later. Its value varies considerably with a change of particle size parameter that are easily viewed from the scattering diagram or phase function. The phase function can be evaluated by considering a particle to scatter independently, when observed at a distance large compared to the individual particle size. \(^{38}\) Figure 2.1 shows polar diagrams of the single-particle phase function for non absorbing particles with different size parameters. The phase function represents the amount of scattered energy and has no relation to the phase of the electromagnetic radiation. \(^{39}\) From Fig. 2.1 it can be seen that for small spherical particles as much as equal energy is scattered to the backward hemispheres as is scattered forward (Rayleigh scattering) whereas for larger particles the forward scattering from the sphere increases and the backward scattering gets smaller.

![Fig. 2.1 Polar diagram of single-particle phase function for non-absorbing particle of refractive index 2.0 calculated at wavelength, \(\lambda_0=0.55 \mu m\) and different size parameters, \(x\). The forward scattering ratio under collimated illumination, \(\zeta_c\) is also shown in the figure. \(^{37}\)](image)

The optical theorem which is a useful quantity yields a relation between extinction cross-section \((C_{ext})\) and the real, \(Re\), part of the forward scattering amplitude, \(S(0)\). \(^{28,40}\) The relation is mathematically given by:

\[
C_{ext} = 4 \cdot \pi \cdot Re \left\{ \frac{S(0)}{k^2} \right\} . \tag{2.8}
\]

More explicit expressions for the extinction \((C_{ext})\), scattering \((C_{sca})\) and absorption \((C_{abs})\) cross-sections follow from the series expansions \(^{28}\):
These cross-sections which are proportional to the particle geometric cross-section are the basis for scattering and/or absorbing particles in a medium. If the size of the particle is much smaller than the wavelength, $C_{\text{abs}}$ is inversely proportional to the wavelength, $\lambda$, and directly proportional to the particle volume\(^{39}\), whereas the scattering cross-section is proportional to the square of the volume but inversely proportional to the fourth power of the wavelength (Rayleigh scattering). On the other hand, if the size of the particle is much greater than the incident wavelength, both $C_{\text{abs}}$ and $C_{\text{sca}}$ approach the geometric cross-section.\(^{39}\)

### 2.2.2 Effective Medium Theory

For inhomogeneous composite media consisting of small particles hosted in a dielectric matrix, the optical constants can be derived from the optical constants of the homogeneous constituents. If the size of the inhomogeneties is much less than the wavelength of the incident light, the electric and magnetic fields are almost constant over this characteristic length, which is the quasistatic approximation. We then describe the response of a material to an electromagnetic field by the dielectric function and magnetic permeability. In the solar and infrared wavelength regions, the magnetic permeability approaches unity and the optical properties can be treated with an effective dielectric function of the medium on the basis of effective medium theory (EMT). The most commonly used effective medium theories are the Maxwell-Garnett\(^{23}\) and Bruggeman\(^{24}\) as well as the Ping Sheng\(^{41}\) models. They can be used to model the effective dielectric function of the composite coating for spherical inclusions and the effective quantity depends only on the dielectric functions of the components and their volume fractions. The Maxwell-Garnett theory, in its simplest form, assumes that the medium has a separated-grain structure (Fig. 2.2a). The Bruggeman and Ping Sheng theories, on the other hand, apply to a two component mixture having aggregate microstructure (Fig. 2.2b). The Ping Sheng model derives for the more general case of coated spheroid particles in an effective medium. The difference in microstructures between the mentioned theories have indeed an effect on the modeled optical properties of the composite.\(^{42}\)

To derive the effective dielectric function, each particle in the composite is considered to be embedded in an effective medium and the composite can be of two or higher component systems.\(^{23-25,41,43-45}\) Here we deal with two components of dielectric constants $\varepsilon_A$ and $\varepsilon_B$ on the work of Niklasson \textit{et al.}\(^{44}\) using the microstructures of Fig. 2a and Fig. 2b. The calculation has been simplified by using the random unit cell (RUC) of Fig. 2c and Fig. 2d that properly accounts for the essential features of the separate and aggregate microstructures, respectively.\(^{25,44}\) Using the Lorenz-Mie theory and the basic definition of EMT, the RUC can be expressed as a function of the scattering amplitude in the forward direction.\(^{27,28}\)
According to the definition of EMT, the RUC should not be detectable by the field in the given electromagnetic wavelength range of the experiment and this is an important condition for the optical theorem of Eq. (2.8) to be equal to zero ($C_{ext} = 0$):

$$S(0) = 0.$$ (2.12)

According to the meaning of the EMT the particles should satisfy a certain size range (smallest and largest size limits). The magnitude of the large-size limits are determined by the onset of the higher order terms in the series expansion whereas the small-size limit is governed in the transition of the bulk-like band structure towards molecular-cluster state. Eq. (2.12) can also be applied for non-spherical shapes by neglecting the higher order series expansion. This is advantageous since particles in practical coatings are found in different shapes. The Bruggeman and Maxwell-Garnett EMT extended to non-spherical particles are discussed below.

The Bruggeman model, which considered aggregate structure (Fig. 2.2b), in its general form has been derived by expanding Eq. (2.12) in terms of the size parameter, $ka$. By considering only the first order expansion (i.e. for small sphere limit) the forward scattering amplitude for an ellipsoid of semi-axes $a_j$ ($j=1,2,3$) is examined. The RUC in Fig. 2.2d for an ellipsoid aligned with the applied electric field polarized along one of the principal axes is applied. The small sphere limit expansion of Eq. (2.12) gives:
where $\varepsilon$ is the dielectric function of either of the constituents A or B, $\overline{\varepsilon}$ is the average dielectric function of the effective medium and $L_j$ is the depolarization factor along the field which satisfies:

$$0 \leq L_j \leq 1,$$  

(2.14a)

and

$$L_1 + L_2 + L_3 = 1.$$  

(2.14b)

Both constituents are treated symmetrically and each ellipsoid is taken to be embedded in the effective medium (Fig. 2.2d). From Eqs. (2.13-14), an implicit equation for Bruggeman effective dielectric function, $\overline{\varepsilon}^{BR}$ for an ellipsoid are obtained given by the expression:

$$f_j \frac{\varepsilon_A - \overline{\varepsilon}^{as}}{\overline{\varepsilon}^{as} + L_j (\varepsilon_A - \overline{\varepsilon}^{as})} + (1 - f_j) \frac{\varepsilon_s - \overline{\varepsilon}^{ms}}{\overline{\varepsilon}^{ms} + L_j (\varepsilon_s - \overline{\varepsilon}^{ms})} = 0,$$  

(2.15a)

where $f_A$ is the filling factor for component A and $(1-f_A)$ that for component B. In a collection of particles randomly oriented it is reasonable to assume an average value. The effective dielectric function for the three principal axes stated above becomes:

$$\frac{1}{3} \sum_{j} f_j \frac{\varepsilon_A - \overline{\varepsilon}^{as}}{\overline{\varepsilon}^{as} + L_j (\varepsilon_A - \overline{\varepsilon}^{as})} + (1 - f_j) \frac{\varepsilon_s - \overline{\varepsilon}^{ms}}{\overline{\varepsilon}^{ms} + L_j (\varepsilon_s - \overline{\varepsilon}^{ms})} = 0,$$  

(2.15b)

The Bruggeman model does not strictly apply to a particulate medium since there is no way to decide which component is the particles and which the surrounding medium. Since it is derived from an aggregate structure it is useful for a higher particle filling factor which is often used for solar energy applications. For spheres, all the depolarization factors in Eq. (2.14) are the same and for spheroids two of them are equal. The Bruggeman effective medium approximation for spherical particles ($L_j = \frac{1}{3}$) follows from Eq. (2.15):

$$f_A \frac{\varepsilon_A - \overline{\varepsilon}^{as}}{\varepsilon_A + 2\overline{\varepsilon}^{as}} + (1 - f_A) \frac{\varepsilon_s - \overline{\varepsilon}^{ms}}{\varepsilon_s + 2\overline{\varepsilon}^{ms}} = 0.$$  

(2.16)

Similarly, the generalized Maxwell-Garnett model can be obtained from an expansion of Eq.(2.12) for a separate grain structure (Fig. 2.2a ) by considering a coated ellipsoid in the RUC (Fig. 2.2c). The effective Maxwell-Garnett dielectric function, $\overline{\varepsilon}^{MG}$ has been given by:

$$\frac{-\varepsilon^{MG}}{\varepsilon} = \varepsilon_B \frac{(\varepsilon_A - \varepsilon_B)L_A^A + f_A(\varepsilon_A - \varepsilon_B)(1 - L_B^B)}{\varepsilon_B + (\varepsilon_A - \varepsilon_B)L_A^A - f_A(\varepsilon_A - \varepsilon_B)L_B^B},$$  

(2.17)

where $L_j^A$ and $L_j^B$ are the depolarization factors along the field for the inner and outer ellipsoid, respectively. Since particle interactions are not taken into account in an explicit manner, Eq. (2.17) is then valid for a low filling factor of particles. For the inverted structure, in which one replaces $A \rightarrow B$ and
B→A, one gets a similar relation. The Maxwell-Garnett expression in its simplest form \((L_j^A = L_j^B = \frac{1}{2})\) reduces to:

\[
\tilde{\varepsilon}_{\text{MG}} = \frac{\varepsilon_A + 2\varepsilon_B + 2f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_A + 2\varepsilon_B - f_A(\varepsilon_A - \varepsilon_B)}.
\]  

(2.18)

There is a basic difference between Maxwell-Garnett and Bruggeman theories. Bruggeman assumes the composite to consist of randomly intermixed particles of dielectric and metal, whereas Maxwell-Garnett considers the metal to be dispersed as particles through the dielectric or vice versa. Their dielectric functions are, however, similar at low filling factors. Both theories have in common that the effective dielectric function does not depend explicitly on the size of the inhomogeneities and this is because the electric dipole term, which is proportional to particle volume, is retained in the series expansion of the amplitude of the electric field scattered by a single particle. The EMT has been applied extensively in optical characterization of spectrally selective absorber composite coatings.

2.2.3 Two and Four Flux Theories

If the inhomogeneities in a composite medium are large enough to give rise to magnetic dipole and higher order multipole radiation, then the effective magnetic permeability of the composite medium cannot be taken to be that of free space even if the particles are non magnetic. Effective medium theories are not valid and instead radiative transfer theories such as two-flux and four-flux models are used. The two flux model proposed by Kubelka and Munk was based on a model of two light fluxes traveling in the forward and backward directions relative to the normal incident radiation. Isotropic directional intensity and isotropic scattering are necessary conditions for the derivation of the two flux expressions.

Consider a composite medium of thickness \(d\) along the z-axis illuminated by diffuse light as shown in Fig. 2.3a. The fluxes have been formulated by a pair of linear differential equations:

\[
\frac{dI_d}{dz} = -(K + S)I_d + SJ_d, \tag{2.19a}
\]

\[
\frac{dJ_d}{dz} = (K + S)J_d - SI_d, \tag{2.19b}
\]

where \(K, S\) are the absorption and scattering coefficients per unit length of the medium, respectively. The differential flux \(I_d\) decreases due to absorption within \(dz\) and scattering in the backward direction but also increases due to the backward scattering contribution from \(J_d\). Similar conditions also apply for the flux \(J_d\) of Eq. (2.19b).
Neglecting surface reflections, the diffuse reflectance, $R_d$ and transmittance, $T_d$ as a function of the thickness of the medium, $d$ are then given by:  

$$R_d = \frac{\sinh(qSd)}{p \cdot \sinh(qSd) + q \cdot \cosh(qSd)}, \quad (2.20)$$

$$T_d = \frac{q}{p \cdot \sinh(qSd) + q \cdot \cosh(qSd)}, \quad (2.21)$$

where $p = 1 + (K / S)$ and $q = \sqrt{p^2 - 1}$. The coefficients, $K$ and $S$, can then easily be extracted from optical measurements of $R_d$ and $T_d$ and a fitting to Eqs. (2.20-21). The diffuse reflectance of the Kubelka-Munk theory when applied on a substrate of reflectance, $R_g$ can easily be modified:  

$$R_g = \frac{1 - R_s \cdot \left[p - (q \cdot \coth(qSd))\right]}{p + (q \cdot \coth(qSd)) - R_s}, \quad (2.22)$$

If the substrate is highly reflecting, $R_g$ can be replaced by unity and if the medium is not supported by a substrate $R_g=0$ and Eq. (2.22) is reduces to Eq. (2.20). The Kubelka-Munk two flux theory which assumes diffuse illumination is a good approximation to calculate the transmittance and reflectance of highly scattering and weakly absorbing coatings. It has, however, limited applicability for partially scattering and absorbing samples.  

The equations were formulated with the assumption of diffuse illumination of the incident light on a diffusely scattering medium which is not applicable to the case of a collimated beam and weakly scattering medium. Instead the four flux theory which includes both diffuse and collimated fluxes should be used. Here we present analytical solutions of collimated as well as diffuse components of reflectance of a four flux model developed by Maheu and his co-authors.
As shown in Fig. 2.3b, the medium is now illuminated perpendicularly by a collimated beam along the $z$-coordinate. In addition to the directly transmitted ($I_c$) and specularly reflected ($J_c$) light, diffusely transmitted ($I_d$) and reflected ($J_d$) light can be considered. The intensities of the collimated beams decay due to scattering and absorption by the particles. The intensity of the diffuse flux $I_d$ is decreased by absorption and scattering into the backward hemisphere, and it is increased by scattering from the $I_c$, $J_c$ and $J_d$ fluxes into the forward hemisphere. A similar analysis corresponds to the flux $J_d$. A set of differential equations for the four flux components is given by:

$$\frac{dI_c}{dz} = -(k + s)I_c,$$

$$\frac{dJ_c}{dz} = (k + s)J_c,$$

$$\frac{dI_d}{dz} = -\xi k I_d - \xi(1 - \xi_c) s I_d + \xi(1 - \xi_c) s J_d + \xi_c s I_c + (1 - \xi_c) s J_c,$$

$$\frac{dJ_d}{dz} = \xi k J_d + \xi(1 - \xi_c) s J_d - \xi(1 - \xi_c) s I_d - \xi_c s J_c - (1 - \xi_c) s I_c,$$

where the intrinsic absorption, $k$ and scattering, $s$ coefficients per unit length, with their sum called extinction coefficient per unit length, can be obtained from the cross-section per unit volume as:

$$\frac{k}{f} = \frac{C_{abs}}{v},$$

$$\frac{s}{f} = \frac{C_{scat}}{v},$$

where $v$ and $f$ are particle volume and particle volume fraction, respectively. (Note the symbol $k$ (italic) for absorption coefficient). If $k$ and $s$ are expressed in $\mu$m$^{-1}$, then the corresponding volumetric cross-sections (cross-section per unit volume) have also units of $\mu$m$^{-1}$. Solutions of the volumetric absorption ($C_{abs}/v$) and scattering ($C_{scat}/v$) cross-sections, are found in Eq. (2.10-11) for single scattering calculation for spherical particles by Lorenz-Mie theory. An alternative way for determining the volumetric cross-sections from optical measurements is described in section 2.2.4. In Eq. (2.23), $\xi$ is the average path length parameter which is introduced to take into account the different path length of the diffuse radiation, as compared to the path length of the collimated component ($\xi=1$ for collimated beam and $\xi=2$ for semi-isotropic diffuse beam). The quantity $\xi_c$ defined in section 2.2.1 is the forward scattering ratio obtained using the Lorenz-Mie theory (see also Fig. 2.1). The differential equations, Eqs. (2.23a-d), have been solved previously, and explicit relations for collimated and diffuse components of the reflectance and transmittance have been obtained. They can easily be modified for the case of a metallic substrate. The collimated, $R_c$ and diffuse, $R_d$ reflectances respectively are given by the following equations:

$$R_c = r_c + \frac{(1 - r_c)^2 F e^{-2(k + s)d}}{1 - r_c F e^{-2(k + s)d}},$$

$$R_d = r_d + \frac{(1 - r_d)^2 F e^{-2(k + s)d}}{1 - r_d F e^{-2(k + s)d}}.$$
The sum of the collimated and diffuse components of reflectance is defined as the total reflectance, $R_t$:

$$R_t = R_c + R_d$$  \hspace{1cm} (2.27)

In the above equations $r_c$ and $r_d$ ($r_c'$ and $r_d'$), are the reflection coefficients for collimated and diffuse radiation at the medium-air (medium-substrate) interface, respectively. The Fresnel formulae are used to evaluate these coefficients, in terms of which the metallic substrate effects are taken into account by means of $F \cong r_c'$ and $G \cong r_d'$. Moreover:

$$C_0 = A_0 \left[ (A_0 + FA_2) - G(A_2 + FA_2) \right].$$ \hspace{1cm} (2.28a)

$$C_1 = \left\{ A_0 (GA_2 - A_3) \cosh(A_4 d) + \left[ A_3 (A_3 - GA_2) + A_1 (GA_2 - A_3) \right] \sinh(A_4 d) \right\}. \hspace{1cm} (2.28b)$$

$$C_2 = F \left\{ A_0 (GA_2 - A_3) \cosh(A_4 d) + \left[ A_3 (A_3 - GA_2) + A_2 (GA_2 - A_3) \right] \sinh(A_4 d) \right\}. \hspace{1cm} (2.28c)$$

with

$$A_1 = \xi \sqrt{k \left[ k + 2s(1 - \zeta_x) \right]}. \hspace{1cm} (2.29a)$$

$$A_2 = s \left[ \xi k \zeta_x + \xi s(1 - \zeta_x) + (k + s) \zeta_x \right]. \hspace{1cm} (2.29b)$$

$$A_3 = s \left\{ \xi \left[ s(1 - \zeta_x) + k(1 - \zeta_x) \right] - (k + s)(1 - \zeta_x) \right\}. \hspace{1cm} (2.29c)$$

$$A_4 = \xi \left[ k + s(1 - \zeta_x) \right]. \hspace{1cm} (2.29d)$$

$$A_5 = A_4 - \xi k. \hspace{1cm} (2.29e)$$

Two and four flux theories have been used extensively in the past for optically related applications such as; oxygen content in blood $^{62}$, minerals $^{63}$, paint or paper industry $^{64,65}$, thickness sensitive spectral selective paints $^{66,67}$ and spectrally selective composite absorbers $^{68}$. 
2.2.4 Cross-Sections from Reflection-Transmission Measurements

As mentioned earlier exact values of the absorption and scattering cross-sections for single particle can be obtained using the Lorenz-Mie theory if a great deal of computing time is applied and the optical constants of the medium are known. But optical constants of some complex materials cannot be found in the literature and are not easily measurable. A method is devised to obtain the single particle absorption and scattering cross-sections of a slab from reflectance and transmittance measurements. In order to apply the concept of single scattering, the incident light traversing the slab that reaches the detector must encounter very few particles. This method is then applicable for sufficiently transparent media i.e. for low volume fractions of the absorbing particles.

The total reflectance ($R_t$) as defined in Eq. (2.27) is given by the sum of collimated ($R_c$) and diffuse ($R_d$) components of reflectance. Similarly, the total transmittance ($T_t$) is defined by:

$$T_t = T_c + T_d$$  \hspace{1cm} (2.30)

where, $T_c$ is the collimated transmittance and $T_d$ diffuse transmittance. Light incident on a medium can either be reflected, transmitted or absorbed. Thus, the absorbed light is represented by the absorptance ($\text{Abs}$) and is defined as:

$$\text{Abs} = 1 - R_t - T_t$$  \hspace{1cm} (2.31)

Scattered light can be defined as the sum of the diffuse components of the total reflectance and transmittance the sum of the scattered light ($R_d, T_d$) and absorptance ($\text{Abs}$) gives the extinction ($\text{Ext}$):

$$\text{Ext} = R_d + T_d + \text{Abs}$$  \hspace{1cm} (2.32)

Inserting Eqs. (2.27), (2.30) and (2.31) into Eq. (2.32), the extinction of light in the scattering-absorbing medium becomes:

$$\text{Ext} = 1 - R_c - T_c$$  \hspace{1cm} (2.33)

From Eqs. (2.31) and (2.33) we see that the absorptance is determined from measurements of the total while the extinction from the collimated reflectance and transmittance. In order to understand scattering by a particle, we take the analogy of reflection-transmission by a slab. 28,69

Consider collimated light passing through a composite slab of thickness $d$ (see Fig. 2.3b) undergoing attenuation by extinction i.e. absorption and scattering. This extinction is due to randomly distributed particles in the medium. A fraction $R_0$ of the incident light is reflected at each interface. The light traversing the medium undergoes attenuation by a factor $\exp(-(K+S)d)$, where K and S are effective absorption and scattering coefficients coefficient per unit length as defined before and K+S effective extinction coefficient per unit length. The collimated transmittance and reflectance of the slab are easily found by addition of the intensities of the multiply reflected beams. The extinction coefficient, can be approximately determined from the ratio:
For weakly absorbing medium, \( \exp(-2(K+S)d) \approx 1 \) and hence for slab materials with refractive indices of 1.5 to 1.6 (like glass, KBr and most polymers), Eq. (2.34) can, within an accuracy better than 5\%, be simplified further to 28,69:

\[
\frac{T}{1 - R} \approx \exp(-(K + S)d).
\] (2.35)

The approximation is especially good when \((K+S)\) is small i.e. when the particle density is small and single scattering prevails.

The effective absorption coefficient, \(K\) can analogously be obtained from the total transmittance and reflectance:

\[
\frac{T}{1 - R} = \exp(-Kd),
\] (2.36)

since the scattered light contributes to either \(T_t\) or \(R_t\). This expression presumes single scattering of light by the particles. The approximation is within 5\% when absorption dominates totally over scattering. 28,69 In our materials, absorption is larger than scattering, as shown below, hence we are close to this limit. The effective scattering coefficient, \(S\) is then obtained from the difference of the extinction and absorption coefficients.

As mentioned earlier, the concentration of the particles in the medium should be very small, and hence multiple scattering can been ignored. A simple test for the absence of multiple scattering is to check the concentration dependence of \(S\) and \(K\). If a linear dependence as a function of the concentration is obtained, then only single scattering is important. 27 By assuming all the particles embedded in the matrix to be identical, the volumetric absorption and scattering cross-sections of Eq. (2.24a-b) are expressed: 28

\[
\frac{C_{\text{abs}}}{V} = \frac{K}{f} \quad \quad (2.37a)
\]

\[
\frac{C_{\text{sca}}}{V} = \frac{S}{f} \quad \quad (2.37b)
\]

Equations (2.24a-b) obtained from Lorenz-Mie theory are analogous to Eqs. (2.37a-b), respectively. The Lorenz-Mie theory considers single scattering for spherical particles but in this work we have used the cross-sections without regard to particle geometry.

In all the theories for inhomogeneous materials discussed earlier, the particle concentration was given in terms of volume fraction, \(f\). In practice we can find particle concentration in weight fraction, \(F\). Thus it is important to relate these two factors provided the density of the constituents is known as:

\[ f = \frac{1}{1 + \frac{\rho_p}{\rho_m} \left( \frac{1 - F}{F} \right)} \]  \hspace{1cm} (2.38)

where \( \rho_p \) and \( \rho_m \) are the mass density of the particle and the medium or matrix, respectively.

2.3 Selectively Solar Absorbing Surfaces

2.3.1 Understanding Selective Solar Absorbers

The blackbody spectrum at a given temperature and the spectral distribution of the sun needed to be known in order to evaluate absorbing surface behavior. The standard spectral solar flux incident at the surface of the earth, after atmospheric absorption, is limited to the range between 0.3 and 2.5 \( \mu \)m i.e. UV/Vis/NIR wavelength ranges. Our eye is sensitive only to the visible part of the solar spectrum. Figure 2.4 shows the hemispherical solar irradiance that reaches the surface of the earth after passing the atmosphere during clear sky conditions. This is adapted from the International Organization for Standardization (ISO) for air mass 1.5 (AM1.5) i.e. when the sun is about 42° above the horizon. The spectrum consists of direct and diffuse radiation and both fluxes contribute to heat-up flat plate solar collectors.

The solar absorptance is one parameter that characterizes the performance of the absorber. It is defined as the fraction of incident radiation at a given wavelength that is absorbed. For an opaque material the spectral absorptance can be expressed in terms of the total reflectance, \( R(\lambda, \theta) \), as:

\[ \alpha_{\text{sol}}(\lambda, \theta) = 1 - R(\lambda, \theta), \]  \hspace{1cm} (2.39)

where \( \lambda \) is the wavelength and \( \theta \) angle of incidence of light measured from the surface normal of the absorber. The solar absorptance is obtained by weighting the spectral absorptance with the spectral solar irradiance and for a given angle of incidence \( \theta \), it can be obtained by integrating over the wavelength dependent solar spectrum, \( G(\lambda) \):

\[ \alpha_{\text{sol}}(\theta) = \frac{\int_{\lambda_1}^{\lambda_2} [1 - R(\lambda, \theta)] G(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} G(\lambda) \, d\lambda}, \]  \hspace{1cm} (2.40)

where \( \lambda_1, \lambda_2 \) denote the lower and upper solar wavelengths, respectively. Since the blackbody spectrum of the sun and the solar irradiance at the surface of the earth are not the same, we cannot use the sun’s blackbody spectrum for weighting solar absorber coatings.
Fig. 2.4 Solar hemispherical spectral irradiance for AM1.5 in the wavelength range 0.3 to 4.045 µm (note the irradiance λ > 2.5 µm is negligible). This measurement was done at ground albedo 0.2, thickness of perceptible water vapor 1.42 cm, ozone layer 0.34 cm and turbidity 0.27. A blackbody radiation spectrum calculated from Planck’s law for three different temperatures is also shown in the infrared wavelength range.

Solar reflectance measurements are usually performed in the wavelength range 0.3-2.5 µm at near normal (θ≈0) angle of incidence using standard spectrophotometers. This means the solar absorptance is characterized at near normal incidence for which the sun is at the zenith angle relative to the absorber. For oblique incidence where the sun is at other elevations than the zenith, the near normal solar absorptance must be modified when characterizing solar thermal collector systems. This is usually done by using the angle of incidence modifier (optical efficiency), $K_{\tau\alpha}(\theta)$ which is a function of $\theta$ given by\(^\text{15}\):

$$K_{\tau\alpha}(\theta) = \frac{(\tau\alpha)}{(\tau\alpha)_o} = 1 - b_o \cdot \left( \frac{1}{\cos\theta} - 1 \right),$$

(2.41)

where $\alpha$ is the solar absorptance defined in Eq. (2.40) and $\tau$ is the transmittance of the collector cover. The subscript “o” represents values at normal (zero) angle of incidence. The constant $b_o$ is called an incidence angle modifier coefficient and its value can be different for different collectors. The collector system and application of the incident angle modifier will be discussed later in section 2.4.

The optical properties of a real body in the infrared wavelength range can be characterized by its thermal emittance compared to the ideal blackbody. Figure 2.4 shows blackbody spectra at three different temperatures calculated from Planck’s law. As the temperature rises, the total amount of radiation increases and the peak wavelength shifts towards shorter wavelength, which can be determined by Wien’s displacement law. The emittance is then defined as the fraction of radiant energy emitted by the heated surface as compared with the radiation energy emitted by a blackbody at a the
same temperature and wavelength. Since the radiation is emitted in all directions, then the thermal emittance is characterized by the hemispherical thermal emittance, \( \epsilon_{\text{therm}}(\lambda, T) \). Using Kirchhoff’s law stating that the absorptance is equal to the emittance and Eq. (2.39) for an opaque object, we get:

\[
\epsilon_{\text{therm}}(\lambda, T) = 1 - R(\lambda, T),
\]

(2.42)

and the total hemispherical emittance at a given temperature, \( T \) can be evaluated by:

\[
\epsilon_{\text{therm}}(T) = \frac{\int_{\lambda_1}^{\lambda_2} \int_0^{\pi/2} [1-R(\lambda, \theta, T)] 2\cos \theta \sin \theta d\theta d\lambda \cdot B(\lambda, T) d\lambda}{\int_{\lambda_1}^{\lambda_2} B(\lambda, T) d\lambda},
\]

(2.43)

where \( B(\lambda, T) \) is the blackbody spectrum given in Eq. (2.1). The absorbers for flat plate solar collectors are normally used at low temperatures and their thermal emittances are usually characterized at temperatures between 50° to 100°C. The emitted radiation from a body at these temperatures are found in the infrared region, and \( \lambda_1, \lambda_2 \) are then 2.5 \( \mu \text{m} \) and 50 \( \mu \text{m} \), respectively. The denominator of Eq. (2.43) is the so called Stephan-Boltzmann law (Eq. 2.2). For a blackbody, \( \epsilon_{\text{therm}}(T) \) is unity and for a real body it varies between 0 and 1.

The blackbody spectrum for temperatures between 50° to 100°C and the solar spectrum do not overlap in any wavelength range, as was shown in Fig. 2.4. It is, therefore, possible to design a surface which absorbs the maximum possible of the incident solar radiation, but does not re-emit the absorbed energy. A material having high absorptance (low reflectance) in the solar spectrum and low emittance (high reflectance) in the thermal infrared is called a selective solar absorber. An ideal spectrally selective surface should have a reflectance of zero in the solar wavelength range and unity in the thermal infrared. For temperatures below 100°C the on-set wavelength for the low to high reflectance is about 3 \( \mu \text{m} \) and for higher temperatures (\( \approx 300°C \)) the critical wavelength is around 2 \( \mu \text{m} \) (see Fig. 2.4).

2.3.2 Selective Solar Absorber Designs

In principle there are several ways of achieving selective solar absorbing surfaces. Descriptions of various selective absorbers produced by different techniques can be found elsewhere. \(^5\text{-7,70-72}\) The coatings are based on different optical absorption mechanisms including light trapping, particulate coatings, semiconductor-metallic layers, multilayer films, quantum size effects and intrinsic absorption. The simplest type of design would be to use materials having intrinsic solar selective properties, but there are no materials in nature that have such ideal solar selective properties. There are, however, reports on some transition metal compounds and semiconductors that indicate the existence of intrinsic selective materials. \(^5,73,74\) The most common absorber type is the absorber-reflector tandem and some of the widely applied designs are discussed below.

An absorber-reflector tandem is obtained by combining two surfaces, one surface which is highly absorbing in the solar region and another highly reflecting in the infrared. \(^75,76\). One way to do this is to cover a base metal of high infrared reflectance by a thin highly solar absorbing coating. This
configuration is called a dark mirror. Most of the commercially available selective absorbers are of this type. An alternative way to achieve the absorber-reflector tandem is to cover a thick absorbing surface by a solar transparent infrared reflecting coating which is normally called a heat mirror. Some of the absorber-reflector tandem designs of the first type are discussed below.

**Semiconductor Coatings**

Spectrally selective semiconductor coatings can be obtained by depositing a semiconductor, which has low band gap so that it absorbs the solar radiation, on a highly infrared reflecting metal substrate. The semiconductor coating absorbs photons having energies greater than the band gap as a result of raising the material’s valence electrons into the conduction band. Photons with energies less than the band gap energy are transmitted through the coating unaffected. To obtain high solar absorptance, the refractive index of the semiconductor should be as low as possible. Unfortunately, semiconductor coatings have high refractive index, which gives high reflectance at the air-coating interface. The reflectance can be reduced through proper thickness control to obtain a destructive interference effect or by applying antireflection coatings. Chemical vapor deposition of silicon in a stack of SiO$_2$/Si$_3$N$_4$/Si/Ag/Cr$_2$O$_3$ on stainless steel was developed for high temperature solar collectors with an antireflection coating on top of the multilayer stack. From this coating, a solar absorptance of 0.85 and a thermal emittance of 0.07 at 500°C was achieved. Ge, PbS and Si produced by gas and vacuum evaporation, chemical vapor deposition and spray pyrolysis are examples of semiconductor materials that have been utilized for solar absorber applications.

**Textured Surface Coatings**

Solar selective absorbing surfaces may be produced by creating texture of a suitable scale on a highly reflecting metal substrate. The rough surface absorbs solar energy by trapping the light through geometric effects of multiple reflection and absorption. For long wavelength radiation, the surface looks fairly smooth, thereby acting like a poor radiator of energy (low $\varepsilon_{\text{therm}}$). A dendrite structure of rhenium, tungsten and nickel made by chemical vapor deposition and textured copper, nickel, and stainless steel made by sputter etching are examples of textured metal surfaces. Al-Si alloy (20 vol.% Si) produced by simultaneous evaporation of the constituents from two electron-beam sources on a glass substrate and chemically etched in a NaOH solution form an irregular textured surface. The textured surface is due to the preferential etching of the aluminum phase, which gives a dark appearance for an appropriate etch time. The microstructure of the above textured absorbers could be interpreted as a top absorbing layer of air filled metal (rough surface) backed by a highly reflecting substrate. The optical properties of such coatings can be obtained using effective medium theories.

**Composite Coatings**

Composite coatings are surfaces consisting of small particles embedded in a dielectric matrix (also called cermet) deposited on a highly infrared reflecting metal substrate. The particles are usually transition metals embedded in an oxide matrix. The particles could either be uniformly distributed in the matrix or gradient index with decreasing content of the particles towards the front surface of the coating. These types of coatings have optical properties appropriate for selective solar absorbers. The coatings absorb solar radiation strongly and are almost transparent in the infrared region and hence the base metal gives the desired infrared properties. Depending on the volume fraction, shape of the particles
and optical constants of the constituents, the wavelength of the transmittance-absorption transition can be controlled by the thickness of the composite coatings. This offers a high degree of flexibility to solar selectivity. The composite coatings have typical values of the order of 0.5 to 1.0 µm in thickness, 0.3 to 0.4 metal volume fraction. Such coatings have a solar absorptance between 0.94 to 0.97 and a thermal emittance of about 0.10 to 0.20. Thicker films with lower particle content is also possible but the thermal emittance is also higher. The optical properties of composite coatings could be understood from effective medium or radiative transfer theory discussed in section 2.2. An advantage of using radiative transfer theory over the EMT is the possibility of predicting size dependent selectivity of composite coating. Recently, it has been reported that solar selectivity of coatings with metallic inclusions in an alumina matrix is not possible for particles with a diameter greater than 0.2 µm.

Figure 2.5 is a schematic cross-sectional diagram of two selective composite coatings one with particles uniformly distributed in the matrix, (nickel pigmented anodic aluminum oxide) and the other with graded index microstructure (sputtered nickel/nickel oxide). In both cases a top layer that reduces the refractive index mismatch (antireflection) between air and the absorbing layer is used. It is convenient to produce the antireflection layer from the same oxide layer as is the case of Fig. 2.5a. These two types of coatings will be discussed in detail in the following sections. There are commercially available metal-dielectric absorbers used for flat plate solar collectors, such as molybdenum/aluminum oxide (Mo-Al2O3), nickel/nickel oxide (Ni-NiOx), both produced by sputtering, electroplated black chrome (Cr-Cr2O3) and nickel pigmented anodic aluminum oxide (Ni-Al2O3).

### Painted Coatings

Selective solar absorbing paints have the potential of being a less expensive alternative to the selectively solar-absorbing coatings described above. They can also be classified as the tandem type of absorbing particles uniformly distributed in a matrix deposited on a metal substrate. Their optical performance is governed by intrinsic optical constants as well as particle size-dependent scattering and absorption. The combined effect gives the effective scattering and absorption coefficients of the pigment particles. Polymers such as silicone, siloxane resin or phenoxy resin are usually used as binders. Unfortunately, binders in general absorb infrared radiation and thereby the thermal emittance is higher. The particles usually agglomerate and their size becomes comparable to or larger than the incident wavelength of light. In order to reduce the agglomeration, fumed silica can be added during the preparation of the paints.
Laboratory studies of a range of pigments (mostly metal oxides) on aluminum substrates have been reported and the best obtained result was for an iron-manganese-copper oxide (FeMnCuOx) pigment with a silicone binder, giving a solar absorptance of 0.92 and a thermal emittance of 0.13. Thickness sensitive spectrally selective (TSSS) paints obtained from FeMnCuOx in a siloxane resin matrix have good optical properties ($\alpha_{\text{sol}}=0.90-0.92$ and $\varepsilon_{\text{therm}}=0.20-0.25$). In addition to the particle volume fraction and thickness, the solar selectivity of such coatings also depend on the dispersion of the particle (size) in the matrix. Paints are thicker ($d=2-3 \, \mu m$) and have a smaller volume fraction ($f=0.2$) than the metal-composite absorbers ($d=0.2-1.0 \, \mu m$ and $f>0.3$). Their optical properties can be studied using radiative transfer theories.

Selectively solar-absorbing paints have also reached commercialization recently, and there are at least two such products on the market, namely, the Solarect-Z, and the SolkoteHI/SORB-II™.

### 2.4. Solar Collectors

#### 2.4.1 Flat Plate Solar Collectors

Figure (2.6) shows a cross sectional view of a commonly used flat plate solar collector design. The major components of the collector as shown in the figure are, transparent cover, absorber, fluid conduit and an insulation.

![Fig. 2.6 Simplified cross-sectional view of a simple flat plate solar collector design used for domestic hot water application.](image)

The function of the collector system is to heat a fluid passing through the conduit by converting incident solar radiation into thermal energy with minimum heat losses. The heat losses can be due to conduction, convection and radiation and these losses are expressed in terms of the collector over all heat coefficient, $U_L$. The relation between thermal losses $U_L$ and the above parameters has been given in detail by Duffie-Beckman. Glass is usually used as cover for the absorber since it is transparent for the solar spectrum but opaque for the infrared wavelength and thereby suppresses thermal radiation emitted from the absorber. Glass reflects some of the incident solar radiation, however, and an antireflection coating can be applied in order to decrease the reflection. The cover also suppresses convection, and for minimum losses the spacing between the cover and absorber should be between 10-15 cm. Convection losses can be further reduced by using an additional transparent insulation material such as a thin transparent foil or honeycomb between the cover and the absorber. Conduction heat losses are avoided by using insulation at the back side of the collector box, as shown in Fig. (2.6).

The most important and critical part of the collector is the absorber surface. Spectral selective solar absorbers increase the useful energy output, $Q_u$, of the collector system as compared with non-selective absorbers. In addition to the intrinsic properties of the selective absorber surface (i.e. $\alpha_{\text{sol}}$ and $\varepsilon_{\text{therm}}$), another useful performance criterion, is the collection efficiency. It involves temperature of operation $(T_i - T_a)$, where $T_i$ is the inlet fluid temperature of the collector and $T_a$ is the ambient temperature. For flat plate collectors the collection efficiency, $\eta$, is the fraction of the available solar energy retained in the collector and is in its simplest form given by:

$$\eta = \frac{Q}{AG_t} = F_r \left( \frac{\alpha(U(T - T_i))}{G_t} \right), \quad (2.44)$$

where $(\alpha)$ from Eq. (2.41) is the optical efficiency that includes the angular dependence of the collector, $A_c$ is the collector (absorber) area and $G_t$ the total solar energy flux. $F_R$ is the collector heat removal factor, a quantity that relates the actual useful energy gain of a collector to the useful gain if the whole collector surface were at the fluid inlet temperature. If most of the radiation is beam radiation that is near normal to the collector, and $F_R$ and $U_L$ do not vary greatly in the range of operation of the collector, then $F_R(\alpha)$ indicates the amount of energy absorbed and $F_RU_L$ is the dissipation of energy in Wm$^{-2}$K$^{-1}$. The collection efficiency decreases with increasing operating temperature and at higher temperatures radiation losses are dominant as compared with conduction and convention losses. It is important, however, to stress that an increase in the solar absorptance, $\alpha_{\text{sol}}$ is more important than an equal decrease in the thermal emittance, $\varepsilon_{\text{therm}}$ for better collector performance.\(^{10,90}\)

To characterize the solar collector during a relatively short testing period with no requirement for steady state climatic conditions, systematic studies of the collector performance are needed. Dynamic testing can be used to predict the energy output of the collector by identifying collector parameters using a multiple linear regression method. The energy output, $q_u$ (Wm$^{-2}$) is determined using the following mathematical model:\(^{91}\)

$$q_u = F'(\alpha)G_{Tb} + F'(\alpha)G_{Td} - F'U_s\Delta T - F'U_t(\Delta T)^2 - (mC)_{\text{eff}} \frac{dT}{dt}, \quad (2.45)$$

where, $F'(\alpha)G_{Tb}$ and $F'(\alpha)G_{Td}$ are the optical efficiency for beam radiation ($G_{Tb}$) and the diffuse radiation ($G_{Td}$) respectively, $F'U_s$ is the heat loss coefficient in units of Wm$^{-2}$K$^{-1}$, $F'U_t$ the temperature dependence of the heat loss coefficient, W(mK)$^{-2}$, $dT/dt$, the mean time derivative for the fluid temperature (°Cs$^{-1}$) and $(mC)_{\text{eff}}$ the collector effective thermal capacitance, Jm$^{-2}$K$^{-1}$. $\Delta T$ is the temperature difference between the mean fluid temperature in the collector and ambient air temperature (°C). The relation between $F'$ and $F_s$ is well described in the book of Duffie-Beckman.\(^{15}\)
3 EXPERIMENTAL METHODS

The experimental methods for preparation of samples will be described in section 3.1. Each sample analyzed in this thesis was a thin film coating obtained from one or more of the following techniques: electrochemical deposition, spray pyrolysis, dip coating or sputtering. Preparation of pellets from black pigments in a non absorbing matrix for studying their optical properties is also given in this section. Oxidation of a solar absorber (metal particles) using accelerating aging technique at high temperature which is important for estimating the durability or life time of an absorber is described in section 3.2 followed by optical and non-optical characterization of the solar absorbers in section 3.3. A dynamic testing of two solar collectors which we have planned to do in the future are briefly described in section 3.4.

3.1 Sample Preparation

3.1.1 Chemical Methods

Anodizing aluminum samples

Aluminum sheet is cheap, has good thermal conductance and high infrared reflectance. By anodizing the aluminum, porous alumina of considerable interests for many practical uses including solar energy applications can be obtained. The formation of anodic oxide is very complex and the coating composition is largely controversial. Without going into details of the theories, we present here the experimental procedure of anodization of aluminum. A 0.5 mm thick rolled electroplated aluminum sheet (99.99% pure) was cut into samples of a size of 5.5 cm x 3.5 cm. These samples were anodized in 2.0 M phosphoric acid (H$_2$PO$_4$) at room temperature using a dc voltage of 15 V (current density about 4 mA/cm$^2$). The time of anodization was set to 12 minutes to produce a film thickness of about 0.5 $\mu$m. An aluminum plate was used as counter electrode. The experimental set-up of the anodizing process is shown in Fig. 3.1.

![Fig. 3.1 Experimental set-up for anodizing aluminum sheet in phosphoric acid electrolyte.](image-url)
The anodizing bath was continuously stirred (not shown in the set-up) to minimize local heating of the substrate which would result in uneven oxide coatings. The oxide thickness was measured using an Alpha step 200 mechanical stylus profilometer.

Pores are formed within preferred cells of the aluminum due to field assisted dissolution and an additional mechanism involved direct loss of \( \text{Al}^{3+} \) ions to the solution.\(^{93,94}\) These conditions produce a transparent porous amorphous aluminum oxide film with a pore fraction as large as 30 to 40 percent by volume.\(^{95,96}\) The pores are columnar of regular morphology and extend through the oxide from the metal-oxide interface to the surface (see also Fig. 2.5a for schematic diagram). The porosity and the thickness of the coating depend on the operating conditions (such as voltage, temperature, time of anodization) as well as on the concentration of the electrolyte.\(^92\) A very thin, about 1.4 nm/V, non-porous barrier alumina layer buffers the aluminum substrate.

**Electrochemical Deposition (Coloration) of Anodized Samples**

Due to aesthetic reasons, processes have been developed for coloration of anodized aluminum products. Coloration can be made either directly (integral coloration) during anodization or as a post treatment.\(^92\) Post treatment coloring of porous aluminum oxide can be made by organic dyes or by chemical or electrochemical deposition of inorganic compounds inside the pores.\(^92,97-99\) By adding inorganic compounds of metal sulfates to the bath of Fig. 3.1 and applying ac electrolysis the alumina film can be colored. In this work coloration of the anodic aluminum oxide was done by using a nickel sulfate salt using a nickel counter electrode.

The composition of the chemical bath was 20 g nickel sulfate, NiSO\(_4\), 20 g magnesium sulfate, MgSO\(_4\), 20 g ammonium sulfate, (NH\(_4\))\(_2\)SO\(_4\) and 20 g boric acid, H\(_3\)BO\(_3\) in one liter distilled water. The ammonium sulfate improves the conductivity of the solution, and magnesium sulfate improves the coloring condition.\(^100\) Boric acid maintains the solution at a pH value of about 7. An ac voltage of 15 V (current density about 20 mA/cm\(^2\)) was applied for 4 minutes at room temperature. Metallic nickel particles of about 300 nm long with a rod shape were grown within the pores of the alumina, one in each pore, starting to grow from the pore base.\(^{101-103}\) In addition to the laboratory produced samples, some commercial nickel pigmented aluminum oxide absorbers obtained from Sunstrip (Sweden) were analyzed in this thesis. The commercial absorber has a total thickness of about 700 nm with a nickel pigmented base layer of 300 nm and an unpigmented alumina top layer of about 400 nm. Rolled aluminum was used as substrate.

**Integral Coloration of Samples**

Although the two step anodization-coloration has been an inexpensive and successful technique for production of solar absorbers, further reduction of cost could be achieved by reducing the coating formation to one step. Direct, or integral coloration of anodized aluminum (99.99 % pure) from a mixture of organic and inorganic electrolyte acids forms metallic aluminum particles embedded in alumina matrix (Al-Al\(_2\)O\(_3\)).\(^{104-106}\) Since the particle volume fraction was very low (< 1%), the alumina had to be thick enough (>10 \(\mu\)m) to change the appearance of the coatings from transparent to a grayish (brownish) color. A darker alumina film (about 50 \(\mu\)m thick and with a 0.002 particle volume fraction) has been reported by anodizing aluminum (99.99 % pure) in a sulfuric acid solution at high current concentrations.
density (>100 mA/cm²). The integrally colored anodized aluminum, however, has high thermal emittance due to the large thickness of the coating and is not feasible for solar absorber applications.

Anodization of aluminum alloys allows the incorporation of alloying elements in the oxide and this has been observed from anodizing commercially available silicon rich Al-Si alloy. This coating has been proposed for use as a solar absorber but its performance as a solar selective coating was not investigated. In this report we have investigated the optical properties of integrally colored Al-Si alloy as a function of oxide thickness. Samples of Al-Si of size 5.5 cm x 3.5 cm and 0.1 mm thick were cut out from a rolled sheet of the Al-Si alloy. The type of the alloy was AA4047, and contains 11.6 wt. % of silicon, which was the highest content of Si commercially found.

The solution in the bath of Fig. 3.1 was replaced by 1.8 M sulfuric acid, H₂SO₄ solution and the samples were anodized at room temperature using a constant anodizing voltage of 15 V dc. An aluminum plate was used as counter electrode and the anodizing bath was continuously stirred to minimize local heating. The time of anodization was between 5 and 120 minutes and this produced 1.0 to 17 µm thick films. The aluminum oxide is integrally colored by the silicon particles when forming the silicon-alumina coating (Si-Al₂O₃) during the anodization process. The appearance of the coatings changes from gray to dark with increasing the Si-Al₂O₃ film thickness. The results are discussed in section 4.

### 3.1.2 Spray Pyrolysis

The pyrolytic spray technique which is inexpensive and well suited for large-scale applications is one of the most suitable techniques for depositing high visible transmission and high infrared reflection (low thermal emittance) coatings. The basic principle of this technique is to transport and disperse a solution in the form of an aerosol through nozzles by means of a carrier gas controlled by a flow rate meter and deposit it onto a heated sample situated in a chamber (See Fig. 3.2). The chamber has an opening channel to let the byproducts out of the chamber. The temperature of the heater is controlled by a temperature controller and a thermocouple can be used to measure the temperature at the sample surface.

The solutions prepared in this work were 2.3 M tin chloride, SnCl₄ in alcohol and 2 M ammonium fluoride, NH₄F in water. Each solution was put in separate nozzles and pyrolytically sprayed simultaneously to a sample held at temperatures between 400 and 500°C. For simplification only one spray nozzle is shown in the figure. The air flow rates of the SnCl₄ and NH₄F solutions were 65 l/min and 22 l/min, respectively. The aerosols evaporate and a solid fluorine doped tin oxide (SnO₂:F) film is grown on the substrate. The samples coated were nickel pigmented aluminum oxide solar absorber (Ni-Al₂O₃) and the deposition rate was about 60 nm/min at 450°C. The reason for covering the Ni-Al₂O₃ absorber is to protect its surface from abrasion and corrosion since it is sensitive to such degradation mechanisms. However, tin oxide has large refractive index (n ≥ 2) resulting in significant reflectance in the visible spectrum and thereby reducing the solar absorptance of the absorber. Thus, a complimentary mechanism such as antireflection is needed to reduce the reflectance of the surface. This has been performed using dip-coating process as explained below.
**3.1.3 Dip-Coating**

A solution of silica was prepared in a bath by first mixing water (25 ml), ethanol (90 ml), methanol (80 ml) and a small amount of sulfuric acid (0.4 ml). Then 50 ml of sol and 250 ml of ethanol were added and used after curing for a few days (approx. 4 days of preparation). The acid stabilizes the sol, (sol is stable at only high or low pH) and prevents it from aggregation to a thick gel. The aging of the sol is important in order to give rise to a larger porosity of the antireflection layer. The samples in section 3.1.2 were immersed into the bath and withdrawn at different rates to produce a silica layer on the surface of the samples for antireflection. The thickness of the layer was controlled by the withdrawal speed ranging from 5 to 10 mm/s. A silica (SiO₂) layer appropriate for antireflection was produced from this process. It is to be noticed that antireflection films prepared from a commercially available colloidal silica sol allows a simple preparation and low cost coatings.

**3.1.4 Sputtering**

Sputtering is one of the most widely used thin film deposition techniques and is clean compared to chemical processing methods, where large quantities of chemical waste products have to be handled. The basic principle of sputtering is to knock out atoms from a source (target) and deposit them on a substrate. A vacuum chamber containing a low pressure inert gas such as argon can set-up a glow discharge by applying a sufficiently large voltage between the target (raw material for coating) and the substrate inside the chamber. Energetic ions can bombard the surface of the target and knock out atoms or particles which are then transported and deposited on the substrate. Sputtering gives the flexibility of selecting different substrates and materials to deposit, uses various kinds of reactive gases, and can also be controlled accurately to make coatings with micro- and multilayer structures. The working principle and description of sputtering can be found in detail elsewhere.

Currently, sputtering technologies are also employed for depositing thin film absorber coatings in large-scale production. Here we mention a roll coating dc magnetron sputtering technique used for...
production of a nickel/nickel oxide absorber (Ni-NiO\textsubscript{x}) on a rolled aluminum substrate. A Ni target is sputtered as the substrate loaded with a 1000 m long coil sheet is moving in the vacuum chamber. Oxygen inlet during the sputtering is designed to give a gradual decrease of nickel content and an increasing amount of nickel oxide from the substrate to the front surface. This produces a grading in the optical refractive index through the coating and a graded nickel/nickel oxide composite absorber is obtained. Meanwhile, an antireflection layer is deposited on top of the graded absorber layer using a second target in a row. The coating is described in detail by Wäckelgård and Hultmark. The schematic microstructure of nickel/nickel oxide coating has been shown in Fig. 2.5b. The total thickness is about 200 nm including the antireflection layer of about 50 nm thickness. This type of absorber was obtained from Sunstrip (Sweden) and its optical properties were compared with nickel pigmented aluminum oxide absorber (Ni-Al\textsubscript{2}O\textsubscript{3}) obtained from the same industry.

3.1.5 Production of Black Pigment Pellets

Characterization of black pigments used for selective solar-absorbing paints have been performed. Two types of pigments, namely, FeMnCuO\textsubscript{x} (Ferro Crop., F-6331) and organic black carbon (Fw2, Degussa) initially in powder form were obtained. Each of them was mixed with potassium bromide (KBr) powder, ground in a pearl mill for about five minutes to disperse the pigment and finally pressed using a load of about 8-tons. Potassium bromide was chosen as matrix for the pigment because of its low absorptance in the solar wavelength range. The light scattering should also be very low due to the hard pressure exerted on the KBr powder during the pellet pressing.

The use of 0.1 grams of the ground material in the press produced pellets with a diameter of 13 mm and a thickness of 0.4 mm. The range of pigment concentration was between 0.1 to 2.0 wt. % for the FeMnCuO\textsubscript{x} and 0.05 to 1.0 wt. % for the black carbon. These ranges correspond to a volume fraction of 0.053-1.07 % and 0.076-1.52 %, respectively. The volume fractions were obtained from Eq. (2.38) using the density of KBr, 2.75 g/cm\textsuperscript{3}\textsuperscript{115}, FeMnCuO\textsubscript{x}, 5.2 g/cm\textsuperscript{3} and black carbon, 1.8 g/cm\textsuperscript{3}. To get high transmittance, the pigment to binder volume fraction was very low. For comparison a KBr pellet without pigment was also produced. Since KBr is hygroscopic, precaution was taken to prevent the samples from being exposed to the environment for longer periods to avoid water absorption that may affect the results. The samples were then kept in a container with a silica-gel from the start of the production to the optical measurements.

3.2 High Temperature Accelerated Aging Test

This section is focused on accelerated aging of the nickel pigmented aluminum oxide solar absorber. The work was divided into two parts: one is oxidation of the nickel particles embedded in the aluminum oxide matrix (Ni-Al\textsubscript{2}O\textsubscript{3}) and the second oxidation of “free” nickel particles (Ni-air) i.e. when the particles are not surrounded by the alumina matrix.

3.2.1 Oxidation of Nickel Particles in Alumina Matrix (Ni-Al\textsubscript{2}O\textsubscript{3})

Samples of Ni-Al\textsubscript{2}O\textsubscript{3} were placed in a pre-heated oven in air at temperatures of 300, 400 and 500°C. Each sample was taken out of the oven at different times from 1 to 500 hours. After the oxidation process the alumina coating was etched for 5 minutes in a bath containing 35 g chromic VI oxide and 20 g H\textsubscript{2}PO\textsubscript{4} at 80°C. The etching does not have a noticeable effect on the nickel and nickel oxide but 5
minutes was enough to remove all of the porous alumina film surrounding the particles. The nickel rods are not washed away by this treatment. They remain as free standing rods perpendicular to the surface loosely attached to the barrier alumina layer. They lean against each other in some areas but they still adhere to the substrate during the experiment (see Fig. 4.1 in section 4). Great care was taken in handling the samples otherwise the particles could easily be wiped off.

### 3.2.2 Oxidation of Nickel Particles in Air Matrix (Ni-air)

The alumina of the Ni-Al₂O₃ samples was first etched away before starting the oxidation process. The chemicals used and the process applied for etching were the same as for the Ni-Al₂O₃ in the previous section. A Heareus RO furnace connected to a Heareus RE 1.1 temperature control unit was used in the oxidation experiment (Fig. 3.3).

![Experimental set-up for oxidation of nickel particles in air matrix (Ni-air). The end piece is disconnected in this figure.](image)

The furnace consisted of a glass tube of 7 cm diameter and length 50 cm with an air tight end-piece on both ends. Each sample together with a thermocouple was then mounted at the end of the tube furnace and connected to a 1 m stainless steel (SS) tube, free to move in and out of the center of the furnace. After inserting the sample, a high rate flow of oxygen gas (99.99 % pure) was admitted into the furnace for five minutes to establish a pure oxygen atmosphere after which the flow was lowered to 0.04 l/min. The sample was then pushed slowly, below 10 °C/min to avoid ignition of the particles, into the center of the oven for oxidation. Different samples were heated at furnace temperatures 260, 280, 300, 320 and 350°C for oxidation times between 5 minutes to 20 hours. After oxidation the samples were pulled out slowly (<10 °C/min) for optical measurements as described in section 3.3.

### 3.3 Optical and Non-Optical Characterization

#### 3.3.1 Spectrophotometers

Spectrophotometers are frequently used for the investigation of the optical properties of solar absorbers. Two kinds of equipment are of interest: UV/Vis/NIR spectrophotometers which measure in the wavelength range of the solar spectrum and the IR spectrophotometers that cover the infrared
wavelength range. Total and diffuse reflectance and transmittance can be measured using spectrophotometers equipped with an integrating sphere. Figure 3.4a-b illustrates the position of a sample for total reflectance (reflectance mode) and transmittance (transmittance mode) measurements using an integrating sphere. For diffuse reflectance measurements, plate-1 in the reflectance mode is removed to let the specular reflectance, $R_s$ out of the sphere and $R_d$ is contained in the sphere. The diffuse transmittance, $T_d$ is measured by trapping the specular component of the transmittance, $T_s$. This is achieved by replacing plate-2 in the transmittance mode with a black cone to damp the specularly transmitted light and thus measuring the remaining diffuse quantity. The specular component is then obtained from the difference of the total and diffuse measurements as in Eq. 2.27 and Eq. 2.30. The interior wall of integrating spheres are coated with almost perfectly diffusing (Lambertian) and highly reflecting materials. In the solar wavelength range barium-sulfate (BaSO$_4$) powder and in the IR gold coated walls are usually used. The theory and design of integrating spheres, spectral measurements and analyses of different kinds of samples, the cause of errors in the measurements and correction algorithms have been extensively reported in the literature.\textsuperscript{116-121}

![Fig. 3.4 Optical measurements of a sample using an integrating sphere. (a) For total and diffuse reflectance (reflectance mode) and (b) total and diffuse transmittance (transmittance mode) measurements.](image)

### 3.3.2 Optical Characterization

Measurements of total and diffuse reflectance and transmittance for absorbers in the solar and infrared wavelength ranges were performed. Depending on the type of measurements to be done, different kinds of spectrophotometers have been used. In the solar spectrum (0.3-2.5 $\mu$m), a Beckman UV 5240 and a Perkin Elmer Lambda 9 UV/Vis/NIR double-beam spectrophotometers with a photomultiplier (0.3-0.8 $\mu$m) and PbS (0.8-2.5 $\mu$m) detectors have been used. The Beckman instrument was equipped with a 150 mm diameter integrating sphere while the Perkin Elmer had a 60 mm diameter sphere. Both instruments were used for measurements at near normal angle of incidence. For oblique angle of incidence a single-beam spectrophotometer built at the Division of Solid State Physics, equipped with an integrating sphere of size 150 mm and a sample holder in the central of the sphere have been used. The instrument has a two color detector; a Si detector that measures in the wavelength 0.3-1.1 $\mu$m but is transparent above 1.1 $\mu$m is combined with a PbS detector which detects signals between 1.1-2.5 $\mu$m.
The sample holder in the central of the sphere can be rotated so non-normal reflectance is measured between 5° and 80° angles of incidence using p- or s- polarized light. The measuring routines and description of the spectrophotometer is found in detail elsewhere.\textsuperscript{121} The inner walls of all the above spheres were painted with BaSO\textsubscript{4} and a BaSO\textsubscript{4} painted plate was used as a reference.

The solar absorptance, $\alpha_{\text{sol}}$ of an absorber is obtained by measuring the total reflectance in the solar wavelength range and weighting by the solar irradiation using Eq. (2.40). The Beckman instrument was used for measuring reflectance to determine $\alpha_{\text{sol}}$ of Si-Al\textsubscript{2}O\textsubscript{3} and Ni-Al\textsubscript{2}O\textsubscript{3} coatings as reported in papers I, II and III. The Perkin-Elmer Lambda 9 was used for measuring transmittance and reflectance to determine scattering and absorption cross-sections for the FeMnCuO\textsubscript{x} and black carbon pigments (paper IX) as well as total reflectance of the TSSS paints (paper X). The solar absorptance of the two commercial absorbers obtained from Sunstrip (Ni-Al\textsubscript{2}O\textsubscript{3} and Ni-NiO\textsubscript{x}) was measured as a function of angle of incidence, using the single beam spectrophotometer. Papers VII and VIII contain results obtained from this instrument.

In the infrared wavelength range a single-beam FT-IR Bomem-Michelson 110 spectrophotometer and a double-beam Perkin Elmer 983 spectrophotometer were used. The FT-IR was equipped with a Labsphere of 4/5-inch inner/outer diameters, infragold-coated integrating sphere and could measure total and diffuse reflectance as well as transmittance at near normal angle of incidence. The instrument had a liquid nitrogen cooled mercury cadmium telluride detector. The Perkin Elmer 983 spectrophotometer had no integrating sphere and could be used to measure only specular reflectance and transmittance. However, it is equipped with accessories for oblique angle of incidence measurements. The instrument has a thermocouple detector and dry air can be circulated in the sample compartment to reduce water and carbon-dioxide absorption during measurements. For both the instruments gold or aluminum mirrors were used as reference.

The FT-IR instrument was used to measure the total reflectance between 2.0 to 20 $\mu$m and from the measurements, the thermal emittance was obtained by applying Eq. (2.43). Papers I, II and III contain results obtained from this instrument. The Perkin Elmer 983 spectrophotometer was used for quantifying the amount of nickel oxide in the annealed Ni-Al\textsubscript{2}O\textsubscript{3} and Ni-air samples (papers IV, V and VI). This was obtained by measuring the reflectance of p-polarized light at higher angles of incidence (60°). The measurements were performed between 1500 to 300 cm\textsuperscript{-1} (6.6-33 $\mu$m) covering the position of the longitudinal optical (LO) phonon mode of nickel oxide. Before these measurements, the porous aluminum oxide matrix for the Ni-Al\textsubscript{2}O\textsubscript{3} samples had been etched away. This was done because aluminum oxide has strong absorption in the 1000 to 900 cm\textsuperscript{-1} range due to absorption by the alumina LO phonon mode\textsuperscript{122} which masks the absorption band of the thermally created nickel oxide.

3.3.3 Non-Optical Characterization

\textit{X-Ray Diffraction (XRD)}

XRD is a well known analysis tool which yields crystallographic information from studying the interaction of monochromatic X-rays with a periodic crystal lattice.\textsuperscript{123} X-ray diffraction measurements are made by causing a beam of X-radiation to fall onto a suitably prepared specimen and measuring the angles at which the specific characteristic X-ray wavelength is diffracted. The diffraction angle, $\theta_0$ can be related to the atomic spacing (or crystallographic information) by Bragg law.\textsuperscript{123} For thicker films
the diffraction peak is recorded at $2\theta_D$ degrees. There are various XRD configurations and in this work a conventional Siemens D-5000 powder diffractometer which scans between $\theta_D$-$2\theta_D$ (degrees) have been used. Samples of Si-Al$_2$O$_3$ and annealed Ni-Al$_2$O$_3$ coatings were analyzed by rotating the source and detector at a constant angular speed for angles between 20 and 100 degrees.

**Scanning Electron Microscopy (SEM)**

When a well-focused electron beam (e-beam) is scanned over a surface of a sample, the interaction between the electrons and the matter gives the emission of X-rays, Auger electrons, backscattered as well as secondary electrons. In SEM the signals of greatest interest are, the secondary electrons which have fairly low energy and the reflected (backscattered) electrons, both give information about sample topography. Using appropriate detectors, the signals from the surface of the sample can be detected and then focused on a screen using cathode ray tube (CRT) to reproduce the image. A schematic diagram of a Scanning Electron Microscope is shown in Fig. 3.5. In general, SEM requires a conducting sample in a low vacuum chamber but for non-conducting samples a very thin gold-palladium film is applied to reduce charging effects. SEMs often have a microprobe for energy dispersive analysis by studying the characteristic X-ray lines for rapid evaluation of elemental constituents. High Resolution Leo 1550 SEM with field emission gun and Zeiss DSM 960 SEM have been used for surface and cross-sectional morphologies, particle size and elemental analyses of different absorbing samples. The samples analyzed were Si-Al$_2$O$_3$ coatings, FeMnCuO$_x$ and black carbon pigments and nickel pigmented aluminum oxide coatings.

![Fig. 3.5 Schematic diagram of Scanning Electron Microscopy (SEM), showing the electron column, the deflection system, and the electron detectors.](image)
3.4 Dynamic Testing of Solar Collectors

In order to evaluate and compare the performance of the two commercial solar absorbers (Ni-Al₂O₃ and Ni-NiOₓ), they have been mounted in two similar collector boxes at Vattenfall’s laboratory at Ålkarleby (Sweden). The evaluation is according to the principle of dynamic testing, with day by day variation of the operating temperature. The actual output can be determined by measuring the water flow and the temperature increase over the collector. These measurements together with Multiple Linear Regression can be used to obtain the collector parameters in the model (see Eq. (2.45)). Angular dependent performances and possible yearly energy output of each of the two collectors, are planned to be carried out in the future using MINSUN simulation program.
4 RESULTS AND DISCUSSION

In this section results of the experiment from section 3 and theoretical modeling for the experiments are discussed. Most of the theoretical models have been introduced in section 2.

4.1 Nickel Pigmented Aluminum Oxide (Ni-Al$_2$O$_3$)

Scanning Electron Microscopy (SEM) pictures of a nickel pigmented aluminum oxide absorber is shown in Fig. 4.1. The aluminum oxide has been dissolved and nickel particles are freely standing on the aluminum substrate (Fig. 4.1a). Figure 4.1b shows a few nickel rods that has fallen on the substrate. The average length of the rods were about 300 nm and from TEM it has been determined that the particles are approximately 30 to 50 nm in diameter.

![SEM picture of nickel pigmented aluminum oxide absorber](image)

(a) (b)

Fig. 4.1. SEM picture of nickel pigmented aluminum oxide absorber. (a) top view of standing nickel rods and (b) a few fallen rods. The alumina matrix is etched away for the SEM micrographs. The length scales, the electron high tension, EHT and microscope working distance, WD are shown in the inset.

The nickel pigmented aluminum oxide solar absorber, was first documented by Andersson et al. in 1979. 52,126 It has a good optical performance ($\alpha_{\text{sol}}=0.95$ and $\varepsilon_{\text{therm}}=0.12-0.20$) but its service life time can be shortened by too high temperature, humidity or atmospheric pollution such as sulfur dioxide. 127 The absorber is also sensitive to abrasion. Thus covering the surface with a chemically and mechanically stable transparent coating can reduce degradation mechanisms. We have applied a pyrolytically deposited fluorine doped tin oxide coating (SnO$_2$:F), on the surface of the absorber. A similar coating was previously applied on a black-enameled/steel absorber and has given a good spectral selective surface for solar collectors. 128 By suitable doping and appropriate substrate temperature one can increase both the solar transmittance and infrared reflectance of the SnO$_2$ coating. The presence of oxygen deficiency in the SnO$_2$ coating also gives high infrared reflection. However, due to the large index of refraction of the transparent oxide, a large amount of the incident light can be reflected. In our work, a significant increase of reflectance (reduction of $\alpha_{\text{sol}} \approx 4\%$) occurs as shown by the dotted curve in Fig.
4.2a. The increase of reflectance in the solar region has been reduced by applying an antireflection coating of silica (SiO$_2$) which has little or no noticeable effect in the infrared (Fig. 4.2a). The best values obtained for this experiment after antireflection was $\alpha_{\text{sol}}=0.94$ and $\varepsilon_{\text{therm}}=0.15$. This is shown in Fig. 4.2b and compared with a commercially produced Ni-Al$_2$O$_3$ absorber ($\alpha_{\text{sol}}=0.95$ and $\varepsilon_{\text{therm}}=0.14$).

![Reflectance spectra of coatings](image)

(a) Reflectance versus wavelength of Ni-Al$_2$O$_3$, SnO$_2$/Ni-Al$_2$O$_3$, and SiO$_2$/SnO$_2$/Ni-Al$_2$O$_3$ coatings. (b) Best values obtained for coatings in (a) as compared with a commercially produced Ni-Al$_2$O$_3$ absorber.

To be of practical use, an antireflection film for solar collectors must show adequate durability and should not deteriorate the optical properties significantly with time. Preliminary test results indicate that SiO$_2$/SnO$_2$/Ni-Al$_2$O$_3$ samples are resistant to high temperatures as well as to corrosion. Figure 4.3a shows reflectance spectra of one sample after heating at 300, 400 and 500°C, each temperature being kept for 24 hours. The optical properties of the sample before and after aging at 300°C are found to be the same. With increasing annealing temperature, the reflectance in the solar region tends to increase and the onset of reflectance shifts toward longer wavelengths. This was also observed previously for SnO$_2$/Ni-Al$_2$O$_3$ samples. An antireflection treated sample was also tested by immersing it in water containing 8% sulfuric acid for three hours, and the result was compared with that of an identically treated Ni-Al$_2$O$_3$ sample. In Fig. 4.3b, it is shown that the Ni-Al$_2$O$_3$ surface is dissolved by the acid and degrades quite severely. The sample with SiO$_2$/SnO$_2$ layer, however, withstands the acid and the reflectance spectra before and after the acid test are found to be practically the same. In summary, the silica (SiO$_2$) antireflection layer is found thermally and chemically stable.
Another degradation mechanism of the nickel pigmented aluminum oxide solar absorber is oxidation of the nickel particles. In order to get information about the durability properties, studies under conditions of accelerated aging are necessary for an estimation of the service life time of the absorber. The International Energy Agency (IEA) has outlined a program for accelerated life testing of commercial solar absorber materials prior to their market introduction. High temperature degradation is one method used in this program in order to develop models from which the service life time of the absorber can be estimated. The rate of oxidation of the nickel particles was previously determined indirectly from the relative decrease of solar absorptance at high temperature accelerated aging test. In this work we report results on thermal oxidation of laboratory prepared nickel pigmented aluminum oxide samples and present a method from which the rate of oxidation can be determined directly from infrared measurements (see section 3 for preparation, oxidation processes and infrared measurements). The growth rate of the oxide has been analyzed by measuring p-polarized reflectance at 60° angle of incidence in the wavelength range around the longitudinal optical (LO) phonon mode frequency of nickel oxide which is around 550 cm\(^{-1}\) (18 µm).

Figure 4.4 shows reflectance spectra of NiO obtained from annealing of the Ni particles in Al\(_2\)O\(_3\) matrix at a temperature of 500°C. There is no absorption band from the porous Al\(_2\)O\(_3\) (LO-phonon between 1000-900 cm\(^{-1}\)) since it has been etched away before the optical measurements. The reflectance minimum at about 540 cm\(^{-1}\) originates from absorption of NiO in the wavelength range around its LO-phonon mode. The depth of the minimum increases with increasing time of exposure i.e. an increasing amount of NiO in the coatings. A similar behavior is seen also for the samples annealed at 300°C and 400°C but with more shallow minima. The absorptance peak height was then determined and used as a measure of the degree of oxidation.
Fig. 4.4 Reflectance spectra (p-polarized light) at 60° incidence angle for NiO obtained by oxidation of Ni particles in alumina matrix as a function of wavenumber (cm⁻¹). The measured spectra are shown before and after annealing at 500°C for different times as shown in the inset.

Reflectance spectra of Ni particles oxidized without the Al₂O₃ matrix, (Ni-air samples) annealed at 280°C is shown in Fig 4.5a. The oxidation time (hour:min) is shown in the inset and is much shorter than for Ni particles embedded in Al₂O₃ (see Fig. 4.4). A similar behavior as in Fig. 4.5a is seen also for Ni-air samples annealed at 260, 300, 325 and 350°C but with more shallow minima for the lower temperature and deeper ones for temperatures higher than 280°C at the corresponding oxidation time.

Fig. 4.5. Reflectance spectra (p-polarized light) at 60° angle of incidence as a function of wavenumber (cm⁻¹). (a) Nickel particles oxidized without Al₂O₃ matrix at 280°C for annealing time (hour:min) is drawn together with unoxidized Ni particles (solid line). (b) Comparison between free nickel particles (Ni-air) and particles embedded in alumina matrix (Ni-Al₂O₃) heated at 500°C for 10 min and 60 min, respectively.
Figure 4.5b shows spectra of two samples heated at 500°C for oxidation times as shown in the inset when the Ni particles are free and when they are kept intact in the Al2O3 matrix. Comparing the oxidation of the particles, it is clear that the alumina acts as a barrier for rapid oxidation. Moreover, the reflectance minimum obtained from the two oxidation processes is found to be different i.e. at 540 cm⁻¹ for the Ni-Al2O3 and 580 cm⁻¹ for the Ni-air.

In order to determine the degree of oxidation, modeling for the NiO absorptance peak has been performed using the Berreman relation and the Bruggeman EMT. From the SEM and TEM analyses, oxidation takes place at the end of the nickel rods facing the pore opening. If oxidation takes place also around the other surfaces of the rods, the amount of oxide must be too small to be detected by TEM. The surface of the treated samples can then be considered as a thin NiO film on top of the metallic Ni particles as shown by the schematic diagram in Fig. 4.6a. Since it is the top NiO which gives rise to the LO-phonon mode absorption, an equivalent system regarding this absorption is found by omitting the unoxidized part of the nickel rods and just treating the film as a single inhomogeneous NiO layer on a metallic substrate (Fig. 4.6b). This consideration helps in the modeling, using the Berreman relation for a thin dielectric film, for which the p-polarized reflectance loss is proportional to the film thickness, $d$ in the wavelength range of the LO-phonon mode. Bruggeman model (Eq. 2.15) was used to calculate the effective dielectric function of the inhomogeneous NiO film. The inhomogeneities are considered to be NiO particles in an air matrix (NiO-air). The optical constants of NiO and Al have been taken from the literature.

![Fig. 4.6](image-url) (a) A cross-sectional view illustrating front surface oxidation of nickel rods and (b) a simplified diagram to describe the effect of the phonon mode by considering a single layer of the oxidized part of the nickel rods on aluminum that was used in the modeling.

Figure 4.7 shows calculated reflectance as a function of wavenumber (cm⁻¹) for different film thicknesses. The shape of the NiO is taken to be similar to that of the Ni rods and hence an appropriate depolarizing factor $L_j$ as defined in Eq. (2.14) is used. A sharp reflectance minimum around 510 cm⁻¹ was obtained for a cylindrical nickel oxide geometry. By varying the depolarization factor the width and depth of the reflectance minimum can be changed to some extent. In this calculation, the particle volume fraction of NiO was taken to be the same as for the nickel rods, which is $f=0.3$, but the volume expansion upon oxidation of Ni to NiO is about 1.67 and this increases the volume fraction of NiO. It has been observed from the calculation that with an increase of the filling factor of NiO the position of the reflectance minimum is shifted towards a higher wavenumber. Experimentally, the minimum appears at a higher wavenumber (540 cm⁻¹, Ni-Al2O3 oxidation) and is also broader, which may be explained by additional surface mode absorption produced by particle shape effects, than the calculated ones. For comparison, a calculated reflectance spectrum of a 30 nm solid nickel oxide film on aluminum substrate is also shown in Fig. 4.7. A sharp and much deeper reflectance minimum at a higher
wavenumber than the corresponding one of the porous film is obtained. The important results of the calculations are that the reflectance in the minimum decreases with increasing NiO film thickness just as we found experimentally and the oxide thickness, \( d \) of the absorber has been validated by the modeling using the Berreman relation.

![Graph showing reflectance vs. wavenumber for different film thicknesses](image)

**Fig. 4.7** Calculated spectral reflectance for \( p \)-polarized light at 60° angle of incidence for given filling (\( f \)) and depolarization (\( L_j \)) factors and varying film thicknesses, \( d \). For comparison the reflectance spectra of a 30 nm isotropic solid film (sf) is also displayed.

If the oxide thickness \( d \) has a general time dependence and an Arrhenius temperature dependence then it can be written as:

\[
\begin{align*}
    d &= \exp\left(-E_a / k_B T\right) \cdot f(t), \\
    &\text{(4.1)}
\end{align*}
\]

where \( k_B \) is the Boltzmann constant and \( E_a \) is the activation energy. The thickness, \( d \) can then be approximated from measurements of the \( p \)-polarized reflectance, \( R_p \) by considering the Berreman relation \(^{134}\):

\[
\begin{align*}
    1 - R_p &\propto d . \\
    &\text{(4.2)}
\end{align*}
\]

The best resolution for the determination of the film thickness, is expected at the LO-phonon frequency with, the largest reflectance losses. The unity in Eq. (4.2) has been modified by the \( p \)-polarized reflectance value of the reference of the unoxidized nickel particles, \( R_p^{\text{ref}} \), since the metal particles also contribute with a background level of absorptance. \(^{133}\) The thickness is then proportional to the absorptance peak height:

\[
\begin{align*}
    R_p^{\text{ref}} - R_p &\propto d . \\
    &\text{(4.3)}
\end{align*}
\]

The relation between the measured reflectance and oxide thickness now makes it possible to quantify the thickness of the thermally created nickel oxide.
From Eq. (4.1) the logarithm of the oxidation time at a specific thickness value, between two different temperatures $T_1$ and $T$ is given by:

$$\ln f(t) - \ln f(t_1) \propto \left( \frac{E_a}{k_b} \right) \left( \frac{1}{T} - \frac{1}{T_1} \right), \quad (4.4a)$$

and for the function $f(t) = t$ the above equation can be written as:

$$\ln(t) - \ln(t_1) \propto \left( \frac{E_a}{k_b} \right) \left( \frac{1}{T} - \frac{1}{T_1} \right). \quad (4.4b)$$

From Eq. (4.4), we can see that the logarithm of the time dependence of the oxide thickness, $\ln(t)$ is a constant translation from $\ln(t_1)$ for any given thickness $d$ at temperature $T$. Similarly, the absorptance peak height of Eq. 4.3 can be expressed by:

$$\ln(\frac{R_s}{R_p} - \frac{R_{s,ref}}{R_{p,ref}}) \propto \left( \frac{E_a}{k_b} \right) \left( \frac{1}{T} \right). \quad (4.5)$$

The oxidation rate of nickel can, therefore, be determined from Eq. (4.5), by extracting the measured reflectance at the wavelength of its minimum value for each temperature and plotted against the oxidation time along a time axis. The isotherms in Eq. (4.4) or Eq. (4.5), should therefore fall onto a single curve in a double logarithmic plot by translating the temperature along the time axis since the translation depends on the temperatures only. This is the master plot technique that have been applied to the measured reflectance data.

From the power-law approximation in the master plot, it is seen that there were fairly large deviations from a single curve for both the Ni-Al$_2$O$_3$ and Ni-air oxidation processes. In the case of Ni-Al$_2$O$_3$ the exponential range (kinetic exponent) was between 0.08 to 0.19 for the temperatures 300 to 500°C and this is much lower than for the Ni-air oxidation process which was between 0.52 to 0.63 for the temperature range 260 to 350°C. Kinetic exponents smaller than the value 0.5 for parabolic law behavior are usually found and have been explained as due to a decreasing number of available grain boundaries because of grain growth observed during oxidation. It then appears that diffusion in the matrix surrounding the metal particles is of prime importance for the durability of the solar absorber coatings. The low observed kinetic exponents of the oxidation of Ni particles situated in the alumina matrix (Ni-Al$_2$O$_3$) are found to be consistent with the previous reports. It should be noted that the nickel particles in the porous alumina are not totally surrounded by the matrix. An even more improved stability is expected for metal-insulator coatings, where the particles are completely surrounded by a dielectric matrix such as the very stable Mo-Al$_2$O$_3$ based coating that was previously investigated in detail. In order to evaluate the life time of the nickel pigmented aluminum oxide, an evaluation mechanism has been presented and hence the activation energy of the particles should first be determined.

The activation energy can be found by plotting either the shifts of the logarithms of the different isotherms $(\ln(t) - \ln(t_1))$ or $(R_s - R_p)$ versus inverse temperature, $1/T$ using Eq. (4.4) or Eq. (4.5), respectively. The slope of the curve then gives the activation energy, $E_a$. Figure 4.8 shows $\ln(t) - \ln(t_1)$ versus $1/T$ for the Ni-air oxidation process and an approximated apparent activation energy of 1.73 eV
was found from the linear fit. For the Ni-Al₂O₃ the activation energy was estimated to be about 1.4 eV but the result could be uncertain since the value of the activation energy below and above the Curie temperature is reported to be different. 

![Graph showing In(t) vs 10^4/T (K⁻¹)](image)

**Fig. 4.8.** Plot of ln(t)-ln(t₁) against inverse temperature for annealing temperatures between 260-350°C and time, t=16 min. The activation energy is found from the slope of the linear fit to the data.

After determining the activation energy using the above methods, then the actual service life time of solar absorber, t_{service}, under a given operating condition, can be estimated using: ¹²⁷

\[
    t_{service} = t_{test} \cdot \exp \left[ \frac{E_a}{k_B} \left( \frac{1}{T_{op}} - \frac{1}{T_{test}} \right) \right],
\]

(4.6)

where, \(T_{op}\) is average operating temperature of the absorber (collector), \(T_{test}\) is the testing temperature, and \(t_{test}\) is the time needed to reach a certain extent of degradation for the optical performance of the absorber during the temperature \(T_{test}\). From the IEA criteria, the service life time of a collector is defined as the time when the optical performance of the absorber is reduced by 5 % of its original value. The effect of high temperature on the degradation of the nickel pigmented aluminum oxide absorber was found to be small since the presence of the alumina around the nickel particle decreases the oxidation rate. If degradation was caused by temperature only, then about 25 years service life has been estimated for this type of coating at stagnation temperature, \(T_{op}=290°C\). ¹²⁷ It is important to mention here that, the Ni-Al₂O₃ absorber is severely degraded in condensation test ¹²⁷,¹⁴⁴ and hence covering the absorber by the transparent oxide mentioned before can minimize this effect. Condensation, on the other hand, may not be a major problem if the absorber is placed in a well ventilated and rain tight collector box.

### 4.2 Anodized Al-Si Alloy (Si-Al₂O₃)

Composite coatings of Si have been produced by co-sputtering of CaF₂ with silicon on an aluminum mirror. Also a paint consisting of silicon particles dispersed in thick silicone binder deposited on
stainless steel has been reported.\textsuperscript{145,146} The optical behavior can be considered as being similar to that of the parent semiconductor with the same energy gap. But the refractive index is dependent on the concentration of the Si particles in the coating and is controlled by the volume fraction of particles.\textsuperscript{7}

Silicon-alumina composite coatings can be produced by anodizing silicon rich aluminum alloys. We have investigated the optical properties of anodized Al-Si alloy (11.6 wt% Si) (see section 3 for sample preparation). The anodization of the sample provides a Si-Al\textsubscript{2}O\textsubscript{3} composite coating growing at a rate of 0.14 µm per minute. From the θ\textsubscript{D}-2θ\textsubscript{D} X-ray diffraction analysis, sharp diffraction patterns for silicon and aluminum (substrate) were detected but not for aluminum oxide. Hence, the alumina (Al\textsubscript{2}O\textsubscript{3}) is found to be amorphous and is integrally colored by the crystalline Si particles during the anodization process. The shape of the Si particles is irregular and their sizes vary between 1 and 10 µm with an average size of about 2 µm as is shown from the Scanning Electron Microscope (SEM) in Fig. 4.9.

![Fig. 4.9 Scanning Electron Microscopy (SEM) picture of Si-Al\textsubscript{2}O\textsubscript{3} coating produced by anodizing Al-Si alloy for two hours.](image)

Figure 4.10a shows the measured reflectance of the Si-Al\textsubscript{2}O\textsubscript{3} coatings for different thicknesses between 1.0 to 10 µm in the wavelength range 0.3 to 20 µm. Thick porous plain aluminum oxide has a broad and deep absorption band in the region of its lattice vibration modes between 10 to 20 µm as seen in Fig. 4.10a. The anodization also produces compounds involving hydrogen, such as aluminum hydroxide, oxyhydroxide, crystal water and sulfate anions causing absorption in the infrared wavelength range. From the figure the characteristic absorption bands of O-H-groups at 3.6 µm and 6.2 µm\textsuperscript{147}, and sulfate anions in the wavelength range 9 to 13 µm,\textsuperscript{148} can be observed. These features of the absorption bands are found from anodized plane alumina (Al\textsubscript{2}O\textsubscript{3}) but the bands are deeper and the reflectance between band regions, 3 to 8 µm, is higher than the Si-Al\textsubscript{2}O\textsubscript{3} coating.

The intrinsic bandgap of crystalline silicon is 1.12 eV which implies that its optical absorption covers the solar spectrum up to 1.11 µm. Impurities, dislocations and non-crystallinity create electron states within the bandgap. The Si particles contain defects and impurities introduced during the manufacturing of the Al-Si, causing the absorption to extend to wavelengths longer than the bandgap edge (Fig. 4.10a). It has been found in earlier work that defects can be removed by annealing, thereby
lowering the infrared absorption. For that reason one sample was annealed at 500°C for 24 hours and the absorptance in the near infrared decreased by 0.03 and the thermal emittance by 0.05.

![Graph](image)

*Fig. 4.10 (a) Total reflectance of anodized Al-Si alloy as a function of wavelength between 0.3 and 20 µm for different anodizing times (film thickness) and (b) solar absorptance and thermal emittance, calculated from the measured reflectance, as a function of coating thickness.*

The optical measurements showed a continuous decrease of the reflectance, i.e. an increase of absorptance, with increasing film thickness. The Si-Al₂O₃ coatings are opaque-grey and become darker for a larger thickness, a higher silicon content and smaller particle size. A maximum solar absorption of 0.85 was achieved for 13 µm or thicker Si-Al₂O₃ coatings (Fig. 4.10b). The deep absorption band of alumina above the wavelength of 10 µm (Fig. 4.10a) is the main cause of the very high thermal emittance as apparent in Fig. 4.10b. This result can be compared with that of the previous work of the composite coatings obtained from co-sputtering or paint with Si pigment. A solar absorptance of 0.70 and a thermal emittance of 0.10 at 300°C was obtained from a 5 µm thick Si-CaF₂ coating. For the paint coating a solar absorptance of 0.83 and a thermal emittance over 0.70 have been reported. The high thermal emittance of the paint was mainly due to the large thickness of the paint. In our experiments, we have used a low concentration of silicon (f=0.138) because that was the highest one commercially found. It was believed that such a low concentration of Si would be far from the optimal one for a selective absorber coatings. Therefore we used a theoretical model to calculate the optical properties as a function of silicon content, particle size and oxide thickness searching for a feasible Si-Al₂O₃ coating for solar selective absorbers.

The optical properties of the Si-Al₂O₃ coatings have been modeled using the four flux model, since the particles are of the order of or larger than the wavelength of the incoming light. The expressions for the total reflectance given in Eq. (2.27) was used to model the optical properties of the Si-Al₂O₃ films and the calculated results are compared to spectroscopic measurements. There is poor agreement between measurements and calculated reflectance when optical constants of pure Si is used.
The predicted reflectance is high in the near infrared wavelength, as shown in Fig. 4.11a. It is known that dielectric functions depend on the type of scattering mechanisms which influence the mean free path of the electron in semiconductors. Contributions to scattering can be originated from defects such as grain boundaries, dislocations, inhomogeneties and impurities. Hence the optical constants of Si has to be modified to account for the contribution from these effects. Our model is simplified and assumed to take into account only Al-doping of silicon introduced during the production of the Al-Si alloy. The simplest approach to describe the contribution of the impurities to the optical properties are by using the Drude model with a plasma frequency, $\omega_p$, as a fitting parameter. The frequency dependent real, $\varepsilon_r$, and imaginary, $\varepsilon_i$, dielectric functions of this additional contribution to the dielectric function of the pure Si are given by:

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2 (\tau')^2}{1 + \omega^2 (\tau')^2},$$

$$\varepsilon_i(\omega) = \frac{\omega \tau'}{\omega^2 + (\tau')^2},$$

where $\tau'$ is the relaxation time of silicon.

The modified optical constants of Si improve the calculated results by lowering the reflectance in the near infrared wavelength range, as shown by the dashed curve in Fig. 4.11a. There is a discrepancy between calculation and experiment and hence further calculation was performed. Theories for frequency dependent ionized impurity scattering suggested that, the impurities act as scattering centers thus decreasing the relaxation time, $\tau'$. It is, therefore, reasonable to consider a frequency...
dependent relaxation time, $\tau' = \tau'(\omega)$ considering the incorporation of ionized Al impurities in the Si during the manufacturing of the alloy. Our calculation is based on the expression outlined by Gerlach \textsuperscript{151,152} since it gives a simplified approach. It can be shown that for most scattering mechanisms in semiconductors the influence on the optical properties can be described by a simple frequency dependent power law as shown in Eq. (4.8). For frequencies between the plasma frequency and the energy gap, the relaxation time due to the presence of charged impurities is proportional to $\omega^{3/2}$ and we write it as $A\omega^{3/2}$. Here A is a proportionality constant which decreases with the ionized impurity concentration, and the atomic number of the impurities. The expression for the total relaxation time is then given by:

$$
\tau'(\omega) = \frac{\tau'_0}{1 + \gamma(\omega r'_0)^{3/2}},
$$

where,

$$
\gamma = \frac{(r'_0)^{3/2}}{A}.
$$

Using $\tau'_0$ and $\gamma$ as fitting parameters in addition to $\omega_p$, a very good agreement is obtained as displayed by the circles in Fig. 4.11a-b. The values of the fitting parameters are displayed in the inset. The model fits well for films of the order of or larger than 5 $\mu$m. As expected, there is no good agreement for films thinner than 5 $\mu$m since the film thickness is comparable to the particle size and the four flux model is not applicable.

The model leads to an understanding of the absorptance of the Si particles with variation of particle size and concentration as well as film thickness. It is well known that the degree of absorption by a particle which is small compared to the measured wavelength is proportional to its volume. As the particle size increases, however, the absorption becomes proportional to the particle surface. It means that there is an optimal particle size which leads to the highest absorption for a given film thickness and particle concentration, as shown in Fig. 4.12a.

![Fig. 4.12](image-url) Calculated solar absorptance of Si-Al2O3 films as a function of (a) particle radius for different particle volume fractions of a 5.0 $\mu$m thick film and (b) particle volume fraction at different film thicknesses using optimum particle radii of each film.
As the particle concentration increases, the optimal particle size increases and for higher particle volume fractions it approaches a constant value. The resulting optimum solar absorptance as a function of particle volume fraction and film thickness using the optimal particle size is shown in Fig. 4.12b. For a high concentration of silicon of sub-micron particle size, a solar absorptance around 0.90 can be achieved from a thick film (~10 µm) but as discussed before the thermal emittance is high. For a thinner film of 1 µm thickness, the infrared emittance is reduced to about 0.27 in the ideal case of smooth surfaces but the solar absorptance is lower, only 0.70. In short, for Si-Al₂O₃ coatings there is no thickness range with high solar absorptance and at the same time low thermal emittance, which indicates that the coating is not a candidate for selective solar absorbers.

4.3 Angular Performance of Selective Solar Absorbers

4.3.1 Angular Solar Absorptance

The optical characterization of solar absorbers for thermal solar collectors is usually performed by measuring spectral reflectance at near normal angle of incidence and calculating the solar absorptance from the measured reflectance. The solar absorptance is, however, a function of the angle of incidence of the light impinging on the absorber. In this section angular solar absorptance of two types of commercial selective solar absorbers; nickel-pigmented aluminum oxide (Ni-Al₂O₃) and sputtered nickel/nickel oxide (Ni-NiOₓ) coatings are discussed. Both coatings contain particles of nickel but they differ in microstructure (particle shape and distribution) as well as coating thickness, d. In section 4.1, SEM pictures of a Ni-Al₂O₃ absorber have been shown (Fig. 4.1) and its microstructure has been discussed. For the Ni-NiOₓ absorber, top and cross sectional views of the coating using Transmission Electron Microscopy (TEM) were investigated. It was observed that the coating consists of nano-sized grains compactly packed in the absorbing base layer and less densely as columns in the antireflection layer. It was beyond the resolution of the instrument to analyze the grain composition in order to determine the nickel and nickel oxide content in a depth profile. Schematic diagrams of both types of absorbers have been shown previously in section 2, Fig. 2.5.

In order to determine the angular solar absorptance of the two absorbers, reflectance measurements at different angles of incidence have been performed (see section 3 for optical measurements). Figure 4.13 presents p- and s polarized spectral reflectance (R₀ and Rₘ) of the Ni-Al₂O₃ coating as a function of wavelength between 0.3 to 2.5 µm for different angles of incidence from 5 to 80°. For clarity we have shown some selected angles of incidence. Due to the coating thickness, optical thin film interference within the measured wavelength range is inevitable. The interference maxima and minima become very pronounced at high angles of incidence. A small shift of the maxima and minima to shorter wavelengths can be noticed for the reflectance curves from 50 to 80°. This is because the layer at higher angles of incidence corresponds to a coating with thinner effective thickness, which is a very characteristic behavior of optical interference coatings. Another feature of thin film interference is that reflectance minima and maxima do not occur at the same wavelengths for p- as for s polarized light. This effect is also clearly seen in the curves of high-angle spectral reflectance in Fig. 4.13.
Fig. 4.13 Total reflectance (a) $R_p$ and (b) $R_s$ for Ni-Al$_2$O$_3$ coating as a function of wavelength in the solar spectrum recorded at different angles of incidence from near normal to 80°.

The p- and s-polarized spectral reflectance of the Ni-NiO$_x$ coating between the wavelengths 0.3 to 2.5 µm for different angles of incidence are shown in Fig. 4.14. Here the interference pattern is suppressed by having a graded-index layer with an antireflection coating on top. The antireflection layer is necessary in order to reduce front surface reflection.

Fig. 4.14 Reflectance (a) $R_p$ and (b) $R_s$ for Ni-NiO$_x$ coating as a function of wavelength in the solar spectrum measured at different angles of incidence from near normal to 80°.
When comparing the spectral angular reflectance of the two types of absorbers it is found that thin film interference patterns dominate the spectral behavior of the two-layer structured Ni-\(\text{Al}_2\text{O}_3\) absorber while the graded Ni-NiO\(_x\) absorber has smoother reflectance curves. It is known that p- and s-polarized reflectance at near normal are the same and this, as expected, has been observed for both the Ni-\(\text{Al}_2\text{O}_3\) and Ni-NiO\(_x\) coatings. As the angle of incidence increases the p- and s- curves split. At higher angels of incidence, \(R_p\) was found to be higher than \(R_s\) but due to the enhanced interference effects, in the case of the Ni-\(\text{Al}_2\text{O}_3\) coating only, the p- polarized reflectance was also higher than the s- ones in certain wavelengths intervals.

The average reflectance of the p- and s- polarized reflectance given by

\[
R(\lambda,\theta) = \frac{1}{2} \left[ R_p(\lambda,\theta) + R_s(\lambda,\theta) \right], \tag{4.10}
\]

over the measured wavelength range is observed to be larger for the Ni-NiO\(_x\) than for the Ni-\(\text{Al}_2\text{O}_3\) coating at higher angles. Using the measured results of the two coatings, the angular solar absorptance was determined from Eq. (2.40), where \(R(\lambda,\theta)\) is replaced by Eq. (4.10). The solar absorptance of the Ni-\(\text{Al}_2\text{O}_3\) absorber is constant over a wide range of angles of incidence. It absorbs about 0.95 of the solar radiation from near normal up to 50° but the absorptance decreases steeply to about 0.70 when approaching 80° as shown in Fig. 4.15. The solar absorptance of the Ni-NiO\(_x\) absorber decreases gradually from near normal up to 40° and beyond this angle it drops steeply (Fig. 4.15). The solar absorptance of the Ni-NiO\(_x\) absorber begins to decrease at lower angles as compared with the Ni-\(\text{Al}_2\text{O}_3\) absorber. The angular solar absorptance at higher angles of incidence is significantly different for the two types of coatings.

Fig. 4.15 Solar absorptance of Ni-\(\text{Al}_2\text{O}_3\) and Ni-NiO\(_x\) absorber coatings against angle of incidence from 5 to 80° obtained from the results of Figs. 4.13 and Fig. 4.14 using Eq. (2.40).

We have already shown that the solar absorptance decreases with increasing angle of incidence. A significant amount of solar absorptance can be gained at higher angles of incidence due to surface roughness of the coatings. As mentioned in section 3 rolled aluminum substrates were used for the two
absorbers. The rolling creates parallel grooves in the aluminum surface, which scatter the reflected light in directions perpendicular to the direction of the rolling grooves. This one-dimensional texture introduces orientation dependent reflectance, i.e. orientation dependent solar absorptance. A noticeable difference in solar absorptance at higher angles was obtained when the groove orientation was perpendicular to the plane of the incident light as compared with parallel oriented grooves for both types of absorbers (see also paper VII). It is therefore advantageous to install a solar collector with grooves of the absorber in the north-south direction in order to gain more solar energy in the mornings and afternoons.

We have also performed theoretical modeling of the solar absorptance as a function of angle of incidence for the two absorbers. The reflectance calculations were based on a 2 x 2 matrix technique using a surface impedance and admittance approach and the Fresnel amplitude coefficients were calculated for each interface in a multi-layer stack of thin films for different angles of incidence between 5 to 80° in the wavelength interval 0.3 to 2.5 µm. The modeling included the calculation of effective optical constants for two component inhomogeneous materials for a given particle shape of appropriate $L_j$ (Eq. 2.14) by use of Bruggeman effective medium model (Eq. 2.15). The surfaces were assumed to be smooth and the effect of surface roughness on absorptance, polarization or coating interference was not considered. The optical constants of nickel, nickel oxide, alumina and the aluminum substrate were taken from the literature.

When the Ni-Al$_2$O$_3$ was modeled, we considered two layers of inhomogeneous media: a base layer of thickness $d_2=300$ nm with nickel rods in alumina and a top unpigmented porous alumina layer of thickness $d_1=200$ nm. The nickel rods and the air filled pores are idealized in the model to be cylinders with the long axis perpendicular to the sample surface. The volume fraction, $f$ of the air-pore in the top layer of the coating was assumed to be the same as that of the nickel particles in the base layer, $f=0.3$. From the calculated reflectance we obtained the solar absorptance for each angle of incidence. The calculated solar absorptance decreases with increasing angle of incidence similar to the measured results. Since the absolute values of the calculated angular solar absorptance are lower than the measured ones, we have chosen to present the angular solar absorptance normalized to its near-normal value. As shown in Fig. 4.16, the calculated normalized solar absorptance models the experimental result quite well. The calculated solar absorptance remains almost constant over a wide range of angles of incidence with maximum solar absorptance around 40° and drops steeply beyond 60°, similar to the experimental data. The existence of this maximum is due to the more pronounced interference effects of the ideal model coating.
Fig. 4.16 Calculated and experimental normalized solar absorptance of Ni-Al$_2$O$_3$ and Ni-NiO$_x$ coatings as a function of angle of incidence from 5° to 80°.

The Ni-NiO$_x$ coating was modeled by considering a single graded-index structure of spherical nickel particles in a nickel oxide matrix. The total thickness which was taken to be about 240 nm was divided into eight equally thick sub-layers. The content of nickel in the sub-layers was assumed to increase when going from the front surface to the substrate. For best fit to the experimental reflectance, the filling factor was found to be greater than 0.6 at the substrate-film interface and zero at the film surface. The composition of the coating at the front surface is considered to consist of homogeneous nickel oxide and hence the porosity was not modeled as it did not improve the fitting. There is no significant difference in the results when the numbers of stratified layers exceed eight. From the reflectance we calculated the solar absorptance for each angle of incidence. The solar absorptance is normalized to the value at near normal and the calculated results model the experiment well, as shown in Fig. 4.16.

In order to sort out the key features that govern the angular behavior of solar absorptance of the selective absorbers, we have also made a thorough theoretical investigation for different types of microstructures. The various microstructures were determined by varying, the shape, $L_j$ and volume fraction, $f$ of the particles inside the matrix as well as the thickness, $d$ and layer structure of the composite coating. From this study, it was found that the difference in particle shape (cylindrical or spherical) has no significant effect on the angular solar absorptance. The main effect was observed from the type of layer structure (double-layer or graded-index layer) of the composite coatings as presented in paper VII. As seen from the experimental and theoretical results, the solar absorptance of the two types of absorbers at higher angles of incidence is significantly different. A higher high-angle solar absorptance is obtained for the nickel-pigmented aluminum oxide coating than for the sputtered nickel/nickel oxide coating and this is found to be due to thin film interference effects which cannot be achieved from a graded-index thin film coating since the interference patterns is suppressed by the graded index layer and the antireflection film on top.
Another way of characterizing absorbers in a system of solar collectors is the use of a model that considers the effect of the angle of incidence of the radiation reaching the absorber. For flat plate solar collectors, the angular optical performance is often modeled with an incident angle modifier, $K_m(\theta)$ (Eq. (2.41)). For an absorber without cover Eq. (2.41) can be modified as:

$$K_m(\theta) = 1 - b_0 \left( \frac{1}{\cos \theta} - 1 \right)^c,$$

(Eq. 4.11)

where $c$ is an additional parameter specific for each type of absorber and $b_0$ (incidence angle modifier coefficient) as was defined in Eq. (2.41). Equation 4.11 has been used to model the experimental angular solar absorptance of the two types of commercial absorbers. As shown in Fig. 4.17, the experimental results are fitted quite well. Since the two absorbers have different absorptance at higher angles, the fitting coefficients differ considerably. The nickel pigmented aluminum oxide has $b_0 = 0.017$ and $c = 1.8$, while the sputtered nickel/nickel oxide absorber has $b_0 = 0.057$ and $c = 1.2$. Both $b_0$ and $c$ are found to be important parameters in order to fit to the angular solar absorptance of unglazed absorbers.

![Graph](image1.png)  
(a) Experimental normalized solar absorptance for Ni-Al$_2$O$_3$ and Ni-NiO$_x$ absorbers as a function of angle of incidence as fitted using Eq. (4.11).  
(b) Optical performance of the absorbers in (a) when they considered to have a glass cover. In both of the figures the fitting parameters are displayed in the inset.

Most solar collectors have some kind of cover glazing and the absorbed radiation is the result of the combined effect of the absorber and the cover. Figure 4.17b shows the transmittance-absorptance product, $(\tau\alpha)/(\tau\alpha)_0$, for the two types of absorbers at different angles of incidence normalized to the near normal angle of incidence $(\theta = 5^\circ)$. In the calculations the transmittance of a 4 mm thick low-iron glass taken from reference 15 was used. The experimental results were fitted using the incident angle modifier expression given in Eq. (4.11) and the fitting parameters are shown in the inset of Fig. 4.17b. From the figure we observe that the exponent, $c$ for both absorbers approaches unity and hence the
original Eq. (2.41) can be applied. This shows that the glass cover has a large impact on the optical performance of the collector at higher angles of incidence. Using the optical measurements obtained in this work, an investigation of collector output for glazed and unglazed systems using dynamic collector testing (Eq. (2.45)) is planned for the future.

4.4 Selective Solar Absorbing Paints

The characterization of the optical properties of two types of pigments, namely, FeMnCuOₓ and black carbon (section 4.4.1 and 4.4.2, respectively) and thickness sensitive solar selective paints (section 4.4.3) produced from these pigments are discussed. The effective volumetric cross-sections defined in section 2 (Eq. 2.37) have been determined from spectral reflectance and transmittance measurements in the wavelength range 0.3 to 2.5 \( \mu m \). Data were obtained using pellets consisting of low volume concentrations of the FeMnCuOₓ \( (f=0.053-0.53 \%) \) and black carbon \( (f=0.076-0.31 \%) \) dispersed in KBr matrix. The sample preparation and optical measurements were described in section 3.

Cross-sectional SEM views of FeMnCuOₓ \( (f=0.21\%) \) and black carbon \( (f=0.21\%) \) as well as KBr pellets are shown in Fig. 4.18. The KBr matrix have large grains as shown in Fig. 4.18a. The small grain clusters appearing in Fig. 4.18b-c were identified from Energy Dispersion Spectrometer (EDS) analyses to be the agglomeration of the primary particles of the FeMnCuOₓ (Fig. 4.18b) and black carbon (Fig. 4.18b) pigments.

Fig. 4.18 Cross-sectional SEM pictures of (a) KBr, (b) FeMnCuOₓ and (c) black carbon pellets. The length scales are shown in the inset of the pictures together with the Electron High Tension EHT and microscope Working Distance WD.
It can be interpreted from these micrographs that the pigments are mainly located in the KBr grain boundaries or at defects. The cluster sizes vary considerably from about 0.05-0.5 µm for the FeMnCuO\textsubscript{x} and 0.02-2.5 µm for the black carbon and are much smaller than the grain size of the KBr. The primary average particle size as observed from the powders were found to be about 0.06 µm for the FeMnCuO\textsubscript{x} and about 0.02 µm for the black carbon. The size of the black carbon was comparable to what has been reported previously \textsuperscript{66,67}, but the primary particle size of the FeMnCuO\textsubscript{x} (≈ 0.06 µm) was much smaller than given by the manufacturer which reported an average size of about 0.4 µm \textsuperscript{66,67}.

### 4.4.1 FeMnCuO\textsubscript{x} Black Pigment

The measured total transmittance, T\textsubscript{t} and reflectance, R\textsubscript{t} of FeMnCuO\textsubscript{x} in KBr matrix as a function of wavelength for different concentrations of the pigment are shown in Fig. 4.19. The total transmittance decreases with increasing pigment volume fraction, f and is mainly collimated. The transmittance (Fig. 4.19a) decreases as the wavelength of the incident radiation is decreased. The total reflectance (Fig. 4.19b) increases at the shortest and longest wavelengths with a minimum value around 0.5 µm. The change of reflectance is insignificant with increasing pigment volume fraction in the 0.053-0.53 % range but significantly increases at the highest volume fraction of 1.07 %. This increase of reflectance at larger f is probably due to the change of refractive index of the pellet material since the reflectance from the back surface of the pellet can be negligible.

![Graphs showing total transmittance and reflectance of FeMnCuO\textsubscript{x} pigment in KBr matrix as a function of wavelength for different volume fractions of the pigment (f=0.053-1.07 percent).](image)

No significant difference was observed when comparing the ratio of diffuse to total reflectance between the different pellets in the volume fraction range 0.053-0.53 %. The ratio of the transmittances, however, increases slowly with increasing pigment concentration. Therefore, a change in the volume fraction of the pigment causes a change in transmittance but not in the reflectance. As a result the
absorptance (Eq. 2.31) and extinction (Eq. 2.33) increase with increasing amount of pigment in the range $f=0.053-0.53\%$.

From the total reflectance and transmittance measurements and the thickness of the pellet ($d=0.4$ mm), the effective absorption coefficient per unit length, $K$, of FeMnCuO$_x$ was calculated using Eq. (2.36). The absorption coefficient increases with increasing pigment volume fraction and decreasing wavelength. The effect of the KBr matrix on the absorption especially at short wavelengths was not negligible. Thus a net absorption coefficient of the pigments has been obtained by subtracting the absorption coefficient of the KBr pellet. A linear relation of the absorption coefficient as a function of the pigment volume fraction was observed. The total and collimated transmittance were very low at short wavelengths (see also Fig. 4.19). In order to apply Eq. (2.36) successfully, the transmittance at a given wavelength should not be too low. Thus for transmittance lower than 0.02 no reasonable values of the coefficients were observed and have been excluded.

Using Eq. (2.35), the effective extinction coefficient per unit length for the FeMnCuO$_x$ pigments as a function of wavelength for the sufficiently transparent samples has been determined. The contribution of KBr to the extinction of the pigment has been subtracted as was done for the absorption coefficient above. The effective scattering coefficient per unit length, $S$ is then numerically obtained by subtracting absorption from extinction. The scattering coefficient increases linearly with increasing pigment concentration but the correlation fails for the higher volume fractions. It can be assumed that the linear region is where single scattering occurs. This can be supported from different scattering experiments. Single scattering by small latex particles, mean size about 0.03 $\mu$m, has been reported to occur for volume fractions lower than 0.64 %. 34 Varadan et al has suggested that multiple scattering effects must be considered for volume concentrations larger than 1% especially for scattering size parameter, $\pi a/\lambda \leq 10$. 158 These results are then comparable to the upper pigment volume fraction limit presented in this work.

The scattering and absorption coefficients obtained in this work are for very low concentration ($f=0.053-0.53\%$) of the pigments, as compared with solar absorbing paints. Absorber paints made from FeMnCuO$_x$ or black carbon have volume concentration of $f=20\%$. 66,67 To compare the results of the low and high volume concentrations, the volumetric cross-sections defined in Eq. (2.37) can easily be used. Figure 4.20 shows volumetric absorption and scattering cross-sections of the FeMnCuO$_x$ pigment in the wavelength range 0.3 to 2.5 $\mu$m. The absorption cross-section of the FeMnCuO$_x$ decreases with increasing wavelength with absorption maximum and minimum obtained at 0.64 $\mu$m and 0.46 $\mu$m, respectively. The scattering cross-section of the pellets (Fig. 4.20) remains almost constant as a function of wavelength but decreases at short wavelengths.
4.4.2 Black Carbon Pigment

The total transmittance, $T_t$ and reflectance, $R_t$ of carbon pigment in KBr matrix as a function of wavelength for volume fractions ranging between 0.076 and 1.52 percent are shown in Fig. 4.21.

The transmittance increases with increasing wavelength but also with decreasing amount of carbon. The total transmitted intensity is dominated by the collimated beam as was also the case for the FeMnCuO$_x$ pigment.
pellet. The total reflectance which remained almost the same for low fractions increases when the amount of pigment is greater than \( f = 0.46\% \). The increased reflectance at larger \( f = 1.52\% \) is probably due to the change of refractive index of the pellet as the reflectance from the back surface of the pellet can be negligible. The collimated component of reflectance increases with increasing pigment filling factor particularly at longer wavelengths. Comparing the ratio of diffuse to total reflectance for different volume fractions results in a very small difference. But the ratio of diffuse to total transmittance increases slowly with increasing carbon concentration. The absorptance (Eq. 2.31) and extinction (Eq. 2.33) of the black carbon, extracted from the reflectance and transmittance measurements, increase with increasing pigment volume concentration.

The effective extinction, absorption and scattering coefficients for the black carbon were obtained using the same method as for the FeMnCuO\(_x\) pigment. The coefficients increase linearly with increasing pigment concentration between \( f = 0.076-0.31\% \) but the correlation fails for higher volume fractions. This linear region is where single scattering prevails. The volumetric cross-section for the black carbon pigments were calculated using the relation in Eq. (2.37). The absorption cross-section decreases with increasing wavelength and no absorption peak has been observed (Fig. 4.22). The scattering cross-section on the other hand remains fairly constant over the wavelength range 0.6-2.5 \( \mu m \) and below 0.6 \( \mu m \) it starts to decrease.

![Graph showing absorption and scattering cross-sections as a function of wavelength for black carbon (f=0.076-0.31 %) pigment.](image)

From Fig. 4.20 and Fig. 4.22 we observe that most of the extinction in the pellets comes from absorption rather than scattering. The scattering cross-section of FeMnCuO\(_x\) (0.12-0.8 \( \mu m^{-1} \)) is larger than the corresponding values for the black carbon (0.004-0.47 \( \mu m^{-1} \)). The absorption cross-section for FeMnCuO\(_x\) (0.61-9.3 \( \mu m^{-1} \)), on the other hand, drops faster than black carbon (1.72-7.01 \( \mu m^{-1} \)) with increasing wavelength and this may indicate a better selectivity of FeMnCuO\(_x\). The absorption to scattering ratio for both types of pigments decreases sharply with increasing wavelength from 0.3-0.75 \( \mu m \). Beyond this wavelength both ratios decrease less rapidly with the rate of FeMnCuO\(_x\) being faster than that of the black carbon. In short, the absorption and scattering cross-sections of the black pigments exhibited a linear function of the volume fraction at low concentrations. The pigment volume
concentrations for the linear region were between 0.053-0.53 % for FeMnCuO\textsubscript{x} and 0.076-0.31 % for the black carbon.

The volumetric cross-sections obtained above were compared to a previous two-flux calculations applied for paints \textsuperscript{66,67}. The absorption maximum and minimum of the FeMnCuO\textsubscript{x} obtained in this work at 0.64 \( \mu \text{m} \) and 0.46 \( \mu \text{m} \) (Fig. 4.20) were found to be at 0.60 \( \mu \text{m} \) and 0.48 \( \mu \text{m} \) for the two-flux calculation on paint \textsuperscript{67}. The scattering cross-section of the pellets (Fig. 4.20) and the two-flux calculation on paint \textsuperscript{67} remains almost constant as a function of wavelength. But it decreases at short wavelengths for the pellets in this work whereas the corresponding values of the paint at short wavelengths increases with decreasing wavelength. The magnitude of the absorption and scattering cross-sections of the FeMnCuO\textsubscript{x} pellet are, however, found to be higher than for the paint. The absorption cross-section for the black carbon determined from pellet (Fig. 4.22) is found to be similar to that of the two-flux calculation for black carbon paint \textsuperscript{66}. The scattering cross-section for the pellet and paint remains fairly constant for longer wavelengths. For shorter wavelengths the scattering cross-section for the pellet starts to decrease whereas for the paint \textsuperscript{66} it increases slightly. The absorption and scattering cross-sections of the pellet are higher compared to the corresponding values of the black carbon paint. The scattering cross-sections of the black pigments determined in this work were found to be different as compared to the two-flux calculation for the corresponding paints especially at the short wavelengths. On the other hand, the absorption cross-sections obtained in this work looked very similar to the corresponding values of the two-flux calculation for paints except that the values obtained here were found to be higher. The reason could be that we have determined the volumetric cross-section for single particle scattering. This condition is satisfied for the small pigment volume fractions used in this work \( f=0.053-0.53\% \) (FeMnCuO\textsubscript{x}) and \( f=0.076-0.31\% \) (black carbon) but the paints have larger concentration \( (f\approx 20\%) \) and are out of this region.

In addition to the above cross-sections, we have determined the real and imaginary part of the refractive index \( (n \text{ and } \kappa \text{ respectively}) \) of the phenoxy resin and the silicone film used as binders for the FeMnCuO\textsubscript{x} and black carbon paints, respectively. The optical constants were determined by measuring the reflectance and transmittance of the film and calculating \( n \text{ and } \kappa \) using a known method from reflectance and transmittance measurements \textsuperscript{159}. The method employs a direct inversion of the Fresnel relations by numerical calculations. A correct solution can be obtained by minimizing the calculated and measured quantities, \( |R_{\text{cal}}-R_{\text{meas}}| \text{ and } |T_{\text{cal}}-T_{\text{meas}}| \), using a Newton-Raphson iteration algorithm. The technique of calculation has been described in detail elsewhere. \textsuperscript{160} In the calculations, optical constants of the glass substrate were taken from the literature \textsuperscript{161}. Figure 4.23 shows calculated \( n \text{ and } \kappa \) as a function of wavelength of phenoxy resin and silicone films. The resin film has \( \kappa \) values that vary between 1x10\textsuperscript{-4} at lower wavelengths up to about 2.5x10\textsuperscript{-3} at longer wavelengths and the silicone film has only slightly lower \( \kappa \) values. The refractive index of both films is in the range of \( n=1.6\pm0.05 \). For comparison the refractive index, \( n \) of KBr obtained from Palik \textsuperscript{162} is shown in the figure and it has been found very similar to the \( n \) value of the films.
From Eqs. (2.9-2.11) we can see that particle cross-sections are functions of the refractive index of the embedding medium. Therefore, the single particle cross-sections of the black pigments in KBr matrix obtained in this paper can used for pigments dispersed in a binder which have similar $n$ value to that of the KBr.

4.4.3 Thickness Sensitive Solar Selective (TSSS) Paints

We have calculated the reflectance of thickness sensitive solar selective paints (TSSS) for FeMnCuO$_x$ in silicone and black carbon in phenoxy resin using four-flux model. The calculated reflectances were compared with measurements for different thicknesses and volume fractions of the paints. In the calculations, the cross-sections of the pigments in Fig. 4.20 and Fig. 4.22 and optical constants for the matrix in Fig. 4.23, were used as input parameters. Additional input factors that have been used in the four flux model were: particle volume fraction, $f$, and coating thickness, $d$, as well as the forward scattering ratio, $\zeta_c$, and average path-length parameter, $\xi$. The thickness, $d$ of the paint coating was taken as a free parameter since the thickness of the paints were given in g/m$^2$. Both $\zeta_c$ and $\xi$ depend on the particle size parameter, $x$ given in Eq. (2.7). Figure 4.24 shows top and cross-sectional SEM pictures of FeMnCuO$_x$ TSSS paint consisting of 2.04 g/m$^2$ coating thickness and 0.20 pigment volume fraction. From the depth profile of the coating, we can observe that the particles are uniformly distributed in the silicone matrix. The pigments in the paint, could be seen as particles with a size distribution similar to the previous investigation on the powder pigments. Using the single scattering albedo, $S/(K+S)$ and the primary size of the pigments ($a=0.06$ µm, FeMnCuO$_x$ and $a=0.02$ µm, black carbon), a $\zeta_c$ value of about 0.5 and $\xi=1.0$ have been chosen for both of the paints. However, the value of $\zeta_c$ and $\xi$ were not crucial to the calculated reflectance of the absorbing paints. It is worth to mention here that a backward average path-length parameter, which is not incorporated in the four flux model, differs from $\xi$ and exceeds 2.0 for absorbing particles.

The calculated reflectances of FeMnCuOₓ and black carbon TSSS paints on aluminum substrate for different thicknesses and \( f=0.20 \) are shown in Fig. 4.25a-b together with the experimental results, respectively.

The calculated reflectance spectra fit the experimental ones well especially for the thicker films. Similar results were also obtained for the FeMnCuOₓ paint with \( f=0.16, 0.18, 0.24 \) and 0.28. For the black carbon we had only one particle volume fraction, \( f=0.20 \). A discrepancy is obtained for thinner films of the black carbon paint at long wavelengths in which the interference patterns seen from the measurements were not reproduced in the calculations. The aluminum substrate has grooves and this
substrate surface roughness could affect the optical properties for the thinner films of the TSSS coating. In the four flux calculations, the surfaces were assumed to be smooth and the effect of surface roughness on absorptance or coating interference was not considered.

In the four flux calculation, the thickness, \( d \) in microns was taken as free parameter since the thickness of the paint coatings were given in mass per unit area (\( g/m^2 \)). The relation between these quantities is linearly fitted as is shown in Fig. 4.26.

![Fig. 4.26 Relation between thickness, \( d \) of the paint in (\( \mu m \)) and weight of the paint per unit surface area (\( g/m^2 \)) of the FeMnCuO\(_{x}\) TSSS paint. The thickness is determined from the fitting of the calculations to the experiments.](image)

Using SEM, the average thickness for the 2.04 \( g/m^2 \) thick FeMnCuO\(_{x}\) paint shown in Fig. 4.24 was analyzed and has been estimated to be of about \( d=1.1 \pm 0.1 \mu m \). Comparing this thickness with the fit in Fig. 4.26 for 2.04 \( g/m^2 \) weight of the paint which corresponds to \( d=1.2 \mu m \), the results were found to be similar within the estimated error of the measured result. The above results conclude that the single scattering and absorption cross-sections obtained from reflectance and transmittance measurements can be used to predict the optical properties of the TSSS paints.
5 CONCLUDING REMARKS

This thesis covers preparation, optical and non-optical investigations and durability tests of the absorbing surfaces used in solar thermal collectors. It also deals with coatings that can improve the quality of the absorbers.

Accelerated aging tests of Ni-Al$_2$O$_3$ absorbers at high temperatures were performed, and the level of oxidation of the Ni particles was quantified using IR spectroscopy. The Ni particles were also annealed without the supporting Al$_2$O$_3$ matrix, free standing on the substrate. A comparison between the free particles and particles embedded in the Al$_2$O$_3$ matrix showed that the matrix reduces the oxidation rate and hence provides long life time of the absorber. However, the Ni-Al$_2$O$_3$ surface degraded when it was exposed to humid air containing sulphur-dioxide or when water condensed on the surface. To protect the coating from degradation, the surface was coated with mechanically and chemically stable SnO$_2$ using the spray pyrolysis technique. The front surface reflection due to the SnO$_2$ coating was reduced by applying a silica antireflection layer using a dipping method in a colloidal silica sol. The silica layer was found to be thermally and chemically stable.

The solar absorptance of commercial Ni-Al$_2$O$_3$ and Ni-NiO$_x$ absorbers as a function of angle of incidence has been determined by measuring the angular spectral reflectance in the solar wavelength range. An enhanced interference pattern was observed in the measured reflectance of the Ni-Al$_2$O$_3$ but not for the Ni-NiO$_x$. This gives a higher solar absorptance for the Ni-Al$_2$O$_3$ at higher angles of incidence. From theoretical modeling, it was found that the double-layer structure of the Ni-Al$_2$O$_3$ causes strong interference and this could not be achieved from the graded index layer structure of the Ni-NiO$_x$ coating. The optical efficiency of the two absorbers with and without glazing has also been determined using an incident angle modifier expression. It was found that the optical efficiency at higher angles is dominated by the transmittance of the cover, irrespective of the type of absorber. The performance of the absorbers in solar collectors as a function of angle of incidence for glazed and unglazed systems is to be evaluated in a future project.

When the Ni-Al$_2$O$_3$ coating is produced, large quantities of chemicals are used in the two-step processes, i.e. anodization and pigmentation. An alternative method, which reduces the use of chemicals and the number of steps, is the integral coloration method. A Si-Al$_2$O$_3$ coating is obtained by anodizing a Si rich Al-Si alloy in a sulfuric acid solution. In order to get high solar absorptance, a thick coating (~10 µm) was required, but this gives high thermal emittance and does not fulfill the requirement of selective absorption. Theoretical calculations were performed searching for a feasible Si-Al$_2$O$_3$ solar selective coating as a function of film thickness, particle size and volume fraction. A solar absorptance of 0.70 and thermal emittance of about 0.27 can be achieved for a 1.0 µm thick film with a high volume fraction and optimum particle size. This indicate that a thickness range with high solar-absorptance and at the same time low thermal-emittance does not exist.

In order to study the performance of selective solar absorbing paints systematically, their optical properties must be known. From optical measurements, scattering and absorption cross-sections of FeMnCuO$_x$ and black carbon pigments were obtained. This was achieved by dispersing the pigments in KBr matrix and measuring the reflectance and transmittance of the pigmented samples in the solar wavelength range. The pigment volume fraction, was low, 0.053-0.53% for the FeMnCuO$_x$ and 0.076-0.31% for the black carbon. The cross-sections exhibit a linear relation to the volume fraction which shows that single scattering dominates. In addition, optical constants of resin and silicone films, used as binders for the selective paints, have been determined from optical measurements. From the cross-sections of the pigments and optical constants of the binders, the reflectance of FeMnCuO$_x$ and black carbon TSSS paints as a function of thickness and/or volume fraction have been calculated using a four-flux model. The calculations were compared with experiments and a good match was found, especially for the thicker layers.
6 ABSTRACTS OF APPENDED PAPERS

Paper I: Optical Properties of Silicon Pigmented Alumina Films

Plates of Al-Si alloy were anodized in a sulfuric acid solution. This treatment provides a Si-Al₂O₃ coating growing at a rate of 0.14 µm/min. The Si particles had sizes between 1 and 10 µm, as seen by scanning electron microscopy. Optical measurements showed a continuous decrease of reflectance with increasing film thickness. The reflectance of the Si-Al₂O₃ coated aluminum could be understood from a four flux radiative transfer theory. In order to explain our measurements it was found necessary to include a free carrier term in the dielectric permittivity of Si. The free carriers are probably due to doping with Al. Hence the relaxation time of the free carriers is determined by scattering from the charged Al impurities.

Paper II: A Feasibility Study of Integrally Colored Al-Si as Solar Selective Absorber

The solar selective properties of integrally colored Al-Si alloy (11.6 wt% Si) have been investigated. Optical measurements showed a continuous decrease of reflectance, i.e. an increase of absorptance, with increasing film thickness. A maximum solar absorption of 0.85 was achieved for Si-Al₂O₃ coatings thicker than 13 µm but such thick aluminum oxide coatings have very high thermal emittance.

The reflectance of the Si-Al₂O₃ coated aluminum could be understood from a four flux radiative transfer theory. Using this theory the optical performance of the coating as a solar absorber was modeled for different size and volume fractions of silicon particles and coating thicknesses. A solar absorptance of barely 0.90 can be achieved from a 10 µm thick coating of about 0.3 volume fraction of silicon. For thinner coatings (1 µm) the solar absorptance was only 0.70 for the same volume fraction and the thermal emittance can only reduced to about 0.27.

Paper III: Antireflection Treatment on Tin Oxide Coated Anodized Aluminum Selective Absorber Surface

Nickel-pigmented anodic aluminum oxide, Ni-Al₂O₃ was pyrolytically coated with tin oxide (SnO₂). The undesirable increase of reflectance in the solar spectrum due to the high refractive index of the SnO₂ film was compensated by an antireflection layer. The layer was applied by a simple dipping technique in a bath containing a commercial colloidal silica sol which forms a silica (SiO₂) layer. The infrared reflectance is nearly unaffected by the silica sol treatment process. Preliminary test results indicate that treated samples are resistant to temperatures as high as 300°C as well as to corrosion when immersed in an 8% sulfuric acid aqueous solution. In addition, the optical properties were unaffected by outdoor exposure for two months.

Paper IV: Study of oxidation kinetics for metal-dielectric films using IR optical measurements

The thermal oxidation of small metallic particles was studied using infrared spectroscopy. The oxidation was quantified by measuring the absorption of p-polarized light at 60° angle of incidence at the wavelengths around the longitudinal optical (LO) phonon mode of the thermally created oxide. The case presented in this report is nickel rods embedded in alumina (Ni-Al₂O₃) exposed to temperatures in the range between 300 and 500°C from 1 to 500 hours. The rate of oxidation was found to be of the same order of magnitude as previously reported for large particles and bulk nickel.

The degradation of selective solar absorbers through oxidation has been studied. We compare the oxidation kinetics of nickel particles of various sizes. Both free particles and particles embedded in an oxide matrix were studied. The oxidation kinetics of polycrystalline nickel nano-rods was determined by IR spectroscopy in the temperature range 300-500°C. The particles were oxidized when situated in the porous alumina matrix of an electrochemically deposited solar absorber coating. The oxidation kinetics was compared to that of free nano-particles at the same temperature and to µm-sized polycrystalline nickel particles, which were studied by thermogravimetry in a wider temperature range. It was found that the oxidation rate of nickel oxide was markedly lower for the particles in the matrix. Implications for the durability of selectively solar absorbing coatings are discussed.


The alumina matrix of an electrolytically deposited solar absorber coating was etched away leaving nickel nano-rods standing on the aluminum surface. The oxidation kinetics of the nickel nano-rods, with an approximate diameter of 30 nm and a height of approximately 300 nm, was determined by IR spectroscopy. The infrared absorption by the LO-phonon mode of nickel oxide was measured before and after exposure to pure oxygen at 260, 280, 300, 320 and 350°C for different times. The absorptance peak height was determined and used as a measure of the amount of the thermally created oxide. The five different isotherms showed a power law behavior with an exponent varying between 0.52 and 0.69. A fit to the homogeneous linear diffusion equation, derived for spherical geometry, gave parabolic rate constants, which are in agreement with data for larger nickel particles and bulk nickel. The deviations in the exponent from that of the parabolic law are discussed in terms of particle geometry and particle agglomeration. The apparent activation energy was determined by the use of a master plot technique to be 1.73 eV.


The optical characterization of solar absorbers for thermal solar collectors is usually performed by measuring spectral reflectance at near normal angle of incidence and calculating the solar absorptance from the measured reflectance. The solar absorptance is, however, a function of the angle of incidence of the light impinging on the absorber. In this report the total reflectance of two types of commercial solar selective absorbers; nickel-pigmented anodized aluminum and sputtered nickel/nickel-oxide coated aluminum are measured at angles of incidence from 5 to 80° in the wavelength range 300 to 2500 nm using an integrating sphere. From these measurements the angular integrated solar absorptance is determined. Experimental data are compared with theoretical calculations and it is found that optical thin film interference effects can explain the significant difference in solar absorptance at higher angles for the two types of absorbers.

Paper VIII: Angular Solar Absorptance and Incident Angle Modifier of Selective Absorbers for Solar Thermal Collectors

The solar absorptance of absorbers for thermal solar collectors is usually characterized at near normal angle of incidence. The solar absorptance is however a function of the angle of the incident light on the absorbers. In this paper the angular solar absorptance of commercial nickel pigmented aluminum oxide
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and sputtered nickel/nickel oxide solar selective absorbers are reported. The solar absorptance was calculated from experimental total reflectance spectra in the wavelength range 300 to 2500 nm for angles of incidence between 5 and 80°. It was found that the solar absorptance at higher angles of incidence is lower for the sputtered nickel/nickel oxide than for the nickel pigmented aluminum oxide coating. This could be understood from theoretical calculations based on microstructure models of the two types of coatings. The nickel pigmented aluminum oxide with a double-layer structure of its coating has an enhanced higher angle solar absorptance due to thin film interference which cannot be achieved from a graded-index thin film coating as the case for the sputtered nickel/nickel oxide absorber. When the absorbers were covered by glass, as is common for most solar collectors, a negligible difference in optical performance at the higher angles of incidence have been obtained. These results were consistent with a theoretical calculations by use of an incident angle modifier model.


The aim of this work is the characterization of the optical properties of two types of pigments, namely, FeMnCuO$_x$ and black carbon. The effective scattering and absorption coefficients per unit length of these pigments have been determined from spectral reflectance and transmittance measurements in the wavelength range 300 to 2500 nm. The data were obtained using pellets consisting of low concentrations of FeMnCuO$_x$ or black carbon pigments dispersed in KBr matrix. The pigment volume concentrations used for evaluating the coefficients were between 0.053-0.53 % for FeMnCuO$_x$ and 0.076-0.31 % for the black carbon. These ranges were found to exhibit the linear dependence of the coefficients as a function of volume fraction, given by single scattering theory.


The performance of black pigments used in thickness sensitive solar selective absorbing paints for solar thermal collectors depend on the optical properties of the pigments. Knowledge of the intrinsic optical properties of most paint pigments is very limited. Pellets made from either FeMnCuO$_x$ or black carbon dispersed in KBr matrix have been used to determine the effective optical coefficients of the pigments. Scattering and absorption cross-sections were derived from reflectance and transmittance measurements at near normal angle of incidence in the wavelength range 0.3 to 2.5 µm. Volume concentrations of the pigments that gave linear dependencies for the coefficients were found to be between 0.053 to 0.53% (FeMnCuO$_x$) and 0.076 to 0.31% (black carbon). Subsequently, a four flux model has been used for calculation of reflectance for thickness sensitive spectrally selective paints. The paints were obtained from the FeMnCuO$_x$ and black carbon pigments embedded in silicone and phenoxy resin, respectively. We have used the experimentally determined scattering and absorption cross-sections of the pigments as input to the four flux theory and the calculations have been performed for different thicknesses and/or pigment volume fraction of the paints. The calculated reflectance spectra were compared with experiments and the results for thick films fit well.
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Uppsala, 2000

Tuquabo Tesfamichael
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