Spectrally selective solar energy materials, properties of reactively sputtered Ni-C films
Sikkens, Marten

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1981

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
CHAPTER I

GENERAL INTRODUCTION TO SPECTRALLY SELECTIVE MATERIALS FOR USE IN PHOTOTHERMAL SOLAR ENERGY CONVERSION.

1.1. Introduction

Renewed interest in solar energy has developed in the last decade as a result of the increasing costs of energy from conventional resources and the technical and social problems associated with nuclear energy application. Different processes exist to convert the solar radiation into a usable energy form, i.e. photovoltaic, photothermal, photochemical and photosynthetic processes. Nowadays, conversion into electricity (photovoltaic conversion) and into heat (photothermal conversion) are the most important methods.

We will restrict ourselves to photothermal conversion processes. The extracted thermal energy can be used for different purposes, which are closely connected with the temperature level at which the heat is extracted. This is summarized in table 1.1 where we have distinguished between five temperature ranges. For each temperature range the main application and collector type used, are indicated (Duffie and Beckman 1974, Meinel and Meinel 1976).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Application</th>
<th>Collector type</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-40</td>
<td>swimming-pool heating</td>
<td>black flat plate without cover</td>
</tr>
<tr>
<td>40-80</td>
<td>space heating, water heating</td>
<td>black flat plate with one or two covers; flat plate with one cover and selective surface</td>
</tr>
</tbody>
</table>
80-150 cooling, industrial heat evaporated tubular collector with selective surface

150-300 industrial heat evaporated tubular collector with cylindrical concentrator (concentration ratio 5-50)

above 300 industrial heat, electricity generation various types with concentrators (concentration ratio 50-1000)

To discuss the efficiency of the photothermal conversion process and its dependence on the temperature level, we consider the most elementary form of a solar energy collector as is illustrated in Fig. 1.1. The instantaneous heat current density $q_u$ which is delivered by the collector can be expressed as (Duffie and Beckman 1974):

$$ q_u = \alpha_a \tau_c E - \sigma (T_a^4 - T_c^4) (\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_c} - 1)^{-1} - h(T_a - T_c), $$

(1.1)

where $\alpha_a$ = total solar absorptance of the absorber,

$\varepsilon_a, \varepsilon_c$ = total thermal emittance of the absorber and cover, respectively,

$\tau_c$ = total solar transmittance of the cover,

Fig. 1.1. Elementary photothermal solar energy collector.
\( \sigma = \text{Stefan-Boltzmann constant} \)

\( T_a, T_c = \text{absolute temperatures of absorber and cover, respectively} \)

\( E = \text{solar irradiance} \)

\( h = \text{heat transfer coefficient for conduction and convection} \).

The first term on the right hand side of eq. (1.1.) represents the absorbed heat current density, the second term represents the thermal radiant heat loss towards the cover, assuming the cover to be opaque for thermal radiation. The last term represents the sum of the conduction and convection heat losses towards the cover. Conduction loss through the insulation has been neglected.

The collector instantaneous efficiency \( \eta \) is generally defined as

\[
\eta = \frac{q_u}{E}. \quad (1.2)
\]

In fig. 1.2., \( \eta \) is plotted versus \( T_a \) for a simple flat-plate collector with a perfect black receiver \( (\alpha = \varepsilon_a = 1) \), assuming normal incidence with \( E = 1 \, \text{kW/m}^2 \), which is about the maximum value obtained at the earth's surface, and \( h = 3.0 \, \text{W/m}^2\text{K} \), which

![Graph showing collector efficiency as a function of the absorber temperature with and without conduction and convection losses.](image)

**Fig. 1.2.** Collector efficiency as a function of the absorber temperature \( T_a \) with and without conduction and convection losses.
is typical for a flat-plate collector at a 45° tilt. The cover material is taken to be glass, with \( \tau_c = 0.85 \) and \( \varepsilon_c = 0.84 \) (Hsieh and Su 1979). For simplicity, \( T_c \) is taken to be constant at 20°C.

From fig. 1.2 it follows that below 60°C only, such a collector has a reasonable efficiency. A slight improvement can be obtained by reducing the conduction and convection losses (for example by evacuating the collector), as is illustrated by the dashed curve in fig. 1.2 where we have taken \( h = 0 \).

To obtain a more significant improvement, \( E \) can be increased by a concentrating optical system. However, high concentration ratios can only be used in areas with a relatively low diffuse component of the solar irradiation and, furthermore, need some form of sun-tracking.

Another method to improve the collector performance is to decrease the thermal radiant heat losses. From eqs. (1.1) and (1.2) it follows that this can be achieved in two ways:

1. reducing \( \varepsilon_a \), while keeping \( \alpha_a = 1 \),
2. reducing \( \varepsilon_c \), while keeping \( \tau_c = 1 \).

Since the spectral distributions of the solar irradiance \( E_\lambda \) and the blackbody radiant exitance \( M_{b\lambda}(T) \) have their main contributions in different wavelength ranges as long as \( T \) is not too high, these demands can be met by requiring that the spectral reflectance \( \rho_\lambda = 0 \) at wavelengths shorter than a cut-off wavelength \( \lambda_c \) and \( \rho_\lambda = 1 \) at longer wavelengths. This is illustrated in fig. 1.3.

In the case of the absorber the total absorptance \( \alpha_{as} \) becomes

\[
\alpha_{as} = \int_{0}^{\infty} \alpha_\lambda E_\lambda d\lambda / \int_{0}^{\infty} E_\lambda d\lambda, 
\]

(1.3)

where \( E_\lambda \) is the spectral solar irradiance. Here, the subscript \( s \) designates the integration over the solar spectrum. The total thermal emittance \( \varepsilon_a(T) \) follows from Kirchhoff's law \( \varepsilon_\lambda = \alpha_\lambda \) (see chapter 2)

\[
\varepsilon_a(T) = \int_{0}^{\infty} \alpha_\lambda M_{b\lambda}(T)d\lambda / \int_{0}^{\infty} M_{b\lambda}(T)d\lambda, 
\]

(1.4)

where \( M_{b\lambda}(T) \) is the blackbody spectral radiant exitance at
temperature T as given by Planck's law.

For an opaque absorber \( a_{\lambda} = 1 - \rho_{\lambda} \) and therefore \( a_{\text{as}} = 1 \) and \( e_{a}(T) = 0 \). Surfaces with these properties are called spectrally selective absorbing surfaces or briefly selective surfaces.

In the case of the transparent cover, apart from the required \( \rho_{\lambda} \), it is also required that \( r_{\lambda} = 1 \) for \( \lambda = \lambda_{c} \). Since \( a_{\lambda} + \rho_{\lambda} + r_{\lambda} = 1 \) (see chapter 2), this additional requirement is identical with \( a_{\lambda} = 0 \) for all wavelengths of interest. The total solar transmittance of the cover is given by

\[
\tau_{cs} = \int_{\lambda}^{\infty} r_{\lambda} E^\lambda d\lambda / \int_{0}^{\infty} E^\lambda d\lambda,
\]

(1.5)

while the total thermal emittance is identical to eq. (1.4).
A cover with $\tau_{cs}=1$ and $\varepsilon_c(T)=0$ is called a spectrally selective transmitting window or briefly selective window.

The optimum cut-off wavelength $\lambda_c$ will be in the overlap region between both energy distributions. Since the maximum of the radiance is a function of temperature, $\lambda_c$ will depend on the operating temperature. Usually, $\lambda_c$ is chosen to be between 1.5 and 2.0 µm, in which case the fractions of the solar irradiance at sea level above these wavelengths are 0.07 and 0.01 respectively (Drummeter and Hass, 1964).

To illustrate the improvement in collector performance obtained by making use of selective surfaces, $\eta$ is depicted in Fig. 1.4 for three sets of values of $a$ and $\varepsilon_a$ that are typical for black paint and two different selective surfaces, respectively.

We have taken $h=0$, while the other parameters are the same as before. As can be observed in Fig. 1.4, the emittance value is dominant at high operating temperatures. However, at low temperatures, $\eta$ is mainly determined by the solar absorptance. For practical selective surfaces, a low $\varepsilon_a$ is generally coupled

![Fig. 1.4. Collector efficiency $\eta$ as a function of the absorber temperature $T_a$ for different selective surfaces. Conduction and convection losses are assumed to be zero.](image)

- 6 -
to a somewhat lower $\alpha_\text{as}$ as a result of the cut-off behaviour. Therefore, the optimum selective surface for a particular application will depend on the operating temperature of the collector.

I.5. Survey of spectrally selective materials

The importance of spectral selectivity for the photothermal conversion of solar energy has been recognized after the work of Tabor (1955) and Gier and Dunkle (1955). Since that time numerous processes for obtaining selective surfaces have been developed. Reviews have been published by Meinel and Meinel (1976), Duffie and Beckman (1974), Peterson and Ramsey (1975) and Seraphin (1979).

Nearly all known selective surfaces consist of an absorbing coating on a metal substrate, the coating providing the high solar absorptance and the metal providing the low thermal emittance. The first selective surfaces were mainly metal oxide and sulphide layers coated onto various metals such as black nickel and black chrome (Tabor 1955 and 1967, Tabor et al. 1964), copper oxide (Edwards et al. 1962, Hottel and Unger 1959, Mattox and Sowell 1974, Christie 1970), iron oxide (Christie 1970, Hottel and Unger 1959, Mar et al. 1976) and cobalt oxide (Kokoropoulos 1959 and 1964, Gillette 1960). Black nickel (Ni/ZnS), black chrome (Cr/Cr$_2$O$_3$) and cobalt oxide (Co$_3$O$_4$) are produced by electrodeposition, copper oxide (CuO) and iron oxide (Fe$_3$O$_4$) by chemical oxidation.

These surfaces have solar absorptances of about 0.90 and thermal emittances at 100°C of about 0.1-0.3. Their long-term thermal stability confines their application to operating temperatures in the range 150-200°C. Possible exceptions are black chrome (Harding 1975, Sowell and Mattox 1978, Zajac and Ignatiev 1980) and cobalt oxide (van der Leij 1979) which seem to remain stable well above 200°C.

Recently, this class of selective surfaces has been extended with some new materials. Transition-metal carbides and nitrides, produced by reactive sputtering, are reported to be stable up to 600°C in vacuum and exhibit a very low emittance of 0.02-0.06 (Harding 1976, Blickensderfer et al. 1977). Also, a very good