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Carl M. Lampert
(Ph.D. thesis)

July 1979

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CHEMICAL, STRUCTURAL AND OPTICAL CHARACTERIZATION OF A BLACK CHROME SOLAR SELECTIVE ABSORBER

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CHEMICAL, STRUCTURAL AND OPTICAL CHARACTERIZATION
OF A BLACK CHROME SOLAR SELECTIVE ABSORBER

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ABSTRACT

The very popular black chrome coating, Harshaw Chemical's "Chromonyx" was analyzed in terms of materials science to determine the nature of its microstructure and relationship to wavelength selectivity. This coating serves as an efficient solar thermal conversion coating for both concentrating and flat plate solar collectors.

General properties of solar energy and selective absorbers were discussed to give a firm footing for analysis. Also, the properties and degradation modes were revealed for samples heat treated at high temperatures for short times.

Several electrodeposited black chrome-substrate combinations were investigated including the favored black chrome with a dull nickel underlayer. It was found that black chrome coating thickness and surface roughness greatly influence spectral hemispherical reflectance. To a minor extent underlayer material also altered infrared reflectance; nickel, copper and steel were evaluated.
Principally, energy dispersive X-ray analysis as well as scanning and transmission electron microscopy were employed for thin film analysis. A wide range of experiments were performed to correlate both the as-plated and annealed microstructure to reflectance measurements. Along with supplemental information on Auger and XPS depth profiling from other investigators, it was possible to develop a physical metallurgical model for the wavelength selectivity properties of this coating.

The microstructure of the as prepared and annealed coating up to $300^\circ C$ consists of agglomerated 0.05 - 0.3 micron size particles with chiefly an oxide surface. Suspended within these oxide particles are $140\,\text{Å}$ (average size) metallic chromium grains. The volume ratio of chromium to oxide increases with depth, finally forming a metal rich region at the substrate interface.

For modeling purposes three general regions are developed, namely: (1) a thin and chiefly amorphous or very fine crystalline $\text{Cr}_2\text{O}_3$ oxide layer; (2) an intermediate layer comprised of ultra fine chromium suspended in a similar oxide and (3) an interfacial layer consisting of a metal-like layer.

Effective medium theories were discussed briefly to describe mathematically the coating's solar selectivity, although such theories fall short when attempting a consistent description of this physically complicated absorber.
Microstructural analysis was performed on 1 - 100 hour annealed specimens over the temperature range of 300 - 600°C, in atmospheres of air and medium vacuum. Black chrome solar selectivity degrades by the nucleation and growth of Cr₂O₃ particles. These particles alter the absorptive properties of the coating by depleting and redistributing metallic chromium. The coating also emanates CO and CO₂ which may break up the coating, enhancing oxidation. At high temperatures above 500°C this coating appears densified and totally oxidized. It is suggested that this black chrome degrades by a simple diffusion controlled oxidation mechanism.
I. INTRODUCTION

A. Historical Background.

In an age where fossil fuels are being depleted, their costs escalated, and often unavailable, due to politics, it is imperative that we look for new sources of supply for our energy hungry world. Advanced technology, such as nuclear fusion and the fast breeder reactors, offer an abundant energy source in theory, but any practical application is plagued with numerous and critical engineering difficulties. At one time, nuclear fission reactors were thought to be our ultimate energy source. Currently, though, these reactors have not only been questioned as to safety, but they seem to present insurmountable problems in the fields of radioactive waste disposal and fuel reclamation.

Along with the disenchantment with nuclear power and depletion of fossil fuels there is a growing movement towards more fundamental and renewable energy sources. The biggest economic challenge is to find and apply the least expensive form of energy to specific end uses.

One of the major sources of energy is that of the sun. This is the very source of energy which promotes life on earth. Ironically, the sun is a large nuclear fusion reactor which has been thoughtfully placed 302,000 kilometers (93,000,000 miles) away from earth. Use of solar radiation along with other natural energies such as wind, geothermal and tidal, offer quite a significant solution and easement of our energy dilemma. However, it must be noted that these forms of energy, although they have the potential to alleviate many of the
current shortages, work well only when applied where they are most suitable. No single or combined energy form will solve all the problems, especially those of political and economic origin.

To overcome our pronounced energy dependence upon fossil fuels, not only do we need to utilize alternative sources of energy in an efficient and economic manner, but public education and widespread conservation as well as energy efficient engineering and architectural designs should also be promoted.

Solar energy commonly can be converted into three forms: thermal, chemical and electrical. Solar thermal and chemical energy are part of the earth's natural processes; thermal radiation being absorbed by all matter and chemical energy produced principally by plants via photosynthesis. Well engineered methods of harnessing the sun's energy include the use of highly absorptive coatings for solar thermal energy conversion, production of hydrogen and alcohol by thermo-chemical reactions; other techniques range from obtaining electricity by means of photovoltaic conversion to passive heating and cooling of buildings.

This study is concerned with the aspect of photothermal conversion exclusively. The most immediate and practical application of solar energy with existing technology appears to be that of heating air, fluids and producing steam for a multitude of domestic, commercial, and industrial purposes. Inevitably, solar energy will be used for the generation of electricity and fuels, possibly by thermal means. To create thermal energy from radiation, a solar collector must be
employed. One of the key components of the collector is the black absorbing material, usually in the form of a coating. The field of thermal absorber coatings offers the materials scientist and related professions a unique opportunity to understand, develop, and to improve materials which offer the desired energy absorptive properties.

B. Nature of the Study.

There are numerous candidates for solar collector coatings, but only a few coatings have been utilized commercially. All of these coatings fall into one of two major classifications: selective and non-selective types. Selective coatings are more efficient and offer lower heat losses and higher operating temperatures than do non-selective absorbers. Basically, the difference between these two categories is that non-selective absorbers are excellent radiators of infrared energy while the selective coatings are poor radiators.

Selectivity is produced by optical properties which vary greatly from one spectral region to another. A solar selective absorber efficiently captures the sun's radiation in the high intensity visible and near infrared spectral regions, while exhibiting poor infrared emitting properties. These are desirable attributes for a collector surface. Accordingly, a selective surface will absorb and retain a high amount of solar energy, while a non-selective surface will lose most of its absorbed energy by radiation. The theory of selectivity will be addressed in detail in a subsequent section.

One of the most promising inexpensive selective absorber coatings is black chrome. Currently, it is a commonly used selective absorber
for commercial solar collectors. This is interesting, considering that only recently has it been tested and its properties evaluated in detail. Black chrome surfaces can be prepared from carbonic acid, urea, acetic acid and fluosilicic acid electroplating baths. Of the processes commercially available, the most popular ones are "Chromonyx" by Harshaw Chemical Company, and "Econo-Chrome BK" produced by DuPont Company. Originally, these coatings were developed for use as decorative finishes and not as solar absorbers. Both coatings are resistant to moisture and appear to be environmentally and operationally stable below 350°C. In this study, the Harshaw coating was investigated mainly due to its slightly superior optical properties and the interest exhibited in it by previous investigators. However, this study may apply to other types of black chrome.

Little is known about the mechanism of selectivity for black chrome and other important properties such as short term high temperature stability. In most cases, a coating like this one will exhibit high solar absorptivity due to basic absorption in the coating and low infrared emittance determined by an underlying metallic substrate. The first step in understanding the mechanism of solar energy collection and its stability to thermal treatments is to investigate the relationship between the chemical, microstructural and optical properties under various conditions. The following study presents a characterization of "Chromonyx" black chrome in terms of material science.
II. THEORETICAL BACKGROUND

A. Solar Collectors.

To properly understand the importance and usage of selective absorbers such as black chrome, it is necessary to discuss the theory of solar collectors. Basically, a solar collector is designed to trap solar radiation and convert it into heat which is transferred easily to a medium such as water. Photothermal conversion of solar energy can be used to supply not only residential heating needs but many industrial and commercial process heat and steam needs, provided adequate temperatures and conversion efficiencies can be obtained.

In many cases, it is the performance and cost effectiveness of the solar collector at a particular temperature level which decides whether a solar energy system will be favored over that of conventional sources of energy. The suitability of a specific collector design depends upon the end use temperature required. The following temperature ranges are commonly encountered:

1. $T < 100^\circ C$ Water and space heating.
2. $100^\circ C < T < 350^\circ C$ Process steam, refrigeration, alcohol production.
3. $350^\circ C < T < 600^\circ C$ High quality steam, mechanical energy prod., catalyzed hydrogen production.
4. $T > 600^\circ C$ High temperature processes, hydrogen production.

The performance of the collector at any one of these ranges results directly from the proper design and specification of the
materials of which it is composed. For example, if we are to use black chrome as an absorber material, which degrades above 350°C, only ranges 1 and 2 can be of interest in this study.

The stagnation temperature of a solar collector is a very important consideration, when choosing a temperature range over which a collector design and coating combination can operate safely. A collector stagnates when fluid flow ceases or is drained off by malfunction or user error. Some collectors are allowed to stagnate during construction, before they are even operational. Residential solar collectors require long term resistance to stagnation degradation, while commercial and industrial installations probably need a smaller margin, due to on-site maintenance personnel. The exact stagnation temperature a collector can realize depends on many site and design specific considerations. Approximate temperatures are tabulated\textsuperscript{14,15} in Table I.

The fundamental principles of photothermal conversion of solar energy are shown graphically in Figure 1. The various losses associated with typical collectors are demonstrated in this figure. Initially, part of the incoming radiation is lost by reflection at various interfaces, after photon absorption takes place in the absorber and surrounding material. Radiation, convection, and conduction are the important heat loss modes. Both convection and conduction are linear functions of temperature, but radiation is proportional to the fourth power of the temperature, according to the Stefan-Boltzmann law:
Table I. Stagnation Temperature Range for Various Collector and Absorber Types\textsuperscript{14,15}

<table>
<thead>
<tr>
<th>Collector Type</th>
<th>Non-Selective, °C</th>
<th>Selective Absorber, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat, unglazed</td>
<td>66 - 92</td>
<td>92</td>
</tr>
<tr>
<td>Flat, single cover</td>
<td></td>
<td>121 - 176</td>
</tr>
<tr>
<td>Flat, double cover</td>
<td>92 - 142</td>
<td>176 - 204</td>
</tr>
<tr>
<td>Evacuated Tube</td>
<td>92 - 142</td>
<td>176 - 204</td>
</tr>
<tr>
<td>Single Axis Concentrating</td>
<td>92 - 142</td>
<td>176 - 204</td>
</tr>
<tr>
<td>Two Axis Concentrating,</td>
<td>92 - 142</td>
<td>176 - 204</td>
</tr>
<tr>
<td>and Central Tower</td>
<td>92 - 142</td>
<td>176 - 204</td>
</tr>
<tr>
<td>*Very few selective absorbers can withstand this range. In practice, non-selective absorbers are used for this application.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1  Idealized model of photothermal energy conversion with associated losses. For high temperatures, radiative losses dominate the other modes.
\[ E = \int_{0}^{\infty} e(w)E_w \, dw = e\sigma T^4, \]  

(2.1)

where \( E \) is hemispherical energy emitted

- \( e \) = total emittance
- \( e(w) \) = emittance of the surface;
- \( E_w \) = spectral emitted energy
- \( w \) = wavelength;
- \( T \) = Temperature \(^\circ\)K;
- \( \sigma = 5.6697 \times 10^{-8} \) W/m\(^2\) K\(^4\).

Below is a simplified heat balance\(^16\) for a solar collector with a certain amount of useful energy being extracted \( E_E \):

\[ E_E = (t_a)eA_cI - A_a(L_r(T - T_a^4) + L_{cc}T) \]  

(2.2)

where \((t_a)e\) is the effective transmission - absorption coefficient;

- \( A_c \) = intercepted area of collector;
- \( A_a \) = area of absorber;
- \( I \) = incident solar radiation;
- \( L_r \) = radiative loss coefficient;
- \( L_{cc} \) = net convective and conductive loss coefficient;
- \( T \) = net temperature above ambient;
- \( T_a \) = ambient temperature.

For high temperatures, radiation becomes the dominant mode compared to conduction and convection losses; therefore, as an approximation:
\[ E_E = (ta)_e A_c I - A_a L_r T_4^4 \quad (2.3) \]

Conversion efficiency can be defined as

\[ \eta_c = \frac{\text{energy extracted}}{\text{energy input}} = \frac{E_E}{A_c I} \quad (2.4) \]

And if we use the concept of concentration \( C = \frac{A_c}{A_a} \),

then \( \eta_c = (ta)_e - \frac{L_r T_4^4}{C I} \quad (2.6) \)

If \( \eta_c \) is to be maximized, then \( L_r \) must be reduced while holding \( C \) and \( (ta)_e \) constant. Also, \( (ta)_e \) should be close to unity. Now from first principles, one would find it difficult, if not impossible, to have a low \( L_r \) or \( e \), emittance, while also having a high absorptance, \( a \), due to the fact that \( a_w = e_w \). (A detailed development of \( a \) and \( e \) along with related quantities will be given in the following section). Now if the spectral distribution of energy is examined for the solar spectrum (roughly, a 5600°C black body), and the absorber radiation spectrum (possibly 100-300°C) as shown in Figure 2, one will note a separation between the distributions. It is that shift between the distributions which allows material to exist which has high solar absorption while maintaining low infrared emittance; hence, the name "selective absorber" evolved. The transition or cut-off wavelength is defined as the wavelength at which both energy spectra intersect, as in Figure 2, where this would be 2.5
Figure 2 Wavelength relationship between an ideal selective absorber in terms of reflectivity, compared to that of the air mass 2 and concentrated solar energy flux, and blackbody spectra, (100°C, 300°C).
microns. Similarly, the selective absorber cut-off wavelength is defined at the 0.5 reflectance value. The dependence between cut-off wavelength and concentration has been developed in Figure 3. By use of selective surfaces, some definite advantages in collection efficiency can be realized. Both a flat plate and concentrating collector are evaluated by computer codes, shown in Figs. 4 and 5, for selective and non-selective absorbers.

Conversion efficiency can be calculated in terms of collector temperature and concentration; this result is shown graphically in Figure 6. If the Carnot efficiency is also considered, as in Figs. 7 and 8, a measure of mechanical work output can be made. Of course, this need not be considered if the end use is only heat.

The Carnot efficiency is defined as the ratio of the work output to the input heat of a particular thermodynamic cycle. The Carnot efficiency is defined mathematically as follows:

$$\eta_{\text{Carnot}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{T_H - T_C}{T_H}$$

where

- $Q_H$ = Input heat;
- $T_H$ = Input temperature;
- $Q_C$ = exhaust heat;
- $T_C$ = exhaust temperature;
- $W$ = output work.

A Carnot cycle utilizing solar thermal energy is shown schematically in Figure 7.
Figure 3 Variation of cut off wavelength shown in terms of concentration factor and absorber operating temperatures. Cut off wavelength increases with concentration due to the amplitude increase in the concentrated solar spectrum. Higher operating temperatures lower the cut off wavelength because the infrared radiation spectrum shifts to shorter wavelengths.
Figure 4 The effect of a selective absorber compared to a non-selective type on collection efficiency for a flat plate collector, operating at 93°C (200°F) with ambient temperature of 21°C (70°F). The non-selective surface has $a = 0.92$ and $e = 0.92$ (93°C), and the selective surface has $a = 0.9$ and $e = 0.1$ (73°C), after Winegarner.17
Figure 5 The effect of using a selective absorber compared to a non-selective one for a concentrating parabolic collector operating at 315°C (600°F) with ambient temperature of 21°C (70°F). Notation (R) net collection efficiency; (ΔR) change in collection efficiency over that of a standard black absorber, after Winegarner.17
Figure 6 Collection efficiency in terms of temperature and solar concentration ratio. Curves are shown for a non-selective surface \((a = e = 1.0)\) and a selective absorber \((a = 0.9, e = 0.1)\). Solar flux is 1 kW/m\(^2\).
Figure 7 Diagram of solar Carnot cycle driven between a selective absorber and black radiator.
Figure 8 Conversion efficiency for combined collector and Carnot conversion for a solar collector. Curves are shown for a non-selective surface \( (\alpha = e = 1.0) \) and a selective absorber \( (\alpha = 0.9, e = 0.1) \). Solar flux is 1 kW/m².
It should be noted that in every case the selective surface shows a gain in efficiency. The greatest efficiency gain due to adding a selective surface is realized for temperatures less than 700°C and for concentrations below 100 and optimally at 10. On the other hand, for lower concentrations, the selective absorber is invaluable as shown in Figs. 4 and 5 for a black chrome type surface.

B. Absorptance, Emittance and Reflectance.

Before the concept of solar selectivity can be fully appreciated definitions of absorptance, emittance, reflectance have to be explained. It is these properties which are to be related to the microstructural properties of black chrome in subsequent sections.

The property of solar absorptance \((a_{w}(q,p))\) dictates the amount of energy absorbed by the surface. Spectral solar absorptance is the fraction of incident solar energy at a given wavelength from the direction \((q,p)\) that is absorbed by the surface, as \(q\) is the cone angle measured from the surface normal and \(p\) is the circumferential angle. The measurement of solar absorptance on the other hand is not as simple as the concept may appear.

Absorptance can be evaluated in two distinct ways. First, by directional absorptance (shown in Figure 9a) which might correspond to the effect of a direct beam of solar radiation on the absorber. Second, hemispherical absorptance (shown in Figure 9b) which could correspond in a similar way to diffuse radiation.

The directional solar absorptance is defined as:
Figure 9 Depiction of two types of solar absorptance measurements 
(a) directional absorptance (b) hemispherical absorptance.
\[ a(q,p) = \frac{\int_0^\infty a_w(q,p) I_w(q,p) \, dw}{\int_0^\infty I_w(q,p) \, dw} \]  \hspace{1cm} (2.7a)

where

\[ a_w(q,p) = \frac{I_a(q,p,w)}{I_w(q,p)} \text{ and} \hspace{1cm} (2.7b)\]

\[ a_w(q,p) = \text{directional spectral absorptance of wavelength } w; \]

\[ I_a(q,p,w) = \text{absorbed radiation at spatial location } (q,p) \text{ and wavelength } w; \]

\[ I_w(q,p) = \text{specific incident solar radiation at wavelength } w; \]

\[ dw = \text{is wavelength interval.} \]

Hemispherical solar absorptance is the fraction of solar energy absorbed from all directions over a hemispherical area, for all wavelengths. A schematic illustrating this concept is shown in Fig. 9b. This type of absorptance can be expressed as follows:

\[ a_H = \frac{\int_0^\infty \int_0^{\pi/2} a_w(q,p) I_w(q,p) \cos q \, ds \, dw}{\int_0^\infty \int_0^{\pi/2} I_w(q,p) \cos q \, ds \, dw} \]  \hspace{1cm} (2.8)

where the notation \( \oint \) signifies integration over a hemisphere,

\[ ds = \sin (q)dq \, dp, \text{ and} \]

\[ \int_0^\alpha ds = \int_0^{\pi/2} \int_0^{\pi/2} \sin (q)dq \, dp \]  \hspace{1cm} (2.9)
Most often, directional absorptance is derived from near normal reflectance measurements. Techniques for this will be outlined subsequently.

Emittance \( e(q,p,t) \) is defined as the ratio of the emitted energy intensity from a surface in the direction \((q,p)\) to a corresponding blackbody intensity. Both the surface and blackbody are isothermal. It must be emphasized that spectral emittance is a direct function of temperature. For selective absorbers, low infrared emittance and high solar or visible emittance are desirable properties. A simple relationship couples emittance to absorptance at a fixed temperature \((T)\),

\[
e_w(q,p,T) = a_w(q,p,T) .
\]  

(2.10)

This equation is strictly correct for blackbody radiation, but in general, both components of radiation must be treated separately if they are not equal. For a perfectly diffuse surface, \( e_w = a_w \) for all angles. Furthermore, if no wavelength dependence is noted, then the surface is termed "grey".

Analogous to absorptance, expressions for specific emittance measurements can be noted. Figure 10a represents the case for solar directional emittance. Solar directional emittance is given by:

\[
e(q,p,T) = \frac{\int_0^\infty e_w(q,p,T) B_w(T) \, dw}{\int_0^\infty B_w(T) \, dw} ,
\]  

(2.11a)
Figure 10 Schematic of solar emittance measurements (a) directional emittance (b) hemispherical emittance.
where

$$e_{w}(q,p,T) = \frac{E_{w}(q,p,T) \ d\Omega}{B_{w}(q,p,T) \ dA} , \text{the spectral emittance,} \quad (2.11b)$$

$d\Omega = \text{solid angle of emitted radiation;}$

$dA = \text{incremental area of emitting surface;}$

$E_{w}(q,p,T) = \text{intensity of emitted spectral radiation;}$

$B_{w}(q,p,T) = \text{corresponding blackbody, spectral intensity.}$

Solar hemispherical emittance (shown in Figure 10b) is the ratio of emitted energy collected over a hemispherical surface to that of an ideal blackbody radiator. Both the surfaces and blackbody are isothermal. An expression for the solar hemispherical emittance is:

$$e(T) = \frac{1}{\pi} \int_{\Omega} e(q,p,T) \cos(q)ds . \quad (2.12)$$

For selective absorbers, $e(T)$ is used often. However, some commercial manufacturers use normal emittance at room temperature with a non solar radiant energy source.

Reflectivity ($r$) measurements are used frequently to obtain both absorptance and emittance values, in practice, both bidirectional and hemispherical measurements are used. However, hemispherical reflectance is favored for general surfaces. Since reflectivity deals with two beams, incident and reflected, there are twice as many geometrical possibilities than for emittance and absorptance. Also, one must be concerned about the nature of the surface; most surfaces exhibit both specular (mirror-like) and diffuse properties.
Bidirectional solar reflectance is the ratio of incident radiation from direction \((q_i, p_i)\) to that of reflected energy at \((q_r, p_r)\), shown in Figure 11a.

Bidirectional solar reflectance is given as:

\[
\begin{align*}
    r(q_r, p_r, q_i, p_i) &= \frac{\int_0^\infty r_w(q_r, p_r, q_i, p_i) I_w(q_i, p_i) \, dw}{\int_0^\infty I_w(q_i, p_i) \, dw}, \quad (2.13a)
\end{align*}
\]

where

\[
    r_w(q_r, p_r, q_i, p_i) = \frac{I_{wr}(q_r, p_r)}{I_{w}(q_i, p_i)}, \quad (2.13b)
\]

where

- \(r_w(q_r, p_r, q_i, p_i) = \) spectral directional reflectance;
- \(I_w(q_i, p_i) = \) incident spectral solar radiation;
- \(I_{wr}(q_r, p_r) = \) reflected spectral radiation.

Many common spectral reflectance apparatus (e.g., Cary, Beckman) use bidirectional reflectance as a basis for reflectance measurements. For specular surfaces, this measurement is adequate. If the surface has a certain amount of optical roughness, then diffuse reflectance can be an important component of the net reflectance. There are three types of diffuse reflectance measurements: (1) directional-hemispherical (2) hemispherical-directional (3) hemispherical reflectivity. Both reflectance types (1) and (2) are reciprocal relationships. Directional-hemispherical reflectance signifies a small angle \((d\Omega)\),
Figure 11 Diagram illustrating two solar reflectance measurements (a) bidirectional reflectance (b) directional-hemispherical reflectance.
entrance beam and hemispherical integration of all reflected beams as shown in Figure 11b. This type of reflectance measurement corresponds to the effect of an integrating sphere (mentioned in the experimental procedures, Section III). By changing the direction of the beams (arrows) in Figure 11b, one can obtain the case for hemispherical-directional reflectance. Here, diffuse radiation falls on a surface with reflected energy measured over a small angle, dΩ. Hemispherical-directional reflectance is used by the heated cavity apparatus. Finally, the most spatially general reflectivity is hemispherical, where both incident and reflected beams have hemispherical orientation.

Mathematically, the case for solar directional-hemispherical reflectivity can be treated as follows:

\[
r(q_{i}, p_{i}) = \frac{\int_{0}^{\infty} r_{W}(q_{i}, p_{i}) I_{W}(q_{i}, p_{i}) \, dw}{\int_{0}^{\infty} I_{W}(q_{i}, p_{i}) \, dw},
\]

where \( r_{W}(q_{i}, p_{i}) \) is the directional-hemispherical spectral reflectivity,

\[
r_{W}(q_{i}, p_{i}) = \int_{0}^{\infty} r_{W}(q_{r}, p_{r}, q_{i}, p_{i}) \cos q_{r} \, ds_{r}.
\]

For uniform irradiation (as for the heated cavity), the solar hemispherical-directional reflectivity is given by:
\[ r(q_r, p_r) = \frac{\int_{0}^{\infty} r_w(q_r, p_r) I_w dw}{\int_{0}^{\infty} I_w dw} \]

where \( r_w(q_r, p_r) \) is the hemispherical-directional spectral reflectivity,

\[ r_w(q_r, p_r) = \frac{\int_{0}^{\infty} r_w(q_r, p_r, q_i, p_i) I_w(q_i, p_i) \cos q_i ds_i}{\frac{1}{\pi} \int_{0}^{\pi} I_w(q_i, p_i) \cos q_i ds_i} \]

Note that equation (2.14a) and (2.15b) are related by reciprocity under the conditions of uniform incident intensity. That is, \( r_w(q_i, p_i) = r_w(q_r, p_r) \), if angles \( (q_i, p_i) \) are equal to \( (q_r, p_r) \) and \( I_w(q_i, p_i) = E_w \).

Finally, for the most generalized case, solar hemispherical reflectance,

\[ r(q_r, p_r) = \frac{\int_{0}^{\infty} r_w(q_r, p_r) I_w dw}{\int_{0}^{\infty} I_w dw} \]

In general, reflectance can be related to the properties of absorptance and emittance. For an opaque surface, the directional spectral absorptance and directional hemispherical spectral reflectance are related by simple energy conservation:

\[ a_w(q, p, T) = 1 - r_w(q, p, T) \]
Also, for directional spectral emittance using equation (2.10)

\[ e_{w}(q,p,T) = 1 - r_{w}(q,p,T) \quad (2.18) \]

Also, relations hold for hemispherical spectral and directional total solar properties. These are detailed elsewhere. In practice, total absorptance and emittance are calculated from the last relations.

For this study, spectral solar absorptance was derived from directional-hemispherical reflectance measurements. Using this data, integrated solar absorptance was obtained by the following relationship:

\[ a_{i}(q,p) = \frac{\int_{0.34}^{2.2} [1 - r_{w}(q,p)] I_{w} \, dw}{\int_{0.34}^{2.2} I_{w} \, dw} \quad (2.19) \]

Integration limits are in microns and \( r_{w}(q,p) \) is taken from a near normal orientation, \( p = 20^\circ \). In general, Harshaw black chrome exhibits fairly isotropic reflectivity values with respect to \( q \), so in this case, \( q \) is arbitrary and can be removed from the reflectivity relation, leaving \( r_{w}(p) \).

In a similar fashion, spectral solar emittance was derived from hemispherical-directional reflectance measurements. Integrated emittance was obtained from the following:
$$e_i(q,p,T,T_b) = \frac{\int_{2.2}^{\infty} \left[ 1 - r_w(q,p,T) \right] B_w \, dw}{\int_{2.2}^{\infty} B_w \, dw}.$$ (2.20)

For this relationship, it is assumed $e_w$ is isotropic in $q$ and $T_b$ corresponds to the temperature of the blackbody spectra $B_w$. $T$ is the sample temperature during reflectivity measurements. It must be noted for accuracy $T_b$ should equal $T$, but most often these are different, and the difference ignored. For increased sample temperatures, $e_w$ is expected to be higher. In this work $T_b = 100^\circ C$ while $T = 25^\circ C$. A correction for the difference between $T_b$ and $T$ has been derived in prior research.20

The limits of the emittance integral are determined by the blackbody spectra selected. For 100$^\circ$C blackbody, the limits used are 4 and 30 microns. In the work to follow, both integrated absorbance and emittance will be designated simply as $a_i$ and $e_i$ with $(p,q,T,T_b)$ held constant.

C. Selective Absorbers.

Solar selectivity can be obtained by a variety of methods.21 Some materials exhibit natural electronic transitions which can affect the reflectivity drastically. These materials would be ideal, except it is uncommon for them to exhibit a transition in the 1-2 micron wavelength region, one of the requirements of a good selective absorber.

Another technique to obtain selectivity is by optical trapping through use of surface irregularities. In this case, the surface is made to appear rough or cavity-like to incoming solar radiation. It
is possible to produce a surface which would appear rough and absorbing to visible energy while appearing mirror-like and poorly emitting in the infrared.

Particulate and composite films can be selective, also. Both reflective and resonant scattering can play an important role in these films. Reflective scattering is obtained purely by geometric multiple reflection means. Resonant scattering, on the other hand, deals with particle size, shape and distribution, including the optical properties of the particles and surrounding media. The Maxwell Garnet Theory describes resonant scattering in an idealized fashion. Description of a real system such as black chrome is difficult because the theories like that of Maxwell Garnet can not generally accommodate three dimensional particle number, size and shape distributions.

Absorbing semiconductor and reflecting metal tandems can serve as selective absorbers. Metals naturally provide high infrared reflectance. However, to improve the solar absorptance properties, they are overlaid with semiconductors. These semiconductors serve as good absorbers in the visible while they appear transparent in the infrared, giving the tandem a metallic character in the infrared, as shown in Figure 12. Black chrome demonstrates tandem effects also.

Finally, two techniques of obtaining solar selectivity are multilayer thin films and quantum size effects (QSE). Multilayer thin films are dielectric metal alternations which act like selective filters for solar energy. Radiation is absorbed by multiple reflection in the dielectric-metallic layers. Wavelengths not corresponding
Figure 12 Schematic cross-section demonstrating the operation of a semiconductor/metal tandem selective absorber.
to the absorption frequency are reflected. Quantum size effects occur in ultrathin films. These effects can result in high visible absorption constants. Currently, QSE is of research importance, since practical selective absorbers have not been devised.\textsuperscript{22}

In later sections it will be shown how some of these various selective absorption processes apply to the effects portrayed by black chrome.
III. EXPERIMENTAL PROCEDURES

A. Electroplating.

In this study, copper test panels were electroplated with black chrome and nickel by the Harshaw Chemical Company under the supervision of Mr. James Long. The following procedure was used throughout:

1. Clean by an electrolytic alkaline kelating process, 88°C @ 76 and 86mA/cm², two cycles.
2. Nickel plate (dull finish, Harshaw NUSAT Process) to thickness of about 12.7 microns.
3. Black chrome (Chromonyx) plate, 216 mA/cm², 24°C for 2 minutes at 24 volts.
4. Water rinse, alcohol rinse and dry.

A relationship between deposit thickness and plating time has been determined experimentally. However, there appear to be some discrepancies in the exact thickness-time relationship because Honeywell states that the thinness factor should be 2-3 or smaller. This uncertainty probably arises from the roughness of the film.

B. Reflectance Measurements.

Spectral reflectance measurements were used to investigate the optical selectivity of each specimen. All reflectance measurements for the wavelength range 0.28-1.8 micron (visible and near infrared) were performed on a Cary 14 integrating spectrophotometer; these measurements were taken with near normal (20°) radiation with
respect to the sample. An integrating sphere$^{25}$ is needed to determine hemispheric reflectance. A schematic is shown in Figure 13. Its basic operation consists of a series of related events. Initially, a monochromatic beam of radiation is focused on the specimen. The radiation source consists of a calibrated tungsten light, although a xenon discharge tube could also be used. This radiant energy passes through a prism monochromator for wavelength discrimination. Monochromatic radiation is thus focused and reflected from the sample on to the integrating sphere. Radiation is reflected from the specimen at all angles (the exact nature depending upon the specularity of the sample). It is the nature of the integrating sphere to be uniformly illuminated by the reflected sample radiation. A detector located on the sphere wall measures the reflected energy flux. Standards are used for calibration; they can be used alternately with the test specimen without disruption: Figure 14 shows the geometrical relationship of the sample to the integrating sphere.

A Gier-Dunkle HC 300 heated cavity reflectometer$^{26}$ was used for measurement of infrared reflectivity over the wavelength range of 2.0 - 25 microns. All measurements (except where noted) were taken near normal ($20^\circ$) with respect the sample.

This device consists of blackened cylindrical nickel cavity heated by a network of resistance heaters, imbedded in the cavity walls. To assure uniform heating, numerous thermocouples are used to monitor the cavity temperature, shown in Figure 15. The sample holder is water or gas cooled and allows the user to specify the angle and temperature at which the sample is to be measured.
Figure 13 Gier-Dunkle integrating sphere and associated optics for directional-hemispherical reflectance measurements.
SCHEMATIC OF INTEGRATING SPHERE APPARATUS FOR HEMISPHERICAL REFLECTANCE OR TRANSMITTANCE MEASUREMENTS, 0.25 – 2.5 MICRONS

Figure 14 Integrating sphere showing the geometry of the measured sample and holder.
Figure 15 Gier-Dunkle heated cavity showing details of holder and sample.
Spectral reflectance is measured by heating the cavity to 760°C (1400°F), corresponding to a particular blackbody distribution of radiant energy. This radiation uniformly irradiates the cool sample. As a result, the sample will exhibit a reflectance spectrum. This spectral energy leaves the heated cavity by means of an exit port after which the radiation is focused and wavelength selected by a monochromator and sensed by a detector, as shown in Figure 16. The resulting reflectance is compared to a standard material of known reflectivity. By rotating the sample, angular spectral reflectance can be obtained.


The surface and cross sectional morphology of the specimens were characterized by use of an AMR 1000 scanning electron microscope (SEM) at 20 kV.

Qualitative elemental analysis was determined by energy dispersive analysis of X-rays (EDAX). This system forms a synergetic combination with the SEM. The principle of the EDAX method consists of energy analysis of fluorescent X-rays generated by the SEM impinging electron beam. Three types of analysis are possible:

1. A point or bulk analysis; 2. Elemental distribution analysis, an X-ray map which corresponds spatially to the electron image in terms of a selected element; 3. Element line scan, relative elemental concentrations are shown along a particular line. For analysis of black chrome, the types 1 and 3 are the most useful.
Figure 16  Associated electronics and optics for the heated cavity system.
Transmission electron microscopy was employed to analyze internal structure, chemistry, and crystallography of black chrome. Also, by use of a heating stage, short term thermal degradation effects can be simulated. A Philips EM 301, 100 kV, research electron microscope (TEM) and Hitachi HU650, 650kV, High Voltage Electron Microscope (HVEM) were used to examine all specimens. Also, by use of gun tilt dark field techniques, a particle size distribution could be obtained.

Specimens for the TEM were obtained by two different methods: chemical etching and ion thinning. Chemical etching was used in the early stages of this experimental study. The chemical techniques consisted of preparing a punched 3 mm diameter sample with one black chrome surface protected by lacquer. This sample was then placed in a jet polishing apparatus containing a solution of liquid nitrogen, acetic acid and nitric acid. Acceptable samples can be made by this technique, but some (lacquer protected) surface etching can result. Higher quality and thinner specimens can be made by ion milling. A schematic cross-section of milled black chrome is shown in Figure 17. Two quite similar ion milling machines was used in this investigation. Commonwealth IMMI Model III and Technics Micro Ion Miller, Model IV. In all cases, argon ions were used for milling. Care must be taken when ion milling; the accelerating voltage must be low enough to minimize ion damage (3-5 kV for black chrome). Also, the ion current or dose must be small enough to keep sample heating within specimen sample tolerance levels.
Figure 17 Schematic cross section of black chrome samples (a) as-plated layers (b) after ion or chemical thinning for TEM investigation.
D. Heating Treating

Heat treating of specimens was performed to gauge the short term temperature stability of black chrome. Experiments were carried out by one of three methods; samples heat treated in air were annealed in dry air at 101325 Pa (1 atm) in a Lindberg tube furnace. Melting point standards and continuous temperature monitoring were used to assure ±5°C accuracy of the heat treatments. Vacuum annealing was carried out either in situ within the TEM hot stage at 1.3 x 10^-3 Pa (10^-5 Torr) or by vacuum encapsulation.

Samples used for spectral reflectance measurements and TEM specimens were encapsulated in long quartz ampules. The encapsulation process consisted of pumping the ampules below 1.3 x 10^-1 Pa (10^-3 ) Torr, backfilling with argon, and resuming pumping. This process was repeated twice and the ampules were sealed off under vacuum. For purely mechanical strength reasons, a partial pressure of argon was allowed to remain in the encapsulated sample tubes.

E. Miscellaneous Techniques.

A Zeiss Particle Size Analyzer was used with the circumscribed circle technique for particle sizing. A large number of particles was needed to give adequate statistical data. Particle sizes were derived from darkfield TEM data taken from many random crystallographic orientations. In most cases, more than 1000 particles were classified by size.
IV. AS-PLATED STRUCTURE OF BLACK CHROME

In this Section, a materials science analysis of "Chromonyx" black chrome will be detailed. First, the process of electrodeposition will be discussed revealing the possible formation reaction which creates black chrome. Further work will show the as-plated structure as seen by electron microscopy and surface science techniques.

A. Electrodeposition of Chromium.

The electrodeposition of chromium is a good starting point to determine the electroplated properties of black chrome. There is much interest in chromium electrodeposits because of its great utility as a corrosion resistant coating. The only real disadvantage with use of chromium is that it exhibits poor ductility and frequently develops cracks in thicker coatings, although this is not true of black chrome. Chromium electroplate resists tarnishing and oxidation to temperatures above 300°C. A thin self healing oxide film is responsible for this very useful property. Deposits ranging in thickness from 0.15 - 0.75 micron are useful for decorative purposes. Thin coatings up to 1 micron are quite porous, and this is also the case in black chrome. Thicker deposits ranging from 0.5 - 60 microns are used in many applications to provide good resistance to wear, abrasion and friction. A crack free chromium plate can be achieved with 85°C solutions or by use of pulsating current in the electroplating bath. Impurities, particularly chromic oxide, Cr₂O₃, have a great effect on the properties of the electrodeposited coating. The oxide content is influenced by the conditions of electrodeposition. One example of
the oxide effects is that if a high solution temperature is used (75-85°C), a high chromium, low resistivity, high density coating results. Whereas, deposits obtained at low operating temperatures (20-40°C) have a high oxide content and exhibit greater resistivity and lower density. Typical black chrome baths operate between 30-40°C, which places them in the low temperature region.

For electroplating chromium, chromic acid solutions containing fluosilicic or sulfuric acid are used. Also, sodium or calcium hydroxide is added in some cases to form a tetrachromate salt. Although commonly trivalent chromium is the principal species in more modern compositions, very little is known about its properties. Oxygen is found as an impurity in chromium electrodeposits; it probably exists as a form of Cr₂O₃ • nH₂O or Cr(OH)₃, usually amorphous. This impurity has been identified in the residue after electrolytic dissolution of chromium metal.

The hydrogen content in chromium electrodeposits ranges from 0.01 to 0.07%. Hydrogen is found in higher concentration in low density (oxide) films. Currently, it is believed that the hydrogen content is associated with the hydrated chromic oxide. Nitrogen is also noted as an impurity in these films; it ranges from 0.001 - 0.1% in concentration for various types of baths.

Resistivity of chromium coatings is directly proportional to oxide content and inversely proportional to density, as expected; Figure 18 shows this relationship. An interesting experiment would be to measure the resistivity of the black chrome film and compare that with
Figure 18  Electrical resistivity and density of chromium electro-deposits shown before and after heat treatments. A range of Cr$_2$O$_3$ densities are shown. Pure chromium exhibits 7.20 g/cm$^3$ and Cr$_2$O$_3$ is 5.21 g/cm$^3$.28
the data in Figure 18 and the resistivity of pure Cr$_2$O$_3$. However, many difficulties exist when doing this. First, the film would have to be measured along with its conductive substrate. Various corrections, including porosity, would have to be used. If the dielectric constant of the film was known, a new microwave technique could be employed. Another obstacle is that a pure form of amorphous Cr$_2$O$_3$ (not commercially available) must be made. However, it can be deposited, using electron beam evaporating techniques. Pure chromium metal has a density of 7.20 g/cm$^3$ and resistivity of $1.2 \times 10^{-5}$ Ωcm (27°C) while pure Cr$_2$O$_3$ has a density of 5.21 g/cm$^3$ and resistivity of about $1.0 \times 10^5$ Ωcm (27°C).

Chromium deposits exhibit densification when they are heated to elevated temperatures. Above 400°C chromium shows appreciable softening. The volume decrease is attributed to the healing or sintering of cracks by oxide formation. This effect amounted to a 1% change in length for heating to 700°C. Such healing consequences may also be noted in soft particulate coatings, possibly one of the annealing processes in black chrome.

Softer chromium coatings exhibit a hexagonal (HCP) structure while the harder coatings exhibit a body centered cubic (BCC) structure.

The removal of hydrogen or water from hydrated chromic oxide is a direct function of temperature and is about 95% complete for heat treatments at 400°C; however, it may not be a permanent reaction.
The loss of water in black chrome may also take place, but it would have to be at a lower temperature, possibly 200°C, for a long time. The amorphous form of Cr₂O₃ is known for its water absorption properties. High purity films after exposure to air have increased in weight with absorbed water; however, they did not in dry air or oxygen. Exposed samples retained a significant amount of water even under vacuum beyond 1.3 x 10⁻⁴ Pa (10⁻⁶ Torr). ³²

A technique for the determination of the effect of trapped water in black chrome coatings is to compare the absorption spectra of water with the infrared spectra of black chrome, annealed at various temperatures and times.

Stress in the chromium deposits (0.1 micron) usually is compressive and may be as high as -80 kg/mm² (-113,000 psi).

Black chromium deposits have been described as mixtures of metallic chromium, chromic oxide and the other oxides of chromium, although it is dubious. The hardness and durability of these deposits depends upon their composition and structure. A common black chrome bath similar to chromonyx is one containing chromic and acetic acid; barium acetate is added to tie up sulfate ions (Chromonyx also contains trivalent chromium Cr⁺³ and Fe⁺³). The bath is operated at 25-40°C at 43-97 mA/cm². The deposit is claimed to consist of 75% metallic chromium and 25% oxide of chromium. ⁶ Another popular process is the Graham process. It consists mainly of chromic oxide with a small amount of fluosilicic acid which serves as a catalyst.
This bath must be entirely free of sulfate and foreign catalyst ions to operate correctly. Barium carbonate is used to precipitate sulfates. An interesting note here is that if sulfate were allowed to be present, a conventional chromium plating bath composition would result. The simplest chromium plating bath consists of chromic trioxide and sulfuric acid. The Graham bath operates at 26°-35°C at current densities of 160-484 mA/cm². Proprietary baths such as Harshaw's "Chromonyx" and DuPont's "Econochrome BK" electrodeposit superior finishes.

The structure of chromium deposits is very interesting. Thin layers of chromium are porous while thicker layers frequently are cracked, as noted before. These cracks or voids are filled with hydrous chromium oxide during electroplating. A structural transformation from an unstable chromium hydride to BCC chromium takes place during or shortly after plating. This structural transformation is said to account for the observed cracking of these coatings. What happens in the very thin chromium deposits is not really known. Other interesting effects have been noted when plating parameters are varied. If a low solution temperature or a low concentration of sulfuric acid or a high current density is used, the formation of HCP chromium hydride is favored. Face centered cubic (FCC) chromium hydride is favored in baths containing a high concentration of trivalent chromium hydride. Both forms of hydride decompose during plating or within a few hours after plating. The resulting composition is BCC chromium and hydrogen. In black chrome, the hexagonal
form of the hydride is favored by temperature and lack of sulfuric
acid, but the FCC form is favored also because ordinarily in these
baths the trivalent chromium content is increased to obtain deposits
of greater stability. Fortunately, the hydride decomposes to BCC
Chromium so it may be of little importance to the stability of black
chrome deposits. 33 Carbon is a common impurity in black chrome
deposits; its presence and concentration coincides with the presence
of organic additives in the basic bath composition.

Two commercial black chrome processes which are favored in the
United States were originally assigned to Diamond Alkali and Corillium
Corporation. These baths contain not only chromic acid, but an
addition of a trivalent species of chromium. The solutions are run at
16-32°C between 150-500mA/cm². Also included in the formulation
are various catalysts described only in the patent literature. As
with the classic black chrome baths, it is essential that all sulfate
ions be eliminated; barium salts are used for this purpose.

Typical chromium deposits exhibit a banded or lamellar structure
when cross sections are etched. A grain size of 179Å has been noted
for crackfree chromium and about 1000Å for cracked chromium; annealing
at 450°C for 1 hour increases the size to 1500Å. A preferred orienta-
tion for conventional chromium is the (111) planes parallel to the
surface of the substrate.

In the following subsection, the actual microstructure of black
chrome will be investigated, then it will be compared with that of
chromium electrodeposits.
B. Electron Microscopy.

To gain a better understanding of the microstructure and mechanism of solar selectivity exhibited by black chrome, the following electron microscopic investigations were performed.


A typical surface morphology for black chrome on nickel-plated copper is shown in Figure 19. The particulate, but physically adherent surface, resembles a partially sintered powder. This surface exhibits 0.05-0.30 micron diameter surface particles which is characteristic of all black chrome surfaces tested. In Figure 19a, the dark "vein like" network separating dome shaped regions of black chrome corresponds to the grain structure of the nickel layer below. The "veins" replicate the grain boundaries and other irregularities of the nickel layer. A low angle cross-section series (Figure 20), shows the rough surface structure of the underlying nickel layer. From EDAX analysis (Figure 19c), the presence of chromium and nickel was detected for the region depicted in Figure 19b. This analysis does not specify whether the chromium is metallic or in a compound, or what its structural form may be.

Black chrome thickness was determined by SEM analysis of mechanically polished specimen cross sections, and by a mechanical stylus apparatus. The mean thickness of the sample investigated in this study was 0.5 microns thick with irregularities ranging ± 0.13 microns of this value, and spacing of 0.05 mm. Careful regard was taken to measure similar regions which were examined by other
Figure 19 Surface topography of black chrome as seen by the SEM at 20 kV; (a) particulate masses separated by vein-like depressions, (b) closeup of particles, (c) EDAX analysis of region b showing the presence of chromium and nickel (from the substrate) only.
Figure 20 Low angle SEM cross section of black chrome on nickel plated copper; (a) bare nickel layer and black chrome interface, showing surface roughness and cracks (outlined), (b) thinner black chrome region, showing how black chrome replicates the underlying nickel layer, (c) top layer, notice resultant dark veins from nickel cracks.
experiments. The normal variation in thickness of the black chrome surface is shown in Figure 21. Under electron illumination, the black chrome layer appeared to "glow" or charge. This charging effect is typical of electrically insulating and some semiconducting materials.

The nickel intermediate layer exhibits a columnar structure (Figure 21a). Second phase impurities are responsible for crystalline discontinuities in structure and produce cleavage planes. The preferred orientation for these deposits is with (100) planes parallel with the surface. Common impurities in nickel are: hydrogen 0.001-0.01%, oxygen 0.003-0.05%, chloride 0.005-0.025%, sulfur 0.001-0.08% and carbon 0.02-0.1%.

For further analysis of black chrome, metallic chromium content and structure, transmission electron microscopy was employed.


Black chrome on nickel plated copper was ion thinned so the thin black chrome region could be analyzed by conventional TEM techniques. Thinned samples were also viewed by SEM to determine if surface damage was created during the sample making process. Damage or changes of the surface was not evident in the samples made by ion thinning in Figure 22a,b. However, samples made by chemical thinning in acetic acid, nitric acid and liquid nitrogen solution showed surface etching, depicted in Figure 22c,d.

The particles revealed by the SEM in Figure 19b appear as a network of islands with the TEM, represented in Figure 22c. A network of chromium particles amassed by an amorphous or fine crystalline
Figure 21 High angle (90°) SEM cross section of black chrome on nickel plated copper; (a) etched nickel-copper interface revealing the columnar structure of Nusat nickel, (b) highly etched region showing the thin black chrome layer, (c) detail of mildly etched black chrome layer and top surface.
Figure 22 SEM (20kV). Comparison of black chrome TEM samples made by ion milling and chemical etching; (a)(b) ion thinned sample showing numerous thin regions, no surface damage noted; (c)(d) chemically etched sample showing over etched edges, with many fewer acceptable areas. The dark edges are intermediate, high chromium content regions.
oxide is shown in Figure 23b. The diffraction pattern for this region (Figure 23c), and for other regions, resulted in the following information:

1. Very fine crystalline chromium was identified with all rings seen up to the Cr (321) ring.
2. Residual single crystal nickel was noted; in this case the zone axis was [001].
3. Two diffuse regions were noticed around the central beam. Their centers of intensity were estimated to correspond to lattice spacing (d) of 3.4Å and 2.55Å.

In Figure 23c, the diffuse halo at 2.55Å is evident. The 3.4Å halo is weak, and although present in the negative, it is not reproduced here. These halos correspond roughly to Cr₂O₃ (012) at 3.4Å, (ASTM data 3.633Å) and Cr₂O₃ (104, 110) at 2.55Å (ASTM data 2.666Å and 2.480Å). The halo spacing also corresponds to what is expected from radial distribution analysis of α-Cr₂O₃. These halos indicate that this unknown substance lacks long range order in bonding or it is to some degree amorphous or extremely fine crystalline. Also, by X-ray powder techniques, weak lines of chromium have been identified along with halo regions within the lattice spacings mentioned above. By use of a high voltage electron microscope (HVEM), both chemically etched and ion thinned black chrome were analyzed. As shown in Figure 25, the microstructure agrees with the ion thinned samples (Figures 23, 24). It must be noted that knock-on damage
Figure 23 The internal structure of black chrome as viewed by TEM at 100 kV; sample was made by ion thinning; (a) bright field and diffraction pattern, (b) gun tilt dark field showing agglomeration of chromium particles and matrix material.

XBB778-8008
Figure 23c Diffraction pattern showing principally metallic chromium and amorphous halos corresponding to a chromium oxide. Single crystal nickel spots arise from the substrate.
Figure 24  The structure of a thick layer of black chrome revealed by HVEM at 650 kV in bright field, with corresponding diffraction pattern. Sample was ion thinned up to black chrome layer.
Figure 25  Chemically thinned black chrome, intermediate layer viewed by HVEM at 650 kV; (a) bright field and diffraction pattern, (b) dark field showing chromium particle exclusively.
becomes an important issue for high accelerating voltages. However, during this investigation, the diffracting patterns remained stable under illumination.

The d-spacings of the chromium and nickel agreed with ASTM data with a high degree of accuracy. Although diffraction patterns were calibrated by use of polycrystalline gold standards, the presence of nickel in the black chrome pattern serves as an internal standard. The only restriction with this technique is that if the chromium (110) ring is used for dark fields, the nickel (111) reflections must be avoided, since their d-spacings are very close to each other (2.04Å and 2.034Å, respectively). In the case presented (Figure 23), nickel has a [001] zone axis, in which nickel type (111) spots do not occur.

The dark field pattern (Figure 23b) is representative of the size distribution of chromium particles within the larger agglomerated regions noted in bright field. By obtaining many dark fields of various regions, a composite particle distribution of 1358 particles was obtained. This distribution was normalized and plotted (Figure 26) using a relative frequency polygon technique. Each point on this plot represents an average value for each class, with the smallest interval 18-54Å. The data for sizes less than this interval is uncertain and is only approximated by projection. There may exist a large number of very fine particles of chromium less than 18Å. Close examination of some large particles revealed that they actually consisted of dense agglomerations of very fine particles. Optically, these agglomerations may act like an equivalent particle with averaged
or modified optical constants. The distribution presented in Figure 26 should be interpreted with this uncertainty in mind. The peak particle size occurred at 72Å with a mean particle size of 139Å.

C. Spectral Reflectance Measurements.

Hemispherical reflectance measurements were used to derive both integrated absorptance \( (a_i) \) and emittance \( (e_i) \) of all samples. In this subsection, various specimens of black chrome are evaluated in terms of surface roughness, thickness, and intermediate layer material. However, in all other sections, only the representative sample designated as H4N is extensively evaluated.

In Table II values for integrated absorptance and net emittance are tabulated along with \( a_i/e_i(20^\circ C) \), a figure of merit for each sample. These values were derived from data shown in Figures 27-29, using the techniques developed in Section IIB.

The overall reflectance spectrum of black chrome (see Figure 27) consists of four definite regions: (1) the low energy ultraviolet and near visible region 0.2 to 0.4 microns, (2) the interference region 0.4 to 1.6 microns, (3) the transition region 1.6 to 10 microns, (4) the infrared region, 10 microns upward. In the ultraviolet and near visible regions are found the lowest reflectance ordinarily. The interference region is created by optical interference between differing strata in black chrome and the black chrome-reflector material layers. This effect is characterized by a rise followed by a fall in reflectance, in the shape of sine wave. If the position of this sine wave is directly related to thickness, the physical thickness of the
Figure 26  Average relative frequency polygon for chromium particles in black chrome. Various regions were examined, consisting of 1358 particles.
Table II. Integrated Absorptance and Emittance (20°C)

Values were obtained by integration with respect to the solar AM1 spectrum for absorptance and the 100°C infrared spectra for emittance.

<table>
<thead>
<tr>
<th>Type</th>
<th>H1N</th>
<th>H2N</th>
<th>H3N</th>
<th>H4N</th>
<th>H5N</th>
<th>H9C</th>
<th>H12S</th>
<th>H16S</th>
</tr>
</thead>
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<tr>
<td>(a_i)</td>
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<td>0.95</td>
<td>0.96</td>
<td>0.96</td>
<td>0.93</td>
<td>0.94</td>
<td>0.95</td>
<td>0.92</td>
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<td>(e_i)</td>
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<td>0.065</td>
<td>0.12</td>
<td>0.08</td>
<td>0.045</td>
<td>0.05</td>
<td>0.245</td>
<td>0.07</td>
</tr>
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<td>14.6</td>
<td>8.0</td>
<td>12.0</td>
<td>20.7</td>
<td>18.8</td>
<td>3.9</td>
<td>13.1</td>
</tr>
<tr>
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<td>Ni</td>
<td>Ni</td>
<td>Ni</td>
<td>Ni</td>
<td>Cu</td>
<td>Steel</td>
<td>Steel</td>
</tr>
<tr>
<td>BC thickness approx ± 0.1 microns</td>
<td>0.5</td>
<td>0.4</td>
<td>0.5*</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5*</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Rough substrate thickness is estimated from plating parameters.*
Figure 27  Spectral hemispherical reflectance for various thicknesses of black chrome on nickel plated substrates.  Thicknesses are approximate.
Figure 28  Hemispherical reflectance of various substrates coated with black chrome. The interfacial reflector material plays a role in the exact shape and position of the transition region.
Figure 29  Hemispherical reflectance for roughened substrates plated with black chrome. In general, heavy surface roughening increases infrared emittance, thereby degrading solar selectivity.
coating may be different, but related to the effective optical thickness, which undoubtedly is wavelength dependent. The influence of black chrome coating thickness upon nickel plated samples can be viewed in Figure 27. In general, the thicker the black chrome layer, the later the transition takes place between low and high reflectivity, with the interference region moving accordingly. The highest selectivity is shown for the thinnest black chrome samples (H5N, H9C), which can be attributed to decreased emittance at the expense of degraded absorptance. Other investigators have found an optimum thickness to be between 0.1 to 0.5 microns \(^{23, 24}\) which supports the above finding.

Black chrome electroplated on copper, steel and nickel all exhibit similar reflectance properties. However, there are differences which appear to be related to the intrinsic reflectivity differences of the various types of metals. Details of the interfacial layer reflectivities are discussed elsewhere. \(^{20}\) For black chrome on copper H9C the transition region exhibits the steepest rise compared with the nickel and steel substrates, in that order, shown in Figure 28. This order is reversed for the initial wavelength at which the transition takes place. The initial transition for H9C is at a higher wavelength (2.0 microns) than all others tested. The sharp rise is due to the inherently high reflectance of copper compared with that of nickel and steel. Also, the high infrared reflectivity of H9C is attributed to this effect.
Overall, reflectance effects witnessed in the visible and near infrared show an optical interaction between the black chrome layer and substrate material, but they cannot be explained merely in terms of substrate reflectance. Such parameters as substrate roughness, grain size and spatial distribution have great influence on the interference and transition regions.

Surface roughness and its relation to reflectance is shown in Figure 29. The addition of nickel layer over a rougher substrate will tend to level and smooth the surface. Sample H12S is heavily roughened and does not have a nickel layer. The results of polishing and slight roughening of the substrate have only minor effects upon solar selectivity.

Angular reflectance is important to the interpretation of the reflecting nature of a surface. Black chrome exhibits an isotropic surface to angles 60° of normal. By surface roughening nearly ideal diffuse isotropic scattering surfaces can be achieved. This evidence is depicted in Figure 30.

In conclusion, the best coating combinations in terms of selectivity were 0.2 microns of black chrome on dull nickel (H5N) and in terms of maximized absorptance 0.5 microns of black chrome on dull nickel (H1N, H4N); also, 0.5 microns of black chrome on copper (H9C). However, it has been reported that copper samples not plated with nickel exhibit degradation during heat cycling with the formation of copper oxide. 34
Figure 30  Angular hemispherical reflectance measurements showing that black chrome is an isotropic scattering surface in nature.
D. Auger and XPS chemical profiling.

Both Auger and X-Ray Photoelectron Spectroscopy (XPS) have been performed on black chrome. These experiments were carried out by other investigators and their results will be detailed here for completeness of the subject. Also, chemical profiling is necessary for optical modeling of black chrome shown in the next section. This work was performed principally at Sandia and Honeywell using equipment at the University of Minnesota and independently at the University of Houston. A brief discussion of these techniques will follow.

Auger Electron Spectroscopy (AES) is a spectroscopic technique for determination of chemical (elemental) composition of surfaces in both a quantitative and qualitative manner. AES can be used with ion sputtering to determine chemical depth profile composition. The latter use is extremely helpful in the analysis of inhomogeneous material such as black chrome.

The physical effect which is responsible for the production of Auger electrons is created or excited by the action of a primary X-ray or incident energetic electron. The incident radiation or particle is powerful enough to eject inner core electrons of the various atoms, making up the substance of investigation. After ejection of this core electron, the local electronic structure is quite unstable; it is stabilized by the transfer of another electron from a higher level. There is excess energy left over from this process which will be released as a secondary fluorescent X-ray or by an ejection of still another electron from one of the upper or intermediate levels. The
energy of ejection is characteristic of the energy of the orbital transition. The Auger effect is of most value for the lighter elements; commonly these elements are the ones hard to detect by other methods. The probability of Auger electron emission drops to about 50% at element 33, Arsenic.

Kinetic energy \( E_a \) of an Auger electron from the L shell is given by: 
\[
E_a = (E_k - E_1) - E_1
\]
where \( E_k \) and \( E_1 \) are binding energies in the \( k \) and \( l \) shells. The quantity \( E_k - E_1 \) is the energy released by the electron falling from the \( l \) to \( k \) shell. The second \( E_1 \) in this expression is the energy required to remove the electron from the L level. The beauty of this process is that the Auger electron is completely independent of the incident radiation energy. This is not the case with X-ray photoelectron spectroscopy (XPS). The only drawback with AES is that there usually is a high background of electrons due to random scattering; So to avoid this shortcoming, the derivative of the signal used is \( \frac{dn}{de} \) rather than the signal itself.

X-Ray Photoelectron Spectroscopy refers usually to ESCA or preferably XPS. XPS relies upon an incident X-ray to eject an electron, this being a core electron. The wavelength of the incident radiation determines whether a deep or outer core electron is ejected. The energy relationship of photoelectron by an X-Ray can be expressed as:
\[ E_b = h\nu - (E_k + C) \]

The term, \( E_b \) is called the binding energy; it represents the difference between the energy \( (h\nu) \) of the X-ray photon and the kinetic energy of the ejected electron, corrected by a spectrometer constant \( (C) \). The binding energy is specific for a given element and is accurate enough for identification of a particular electronic state. The oxidation state does, however, influence the exact binding energy noted for a particular element. Different types of molecular bonds affect the effective force field of a nucleus, thus affecting the nature of the binding energy. It has been noted experimentally that the binding energy will vary by about 10eV for most elements. XPS like other types of electron spectroscopy, is a surface analyzer essentially, because excited electrons have little chance of escape if they originate greater than 50Å below the surface. To analyze chemical information at greater depths ion etching is used. Auger and XPS offer accurate methods of determining surface composition. When ion sputtering is coupled with these techniques it becomes shadowed with inaccuracies and uncertainties. Three major problems can arise with ion sputtering; it tends to alter surface composition, induce false topography, and artificially induce diffusion of sample constituents. 35-36

The major reason surface composition is altered during ion bombardment is that different atomic species have differing sputter yields. It is not uncommon for a particular light mass or high
sputter yield element to be sputtered preferentially, leaving the surface enriched with a lower sputter yield element. In a homogeneous material, this process will continue until a steady state condition is reached, which can be after several hundred Angstroms of sputtering. In general, due to this effect, it is recognized that the sputtered surface is not necessarily characteristic of the actual composition.\textsuperscript{37} Surprisingly, for Cr\textsubscript{2}O\textsubscript{3} preferential sputtering of oxygen (3kV argon) is not evident.\textsuperscript{38} The range of compositions studied here was 20-80 volume percent Cr and the composition of black chrome lies within this range. When electron probe beams are used such as in Auger spectroscopy, electron bombardment can preferentially desorb oxygen in stable oxides. This is further complicated by reoxidation from imperfect vacuum systems containing oxygen.

Topological alterations can influence depth profiling techniques. Both sputter rate and sensitivity are affected adversely by rough topology. Depth resolution is degraded proportionally to degree of topological alteration. One noticeable topological consequence is the broadening of interfaces, such as the nickel-black chrome interface.

By use of ion bombardment local diffusion is induced. With ion sputtering or thinning, diffusion effects are expected over a 50Å range within the damage region for 5 kV ions.\textsuperscript{39} Ion impact can displace or drive surface atoms deeper into the sample by recoil implantation, knock-on process or collision cascade.\textsuperscript{40}
Unfortunately, it is very difficult to assess which effects might predominate in a particular homogeneous material, and the case is worse for an inhomogeneous Cr-Cr$_2$O$_3$ cermet such as black chrome. Currently, the area of ion and electron bombardment effects is very active and hopefully many of these shortcomings will be resolved or understood in the near future. Two approaches might be used to investigate and separate various artifacts of the sputtering process. By varying ion profiling parameters, relationships between ion energy, beam heating (discussed in Appendix I) and ion types can be correlated to profile accuracy. Also, better accuracy may be obtained by profiling samples in two directions, surface to substrate and reverse. Another approach might be to perform auxillary measurements, such as very high energy ion beam spectrometry (Rutherford Backscattering) which enables depth profiling without sputtering. Yet another experiment, which avoids many problems, is to use a low angle cross section and analyze it directly, using a high spatially resolved surface analysis system.

The following results have been reported separately by the authors cited. Although their samples vary, the data is representative of the Harshaw coating.

Auger depth profiling has been performed (shown in Figure 31) by Sandia Labs.\textsuperscript{41} and it agrees with prior investigations.\textsuperscript{42,43} The sample consisted of Chromonyx deposited at 188 mA/cm$^2$ for 3.5 minutes at 20-26$^\circ$C, on a nickel plated substrate. During analysis, this sample was ion etched with Argon at 5 kV and 25mA. A single
Figure 31 Auger depth profile of black chrome. The sputtering was performed with Argon ion at 5 kV and 25 mA. The oxygen to chromium ratio equals 2.4:1 for crystalline Cr₂O₃. (after R. Pettit and R. Sowell, Sandia Labs.)
crystal Cr₂O₃ sample was used to calibrate the oxygen to chromium ratio which was necessary for semiquantitative analysis. It was found that the first few hundred Angstroms were comprised chiefly of Cr₂O₃, assuming the data was not altered by sputtering artifacts and simple inhomogeneity. The remainder of the coating consisted of chromium and oxygen, which had been verified in an early section as metallic chromium in a Cr₂O₃ matrix. By integrating the chromium and oxygen curves, the bulk ratio result was, respectively, 86:14. Only idealized Cr³⁺ and Cr⁰ concentrations are shown in Figure 31. They have been derived assuming all oxygen is in the form of Cr₂O₃, disregarding water vapor and O₂ (this may not be legitimate). XPS measurements were employed to clarify the Cr³⁺ and Cr⁰ concentrations. Also, in Figure 31, the black chrome nickel interface was poorly defined; this was due mainly to the roughness of nickel and sputtering effects.

To resolve the question about chromium oxidation states, XPS measurements were performed, coupled with Argon ion sputtering. Usually, with these measurements, oxidation states can be identified as binding energy shifts in simple systems. Investigators at the University of Houston have performed this work⁴⁴ although their model differs from the one developed in this study. The black chrome sample was plated with Chromonyx at 200 mA/cm² on polished nickel. The XPS profile shown in Figure 32 was obtained by sputtering at 3 kV. This curve was plated from the few data points given. High concentrations of Cr³⁺ and O²⁻ can be noted close to the surface
Figure 32 XPS depth profile of black chrome. The sputtering was done with Argon ions at 3 kV. (Data from A. Ignatiev, et al., Univ. of Houston)
of the sample, signifying that a major constituent was Cr\(_2\)O\(_3\).
Deeper into the black chrome the major constituent becomes metallic chromium which appears to increase with depth as noted. However, the oxygen curve does not drop off, as expected from the Auger data if it is assumed that all the oxygen is in the O\(^{2-}\) state, so this may not be the case.

The results do appear plausible since one would expect a chromium oxide film to form readily on the exposed surface of metallic chromium. Ion yield ratios have been derived from the Sandia study\(^{41}\) and presented in Figure 33; these results agree with the XPS study.

Additional XPS research was performed on a different black chrome coating of nickel in France.\(^{45}\) Their work has resulted in a similar volume fill factor function for metallic chromium, but lower in magnitude. There remains some disagreement about the thickness of the Cr\(_2\)O\(_3\) layer, as it is between 400-1000Å.

With these combined results, coupled with the current study, a solar selectivity model for black chrome can be devised.
Figure 33 Chromium fill factor ratios for black chrome. Data was derived from Figure 31 (after R. Pettit and R. Sowell, Sandia Labs)\textsuperscript{43}
V. SOLAR SELECTIVITY MODEL FOR BLACK CHROME

From the combined research material presented thus far, a model can be devised for the as-plated structure of black chrome. Also, this microstructural model will be compared with the theoretical modeling performed by international investigators, principally of Sweden, France and Australia. These effective medium mathematical models will consist of Maxwell Garnett,\textsuperscript{46,47} the CCCA modified Maxwell Garnett,\textsuperscript{48} and Bruggeman theory.\textsuperscript{49}

A. Microstructural Model

As a result of chemical and structural investigations, the Harshaw black chrome consists of three distinct regions: 1) a thin \( \text{Cr}_2\text{O}_3 \) top layer, 2) an intermediate \( \text{Cr}_2\text{O}_3\text{-Cr} \) cermet and 3) a \( \text{Cr- Cr}_2\text{O}_3 \) cermet dominated with metallic Cr and nearby Ni interface. In all regions \( \text{Cr}_2\text{O}_3 \) is either amorphous or very fine crystalline. Basically, this absorber exhibits solar selectivity (shown in Figure 34) as follows: The top oxide layer acts like a transparent antireflective layer to incoming solar radiation (also as an oxidation barrier). Amorphous \( \text{Cr}_2\text{O}_3 \) probably is a p-type semiconductor with bandgap of 3eV or higher.\textsuperscript{50}

The intermediate cermet layer is where most of the visible absorption takes place. In the infrared, this layer becomes ineffective as an absorber and appears transparent like the top layer. The lowest layer has a metallic character, which exhibits a reflectance dependency and interaction with the interfacial nickel layer. However, this interaction appears to be mild. The greatest effect the
nickel layer may have on the exact nature of the black chrome morphology is its columnar structure, roughness, grain size boundaries and electrochemical properties during plating. Low infrared emittance is governed by the metallic layer mixed with some nickel effects.

An experiment to verify the substrate influence might be to compare the reflectance of black chrome coated gold, copper and nickel substrates. Care must be taken to use polished substrates and very smooth deposits; also a microstructural investigation would be necessary to determine any electrochemical effects the substrate might have on the black chrome deposits. In general, the structure of black chrome deposits do vary, depending upon types of substrates. Of these substrates, however, deposits on copper, nickel and steel are very similar, but this is not true of zinc.

Notice that in Figure 34, these three layers are not clearly defined as separate regions and they vary in depth with the surface particle morphology. This transition nature is expected, with the steepest interface lying between a-Cr$_2$O$_3$ and a-Cr$_2$O$_3$-Cr (Figure 31, 32) cermet region. The mechanism of chromium oxidation probably is responsible for the metallic depleted region (steep interface); in this system the principal diffusing species is Cr$^{+3}$, which will diffuse through the oxide layer to react with chemiabsorbed oxygen at the surface. The theory of chromium oxidation is covered in Section VI.

During black chrome deposition the layers exhibit additivity, that is to say, two separate 2 minute layers of black chrome equal
Figure 34 Schematic cross section of black chrome. Three distinct regions are shown in the as-plated structure.
1. Top layer of amorphous or fine crystalline $\text{Cr}_2\text{O}_3$.
2. Intermediate area of metallic Cr in $\text{Cr}_2\text{O}_3$.
3. Bottom layer, consisting principally of Cr and the Ni substrate.
Also, not shown is the presence of trapped water, in the form of hydrated $\text{Cr}_2\text{O}_3$ or chromium hydride. XBL 799-11767
that of a single 4 minute layer, without change in reflectance properties. The process of deposition begins with the codeposition of Cr + Cr$_2$O$_3$ species and as the layer thickens, more oxide is deposited. If deposition is stopped, the coating is allowed to oxidize in air resulting in a top oxide layer. Now, if deposition is continued, then initially this oxide layer is partially reduced to metallic chromium, after which deposition continues as before.

The ratio of Cr to Cr$_2$O$_3$ undoubtedly is determined by local concentration of species in the bath, layer conductivity, local field gradients, and deposition conditions. As plating time and coating thickness increase, the resistivity of the coating increases and emittance sharply increases. Black chrome has a limiting thickness about 1 micron, which probably is caused by the rising insulating nature of the coating as thickness grows. The sharp increase seen in thick coatings may be caused from an expanded intermediate region (2) as seen in Figure 34. This region might only be semitransparent in the infrared, thereby imparting a higher net emittance to the metallic like region (3).

Obviously, many of these hypotheses are unproven, but they appear to be consistent with the microstructural model presented. Further experimentation is necessary to obtain the significant evidence.

B. Optical and Electrical Properties of Cr$_2$O$_3$, Chromium and Nickel.

To develop a mathematical model for black chrome, characteristic optical parameters must be known. Unfortunately, the optical constants, especially those with depth, are unknown for black chrome.
However, the following optical and related electrical properties have been measured in various investigations. This data is commonly used in mathematical models for black chrome. One should be warned that these values rely heavily upon the condition of the material at the time of analysis. In other words, the presence of oxide layers, contamination and surface irregularities can all influence the optical properties of a material. When optical property measurements are taken, various conditions are implied. Optical constants of importance are typically, refractive index \( n \) and the extinction coefficient \( k \), both functions of wavelength and temperature.

1. \( \text{Cr}_2\text{O}_3 \)

Chromium sesquioxide, \( \text{Cr}_2\text{O}_3 \), behaves as a p-type semiconductor over the range of 27-1327\(^{0}\)C. It has an energy gap of \( \text{E}_g = 3 \text{ eV} \) for the single crystal\(^5\)\(^1\) and \( \text{E}_g = 7.68 \text{ eV} \) has been reported for sintered samples,\(^5\)\(^2\) and activation energy of \( \text{E}_a = 0.32 - 0.4 \text{ eV} \).\(^5\)\(^3\) Conduction for this material is extrinsic below 927\(^{0}\)C. That is, conduction is dominated by impurities or native defects with the jumping of holes between \( \text{Cr}^{4+} \) and \( \text{Cr}^{3+} \) sites. This oxide exhibits a dielectric constant of \( \epsilon = 8 \) in its single crystal form. The optical properties of \( \text{Cr}_2\text{O}_3 \) reveal absorption bands at 0.25, 0.367, 0.461, 0.602, and 0.695 microns which are attributed to crystal field transitions. Infrared bands are encountered in the region of 13.3 - 33.3 microns, chiefly at 19.5 microns and are due to vibrations of the \( \text{Cr-O} \) bond. This data indicates the localized nature of the electrons in \( \text{Cr}_2\text{O}_3 \).
Although limited reflectance data is available for \( \text{Cr}_2\text{O}_3 \), none appears to be directly applicable to amorphous \( \text{Cr}_2\text{O}_3 \) in black chrome. Limited data for amorphous very fine crystalline films with \( n = 2.4 \) is available.\(^54\) Also, single crystal\(^55\) and sintered crystalline\(^56\) reflectance has been measured over various wavelength regions. Several values have been used for \( n \) and \( k \) of \( \text{Cr}_2\text{O}_3 \). As an average value representing electrodeposited film, \( n - ik = 2.0 - 0.5i \) has been suggested.\(^57\) In more recent work, a wavelength dependent function \( 1.8 - 0.003i \) ranging to \( 1.8 - 0.2i \) with a strong resonance at 3 microns was used over the range 0.4 to 3.5 microns.\(^58\) Another investigation has picked \( n = 2.45 \) to represent \( \text{Cr}_2\text{O}_3 \).\(^59\) Obviously, there is a need to better optically characterize \( \text{a-Cr}_2\text{O}_3 \) in electroplated films. Except in one case for electron beam evaporation,\(^53\) a pure film of this material has not been produced.

2. Chromium and Nickel

The properties of both chromium and nickel are well known and bulk optical property information exists for the pure film.\(^60,61\) Composite data is shown in Figure 35. Although these data are used commonly, it is difficult to say that bulk values for chromium are characteristic of small chromium particles.

C. Mathematical Models for Black Chrome

Scattering and effective medium theories with their modifications are presented in the following subsection. No single theory completely explains the reflectance properties of black chrome, but
Figure 35 Index of refraction and extinction coefficient for chromium and nickel. Data designated (JC) is from Johnson and Christy's high purity evaporated films. Data from Barker and Ditzenberger (BD) is also shown for chromium. The authors have not explained the discrepancies in their data.
altogether they do serve a purpose as approximations. The effect of large particle scattering \((\text{dia} > \text{w})\) will not be covered here as it lies within the realm of geometrical or diffractive scattering.

D. Maxwell Garnett Theory

The Maxwell Garnett Theory (MG) is employed to help elucidate the absorption properties of extremely fine particles in a solid matrix. The MG theory was developed from the Mie Scattering Theory, which describes the scattering properties of spherical particles larger than those which could be handled by Rayleigh theory. The original MG theory treated isolated spherical metal particles in a dielectric matrix. Also, it was assumed that the particles exhibited identical properties to the bulk metal, which is much too simplified. The MG theory was further developed to take a random distribution of particles characterized by a metal filling factor \((f)\).\(^{62}\) The diameter \((d)\) of the particles is small compared to the film dimensions and wavelength \((\lambda)\), so \(d < 0.1\lambda\).

Historically, the MG theory has been used to describe the color obtained from colloidal suspension of metal in glass,\(^{47}\) and currently used to predict the properties of uniform ultrafine particulate solar absorbers.\(^{63}\) Here the MG theory will be used to model the absorption effect in black chrome.

In general, a homogeneous isotropic material is optically characterized when the refractive index \((n(\lambda))\) and the absorption coefficient \((a(\lambda))\) are known as a function of all wavelengths of interest. A related term, the extinction coefficient, \(k = na\), is also used to characterize optical materials.
1. Theory

Consider a medium composed of metal spheres suspended in a vacuum. There are $N$ spheres per unit volume. Each sphere behaves like an electric dipole with dipole moment $\vec{P}$ in a applied external field $\vec{E}$. The external field is the sum of the field due to the incident light or energy $\vec{E}_i$ plus contributions from other dipoles, as expressed in the following relationship:

$$\vec{E} = \vec{E}_i + \frac{4}{3} \frac{\vec{P}}{N}.$$  \hspace{1cm} (5.1)

Where $\vec{P}$ due to $N$ individual dipole moments per unit volume is given as

$$\vec{P} = \overline{Np} = Na^3 \left( \frac{e - 1}{e + i} \right) .$$  \hspace{1cm} (Clausius Massotti equation) \hspace{1cm} (5.2)

The complex dielectric constant is given as $\varepsilon$ and is defined as:

$$\varepsilon = (n - i \kappa)^2 = \varepsilon_1 + i\varepsilon_2 .$$  \hspace{1cm} (5.3)

The wavelengths of interest for solar energy applications are orders of magnitude larger than the particle sizes, showing that the optical properties should be discussed in terms of a spatially averaged dielectric constant

$$\overline{\varepsilon} = \varepsilon_1 + i\varepsilon_2 .$$  \hspace{1cm} (5.4)
To use the Maxwell Garnett theory, the fill factors of metal to matrix ratio must be $f \leq 0.2$. Otherwise, corrections have to be made for retardation effects. The Maxwell-Garnett theory gives:

$$
\bar{\varepsilon} = \frac{2\varepsilon_{ox}}{1 - \frac{3}{3}f\alpha} + \frac{1}{1 - \frac{3}{3}f\alpha},
$$

(5.5a)

where $\alpha$ is the polarizability factor; for metal spheres particles in dielectric:

$$
a = \frac{(\varepsilon_{m} - \varepsilon_{ox})}{\varepsilon_{ox} + Q(\varepsilon_{m} - \varepsilon_{ox})}, \quad Q = \frac{1}{3},
$$

(5.5b)

$\varepsilon_{m}$ = the complex dielectric constant for the metal;

$\varepsilon_{ox}$ = the dielectric constant for the oxide.

$Q$ = the total depolarization factor

Also $\bar{\varepsilon}$ can be expressed as:

$$
\bar{\varepsilon} = \frac{\varepsilon_{ox}[2\varepsilon_{ox}(1-f) + \varepsilon_{m}(2f+1)]}{\varepsilon_{ox}(f+2) + \varepsilon_{m}(1-f)},
$$

(5.6a)

or

$$
\frac{\bar{\varepsilon} - \varepsilon_{ox}}{\bar{\varepsilon} + 2\varepsilon_{ox}} = f \left[ \frac{\varepsilon_{m} - \varepsilon_{ox}}{\varepsilon_{m} - 2\varepsilon_{ox}} \right].
$$

(5.6b)
For the simplest case of metal spherical particles surrounded by a vacuum, the transmittance of the film can be written as:

\[ T \approx \exp \left[ \frac{-18\pi fde_2}{w} \frac{1}{(e_1+2)^2 + e_2^2} \right], \quad (5.7) \]

and \( e_m = e_1 + ie_2 \), \( d = \) coating thickness and \( w = \) wavelength \( (5.8) \)

Another treatment of \( e_m \) is to consider it as a sum of two separate contributions, that of interband transition (\( e_b \)) and free electron contribution (\( e_d \)), so

\[ e_m = e_b + e_d. \quad (5.9) \]

The Drude part of the dielectric constant for the metal is given by:

\[ e_d = 1 + \frac{W_p^2}{iW_a(1+iW_a t)}, \quad (5.10) \]

where \( W_a \) = the angular frequency of the light;
\( W_p \) = the plasma frequency;
\( t \) = the mean scattering time of the conduction electrons.

2. Particle Shape

The Maxwell Garnett expression (5.5b) may be modified to describe particles of shapes other than spheres.
For spheroids with their symmetry axis in the field direction these can be treated as follows:

\[ a = \frac{e_m - e_{ox}}{e_{ox} + L(e_m - e_{ox})} \]  

(5.11)

where \( L \) is the depolarization factor for a particular symmetry axis.

This equation can be generalized for randomly oriented spheroids:

\[ a = \frac{1}{3} \sum_{i=1}^{3} \frac{e_m - e_{ox}}{e_{ox} + L_i(e_m - e_{ox})} \]  

(5.12)

\( L_i \) denotes the appropriate triplet of depolarization factors, which accounts for shape and aspect ratios (eccentricities).

Ellipsoids, with one of their axes perpendicular to the field, but otherwise randomly oriented have a total depolarization factor of \( Q = 0.5 \).

The influence of an oxide shell over a metal particle different than that of the oxide matrix can be shown as:

\[ a = \frac{3(e_{os} - e_{ox})(e_m + 2e_{os}) + V(2e_{os} + e_{ox})(e_m - e_{os})}{(e_{os} + 2e_{ox})(e_m + 2e_{os}) + V(2e_{os} - 2e_{ox})(e_m - e_{os})} \]  

(5.13a)

where

\[ e_{os} = \text{Dielectric constant for oxide shell} \]

\[ V = \text{Volume ratio between oxide shell and metal core.} \]
The above equation can also be derived for ellipsoids.\(^{65}\)

3. Graded Index Coatings

A method used to describe coatings with a linear graded index (the simplest case) follows an easy linear mixing theory.\(^{57}\) The composite dielectric constant is given by

\[
\bar{\varepsilon} = f\varepsilon_m + (1+f)\varepsilon_{ox}
\]  

(5.14)

where \(\varepsilon_m\) = the dielectric constant of metal  
\(\varepsilon_{ox}\) = the dielectric constant of the oxide  
\(f\) = the fill factor of metal in oxide (volume fraction).

The above equation is the equivalent to treating atoms as independent polarizable units and neglecting the Lorentz field correction to obtain the local field from the average field. If we include the Lorentz correction the following formula (5.15) is obtained. This correction is only necessary for well localized electron systems and is negligible for free electron systems. That is, this correction is used for dielectric material, and is not necessarily correct for metallic systems.

\[
\frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2} = f \left[ \frac{\varepsilon_m - 1}{\varepsilon_m + 2} \right] + (1+f) \frac{\varepsilon_{ox} - 1}{\varepsilon_{ox} + 2} .
\]  

(5.15)

Usually, the dependence of \(q\) on the distance \(t\) from the surface is derived from the rates of deposition, although this would be quite different for black chrome.
A relationship can be derived for the variation of the dielectric with depth into the coating, using the linear mixing theory.

\[
e(t) = \frac{e_m - ae_{ox}}{1-a} - \frac{a(e_m - e_{ox})}{(1-a)\left[1 - (1-a)\frac{t}{d}\right]^\frac{1}{2}},
\]

(5.16)

where \(a\) = grading constant;

\(d\) = the thickness of the film;

\(t\) = fractional depth from surface (\(t_s = 0\))

Basically, the theories of linear mixing and Lorentz-Lorenz are all based on, A and B forming a solid solution; that is, intimate mixtures of A and B atoms.

However, in many systems, A and B are insoluble and have different equilibrium phases, such as the case of Cr in Cr\(_2\)O\(_3\). In this case, material of the minority phase will agglomerate to form a precipitate in the majority material.

When the volume fraction of the minority constituent is less than about 0.2 the classic MG theory can be used to describe this system. The low filling factor accounts for the necessity for particles of the minority phase to have non-interacting scattering functions. We assume that the particles are spherical, greater than atomic dimensions but smaller than the wavelength of visible energy. Also, particle spacings must be closer than a visible wavelength.

The key MG formula for a graded index is as follows:
\[
\frac{\epsilon(t)}{\epsilon(t) + 2\epsilon_{ox}} = \left[\frac{\epsilon_m - \epsilon_{ox}}{\epsilon_m + 2\epsilon_{ox}}\right] \left[\frac{a}{a-1}\right] \left[1 - \frac{1}{1-(1-a^2)\frac{t}{a}}^{0.5}\right]. \tag{5.17}
\]

For highly absorbing films \(a_i \approx 0.9\), one expects that a composite film would have \(n \leq 1.5\) and \(0.2 < k < 0.8\). Materials with higher \(n\) values tend to be too refractive and lower \(k\) values are too dielectric like while higher \(k\) values are metallic in nature. Intrinsic materials in this region are uncommon; that is why composites are so desirable.

4. Metal Rich Fill Factors

For high metal content, an inverse procedure can be used to obtain an expression for the effective dielectric constant. In this case, the physical system consists of a metal matrix containing spherical dielectric islands. It has been shown that for the metal rich limit: 48, 66

\[
\epsilon = \frac{\epsilon_m(3\epsilon_{ox} - 2f(\epsilon_{ox} - \epsilon_m))}{3\epsilon_m + f(\epsilon_{ox} - \epsilon_m)}. \tag{5.18}
\]

A self-consistent method does not, however, cover the intermediate range of \(f\)'s, when both phases appear as particles. The MG theory works for all \(f\)'s only when one phase is particulate and the other continuous.

5. Surface Roughness Effects

An expression for the decrease in reflectance has been derived for surface roughness effects: 67
where \( R_i \) is the spectral reflectance of the smooth surface; 
\( R \) is the spectral reflectance of the rough surface; 
\( r \) is the R.M.S. surface roughness 
\( w \) is the wavelength.

6. Computed Results

Several studies have modelled black chrome, in general. However, in most cases, constant fill factors were used with low enough \((f < 0.2)\) or high enough \((f > 0.8)\) to fit into the MG theory. Unfortunately, intermediate fill factors exist in black chrome; their effect on absorption cannot be described in terms of MG theory. Self consistent theories such as the Bruggeman effective medium theory have to be employed in this case.

Shown in Figure 36 are various attempts to model the black chrome surface using the Maxwell Garnett Theory. The better fitting curves consist of the modified MG theory \(^4_8\) to take into account the high metal content coatings. The data here is from recent French (BL) work. \(^4_5\) It models black chrome on copper. The form of the (BC) curve is close to the experimental data shown here except for a shift of the cut-off wavelength further into the infrared. Other works shown here are homogeneous Cr layers and graded \( \text{Cr}_2\text{O}_3 - \text{Cr} \) films with low filling factors, \( f = 0.1 \), developed in Scandinavia. \(^6_8\) A graded interference film is also shown which models the \( \text{Cr}_2\text{O}_3 - \text{Cr} \) cermet with \( f = 0.1 \). This Australian work \(^5_7\) comes the closest to
Figure 36 Maxwell Garnett modeling of black chrome showing various modifications. The cosinusoidal graded cermet has been developed by Ritchie and Window (RW).\textsuperscript{57} Also, uniform cermets with spheroid inclusions modeled for dielectric permeabilities of 1 and 3, by Granqvist and Hunderi (GH).\textsuperscript{68} Finally, a modified MG model for metal rich cermet has been investigated by Berthier and Lafait.\textsuperscript{45}
the experimental data shown here, but it uses consinusoidal grading and \( f = 0.1 \) which does not agree with the experimental data. Another model for the Harshaw coating is the continuous Theory of Spheroidal Chains,\(^4\) however, this model is inconsistent with the materials science characterization presented here.

Further modifications are needed if the MG Theory is used to model black chrome. Such details as particle size and shape distributions and intermediate fill factors need to be considered; also correction terms are necessary for scattering interactions between particles\(^6\) and particle clustering effects.

Also, there are experimental unknowns associated with the amount of information one can obtain by the analysis of a black chrome type solar absorber. We need a more adequate characterization of the following:

1. Actual dielectric constant of chromium metal phase as electrodeposited. Up to now, only textbook values have been used.
2. Actual dielectric constant of the matrix oxide. It consists of amorphous \( \text{Cr}_2\text{O}_3 \) with impurities and porosity.
3. Analysis of shape and size distributions at various levels of grading.

E. Bruggeman Effective Medium Theory.

1. Theoretical outline

In the Bruggeman Theory (BR) an inhomogeneous two phase material is treated as a system of spherical particles. These particles are
comprised separately of pure phase A and pure phase B. The theory solves for the local electric field around a typical two phase element, embedded in an effective medium. In the BR Theory first-order scattering shall vanish on the average; that is, all field fluctuations will average to zero. In this fashion, a self consistent local field is equivalent to the choice of an active medium such that the average single site scattering is zero. Considering the black chrome system, the effective medium permeability results as:

$$\bar{e} = e_{\text{ox}} \frac{(1 - f + \frac{1}{3} f a)}{(1 - f - \frac{2}{3} f a)} ;$$  \hspace{1cm} (5.20a)

where

$$a = \frac{e_m - \bar{e}}{\bar{e} + \frac{1}{3} (e_m - \bar{e})} \quad \text{for spheres,} \hspace{1cm} (5.20b)$$

and $e_{\text{ox}}$ = dielectric permeability of oxide;
$e_m$ = dielectric permeability of chromium;
$\bar{e}$ = effective dielectric permeability
$f$ = chromium fill factor.

This equation (5.20b) can be generalized to account for ellipsoidal shapes:

$$a = \frac{1}{3} \sum_{i=1}^{3} \frac{e_m - \bar{e}}{\bar{e} + L_i (e_m - \bar{e})} ,$$  \hspace{1cm} (5.21)
where $L_i$ = triplet of depolarization factors. Also, expression (5.20) can be seen in its symmetric form:

$$f \left[ \frac{e_m - \bar{e}}{e_m + 2\bar{e}} \right] + (1-f) \left[ \frac{e_{ox} - \bar{e}}{e_{ox} + 2\bar{e}} \right] = 0$$

(5.22)

2. Computed Results

The Bruggeman Theory has been used to describe black chrome. In this theory, fill factors from 0 to 1 can be used. French investigators used this theoretical model to describe black chrome.45 In Figure 37, a curve is shown which models the experimental data in this study. The response in the visible range should be flatter for the modeled curve and the transition slope should be sharper in the infrared.

Other hypothetical effective medium theories exist,70 but they have yet to be tried on the black chrome model.
Figure 37 Bruggeman effective medium theory modeling of black chrome. Shown is the simple model for $\text{Cr}_2\text{O}_3$ - Cr cermet coating with spherical roughness. After Berthier and Lafait.45
VI. OXIDATION PROPERTIES OF BLACK CHROME CONSTITUENTS

Before the experimental results are discussed for the thermal stability of black chrome, it is necessary to consider the oxidation properties of its principal chemical species. With this knowledge, one may justify various physical and chemical observations reviewed by electron microscopy.

Oxidation properties frequently are split into two categories, tarnish films and high temperature oxidation scaling systems. The separation between both these categories is not well defined; tarnish films occur from 0 - 700°C and scaling might occur from 500°C upwards. For black chrome studies we are mainly interested in tarnish reactions roughly, 100 - 500°C, but high temperature oxidation should not be ignored. Spinel phases are known to form in scaling systems, as has been detected in black chrome. The following discussion will deal with both low and high temperature oxidation of chromium and nickel. Nickel-chromium reactions are important because nickel is the favored reflector layer in black chrome absorbers.

For oxidation occurrence there are usually a number of factors which can be the rate determining steps. These steps are listed below:

1. Phase boundary reactions, nucleation and crystal growth.
2. Diffusion or transport of cations, anions or electrons through the oxide.
3. Transport in space change boundary layers (thin oxides).
4. Thermodynamic stability of oxides.
5. Crystal structure and mismatch of oxide and metal.
Phase boundary reactions take in the chemisorption of oxygen, exchange of electrons, splitting of molecules at the interface, transfer of the metal ions and electrons to the interface and react to form the oxide layers. Transport of ions and electrons can be hampered by the presence of chemical and electrical gradients in the various layers.

The parabolic rate law is used to describe ideal oxidation rates at high temperatures and gas pressures.

This law is given as follows:

\[
\frac{dL}{dt} = \frac{K_p}{L} \quad (6.1a)
\]

where \( L \) is the oxide thickness, \( K_p \) is the parabolic scaling constant and \( t \) is the oxidation time.

Integrated, this law is as follows, if the rate determining factor is transport of one type of charged species,

\[
L = (2k_p t)^{1/2}, \quad k_p = V_i D(N_a - N_i) \quad \text{ (6.1b)}
\]

where \( V_i \) is the volume per metal ion and \( N_a \) and \( N_i \) are respectively, the number of vacancies or interstitials per volume at the phase boundary.

For intermediate temperatures a cubic rate law is often approached:

\[
\frac{dL}{dt} = \frac{K_c}{L^2}, \quad (6.2a)
\]
where $K_c$ is the cubic rate constant.

Integrating equation (6.3), the cubic law becomes,

$$L(t) = (At + B)^{1/3}, \quad (6.2b)$$

where $A, B$ are constants.

For even lower temperatures (0-200°C) and thicknesses of 20-80Å tarnish layers follow either a normal or reciprocal logarithmic law of oxidation, as follows:

$$L = L_0 \ln(t + t_0) - C \quad \text{(normal)} \quad (6.3)$$

$$\frac{1}{L} = A - B \ln t \quad \text{(reciprocal log.)} \quad (6.4)$$

Finally, for very fast transport of the necessary ions, oxidation can follow a linear law which is simply:

$$L = K_1 t, \quad (6.5)$$

where $K_1$ is linear rate constant.

In the following treatment these rate laws will be applied to the specific cases of chromium, nickel and a mixed Cr-Ni system, as might be expected from black chrome at various temperatures.

A. Tarnish Oxidation of Chromium

The presence of space charge layers in oxidized chromium can cause field transport of ionic defects. The electrical field set up during oxidation is the result of a negative surface charge and a positive oxide charge developed during the chemisorption of oxygen.
The positive space charge layer in the oxide can be several thousand angstroms wide.

For chromium oxidation (p-type conductor) there is a high concentration of holes in the space charge region, and only in films as small as 10 Å can space charge effects be neglected. For this process of oxidation, the cubic law holds the best, because the space charge can be in excess of 1000 Å wide.

For low temperature oxidation premature rupture of the oxide layer can take place. This failure is caused by the build up of internal stresses. The formation of stress arises from the formation of void regions. Voids form from coalescence of vacancies as described previously. High temperature oxidation doesn't present this problem because at such temperature: plastic flow allows material to fill in these natural voids. For chromium and nickel it is expected that these cavities will form at the metal/oxide interface and, with time, migrate outward. The rate laws mentioned will be affected greatly by this action.

B. Oxidation of Cr₂O₃

The only known high temperature stable oxide phase is Chromium Sesquioxide (Cr₂O₃). Other common phases of chromium oxide are oxygen rich phases, see Table III, and Figure 38 for a suggested phase diagram.

Chromium sesquioxide exhibits the corundum structure like that of α-Al₂O₃, Fe₂O₃, Ti₂O₃, etc. This structure can be described as a hexagonal close pack array of oxygen atoms with metal
Table III. Known Properties of Chromium Oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>O/Cr Ratio</th>
<th>Structure</th>
<th>Lattice, Å</th>
<th>Density</th>
<th>Melting Point, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃</td>
<td>1.33</td>
<td>cubic A-15 (β-W type)</td>
<td>a = 4.54 Å</td>
<td>m = 3</td>
<td>--</td>
</tr>
<tr>
<td>Cr₂O₅</td>
<td>1.50</td>
<td>rhomb. D5, carborund.</td>
<td>a = 5.35 Å</td>
<td>m = 2</td>
<td>2435 (Dec.)</td>
</tr>
<tr>
<td>Cr₂O₆</td>
<td>2.00</td>
<td>tetrag. (rutile)</td>
<td>a = 4.41 Å</td>
<td>m = 2</td>
<td>300</td>
</tr>
<tr>
<td>Cr₅O₁₂</td>
<td>2.4</td>
<td>orthorh.</td>
<td>a = 12.04 Å</td>
<td>b = 8.21 Å</td>
<td>c = 8.18 Å</td>
</tr>
<tr>
<td>Cr₂₅O₆₁</td>
<td>2.44</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cr₂₇O₅</td>
<td>2.5</td>
<td>orthorh.</td>
<td>a = 8.47 Å</td>
<td>b = 12.90 Å</td>
<td>c = 10.08 Å</td>
</tr>
<tr>
<td>Cr₇O₉₃</td>
<td>2.65</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cr₃O₈</td>
<td>2.66</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CrO₃</td>
<td>3.0</td>
<td>Orthorh.</td>
<td>a = 5.743 Å</td>
<td>b = 8.567 Å</td>
<td>c = 4.789 Å</td>
</tr>
<tr>
<td>Oxide</td>
<td>Notes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₃O₇</td>
<td>little details of properties known.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₃O₂</td>
<td>few details of properties known.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrO</td>
<td>does not exist in state state, exists in solid solutions only.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₃O₄</td>
<td>metastable, identified and stabilized as FeCr₂O₄ or NiCr₂O₄, etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>stable, frequently found in hydrated form.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₂O₂</td>
<td>metastable, decomposes to Cr₂O₃ at 447°C, metal like conductivity.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₅O₁₂</td>
<td>formed under high pressure at 227°C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₂₅O₆₁</td>
<td>formed by decomposition of CrO₃ at 600 bar and 237°C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₂O₅</td>
<td>formed under 1 Kbar at 217°C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₂₀O₅₃</td>
<td>formed by decomposition of CrO₃ in Air at 267-297°C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr₃O₈</td>
<td>formed by decomposition of CrO₃, decomposes at 337°C.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrO₃</td>
<td>semiconductor, absorbs moisture.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 38 Proposed phase diagram for chromium-oxygen system. Data is from composite sources 71-78 using the basic diagram presented by Goldschmidt. 69
in only 2/3 of the octahedrally coordinated interstices. In this way each chromium atom is thus coordinated by six oxygen atoms, each of which are surrounded by four chromium atoms.

Self diffusion experiments concluded that in Cr₂O₃ chromium ions diffuse about 1000 times faster than oxygen ions. So the controlling mechanism for oxidation in an oxygen atmosphere is transporting chromium to the free surfaces to combine with adsorbed oxygen. For oxidation of black chrome in a vacuum, assuming this happens, free oxygen ions would have to be present in the black chrome structure. Also the presence of water may help accelerate oxidation by serving as an ion transport media.

In Cr₂O₃ the diffusion coefficient of Cr is given by: \( D_{cr} = D_0 \exp(-\Delta H/RT) \), \( \text{where } \Delta H = 100 \text{Kcal/mole and } D_0 = 4 \times 10^3 \text{ cm}^2/\text{sec, for sintered specimens in air and inert atmospheres. These samples were thought to be somewhat porous. For hot pressed samples } D_{cr} \text{ differs with the sintered specimens but agrees with recent single crystal studies. The diffusion parameters for hot pressed samples are } \Delta H = 61.1 \text{ Kcal/mole and } D_0 = 1.67 \times 10^{-1} \text{ cm}^2/\text{sec. All of these values are valid over, roughly, the 1000 - 1500°C temperature range. At lower temperatures, of interest in black chrome, it is not known if the same mechanisms of diffusion hold as for high temperatures. Electrical conductivity measurements may help elucidate this point.} \)
The diffusion of oxygen in Cr$_2$O$_3$ is also of interest. The diffusion parameters are, $\Delta H = 100.8$ Kcal/mole and $D_0 = 15.9$ cm$^2$/sec. This data was obtained with $^{18}$O tracers at 16625 Pa over the range 1200-1500°C, see Figure 5. The consensus of opinion is that chromium diffusion is independent of external oxygen pressure over the entire homogeneity range of Cr$_2$O$_3$. Also, the presence of impurities may alter the defect concentration and subsequent diffusion properties.

C. Tarnish Oxidation of Nickel

Nickel has only one stable oxide, NiO, involved in the oxidation process. The dependence upon oxygen pressure is $P_0 = 1/6$, which follows the Wagner Theory. Pore structures are known to form in NiO as a result of insufficient plastic flow of the oxide. As a consequence of the oxidation process voids are formed near the parent metal. NiO is known as metal deficient, p-type semiconductor. It forms by cation and electron diffusion, somewhat similar to Cr$_2$O$_3$, with metal ions migrating to a source of chemiabsorbed oxygen. It is possible that the black chrome over layer at high temperatures transfers oxygen ions to the nickel interface. This premise is founded because chromium undergoes oxidation near the nickel interface at high temperature (discussed in the following sections). Also it is expected that nickel ions will interdiffuse into the black chrome layer.

Oxidation of nickel follows a logarithmic law up to 300°C (where $L_0 = 1-2\text{Å}$), above which it follows a cubic law to 400°C and finally becomes parabolic at high temperature.
D. Side Reactions Due to Interdiffusion or Impurities

Various side reactions can take place which complicate black chrome oxidation. Carbon is noted as an impurity in black chrome. It appears to have very little to do with the energy absorptive process of the coating since very selective Cr-Cr$_2$O$_3$ cermets have been prepared without carbon. The most likely chromium carbides might be Cr$_7$C$_3$ or Cr$_3$C$_2$; however, they are known to form between 550-1200°C. In this study carbide has not been identified from electron diffraction.

The presence of carbon can play an important role in black chrome degradation in air. If CO or CO$_2$ is formed, it has the effect of breaking up the oxide. In this manner the effective oxidation rate is increased. The outgassing of CO and CO$_2$ might explain surface eruptions seen in heat treated black chrome (refer to next section). Recent outgassing experiments have verified that both CO$_2$ and CO are given off at the surface.

Another consideration is the NiO-Cr$_2$O$_3$ system. The cubic form of NiCr$_2$O$_4$ is noted to form in vacuum at high temperatures (see next section). However, it has been observed that under certain conditions below 660°C, NiCr$_2$O$_4$ decomposes to NiO and Cr$_2$O$_3$. Although it is believed that NiCr$_2$O$_3$ may exist at lower temperatures. The presence of this spinel phase appears to hinge on the presence of NiO. At room temperature an oxide layer of 10-50Å can be found on nickel, thicker at higher temperatures.
If the CO and CO₂ formation is considered here also, it is easy to see how the nickel substrate can be oxidized even through a black chrome overlayer.

Also of importance are hydrated reactions. Since Cr₂O₃ has an affinity for water, it is necessary to examine any possible reactions which might take place. In many oxides the presence of water accelerates oxidation kinetics. Principally three reactions have been observed for Cr₂O₃ • nH₂O. For low H₂O pressures and temperatures below 700°C, Cr(OH)₃ can form. Over the interval 70°C-500°C, CrOOH prevails and above 500°C, Cr₂O₃ is the favored phase. Earlier in this study it was stated that even above 600°C water was still present in Cr₂O₃; possibly it is in the free form. Both infrared and secondary ion mass spectroscopy might be viable techniques to investigate the presence of water and ions in black chrome. Recently it has been suggested that CrOOH may play an important role in the degradation of this coating. However, the Cr(OH)₃ phase should be considered also.
VII. THERMAL STABILITY OF BLACK CHROME

The stability of the black chrome absorber is a very important issue. One of the justifications for using this coating is its assumed stability, at least below 300°C. It is necessary to understand the effect of stagnation events, humidity, and long term thermal aging in both air and vacuum atmospheres. The quality of the vacuum commonly used in evacuated collectors is about 10^{-4} Torr or less. Higher vacuums are of little interest to the commercial manufacturers. However, for detailed oxidation studies, a range of vacuum conditions must be employed. Very high vacuum atmospheres are required to determine if other mechanisms in addition to oxidation play an important role in the degradation of black chrome.

The following work focuses upon the influence of short term heat treatments in both dry air and medium vacuum, 1.3x10^{-1} - 1.3x10^{-3} Pa (10^{-3} - 10^{-5} Torr) on microstructure and optical properties of black chrome.

A. One Hour Heat Treatments and In Situ Hot stage Microscopy.

Heat treatments ranging from 200°C - 700°C were performed on encapsulated and air exposed specimens. Hot stage transmission electron microscopy was employed to view in situ annealing under medium vacuum conditions.

1. Spectral reflectance.

In Table IV and V values for \( a_1 \) and \( e_1 \) are tabulated for various short term heat treatments. The data shown in Tables IV and V is derived in part from the curves shown in Figures 39 - 41. For
Table IV. Integrated Absorptance and Emittance (27°C) for Heat Treated Black Chrome in Vacuum**

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>$e_i$</th>
<th>$a_i$</th>
<th>$a_i/e_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None, as plated</td>
<td>0.12</td>
<td>0.93</td>
<td>7.75</td>
</tr>
<tr>
<td>200°C, 1 hr.</td>
<td>0.11</td>
<td>0.93</td>
<td>8.45</td>
</tr>
<tr>
<td>300°C, 1 hr.</td>
<td>0.11</td>
<td>0.93</td>
<td>8.45</td>
</tr>
<tr>
<td>400°C, 1 hr.</td>
<td>0.12</td>
<td>0.94</td>
<td>7.83</td>
</tr>
<tr>
<td>500°C, 1 hr.</td>
<td>0.08</td>
<td>0.92</td>
<td>11.5</td>
</tr>
<tr>
<td>600°C, 1 hr.</td>
<td>0.08</td>
<td>0.8</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Values rounded to 2 places.

**Residual atmosphere is inert gas.

Table V. Integrated Absorptance and Emittance (27°C) for Heat Treated Black Chrome in Dry Air.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>$e_i$</th>
<th>$a_i$</th>
<th>$a_i/e_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None, as plated</td>
<td>0.12</td>
<td>0.93</td>
<td>7.75</td>
</tr>
<tr>
<td>200°C, 1 hr.</td>
<td>0.11</td>
<td>0.93</td>
<td>8.45</td>
</tr>
<tr>
<td>300°C, 1 hr.</td>
<td>0.09</td>
<td>0.93</td>
<td>10.3</td>
</tr>
<tr>
<td>400°C, 1 hr.</td>
<td>0.10</td>
<td>0.93</td>
<td>9.3</td>
</tr>
<tr>
<td>500°C, 1 hr.</td>
<td>0.07</td>
<td>0.90</td>
<td>12.86</td>
</tr>
<tr>
<td>600°C, 1 hr.</td>
<td>0.10</td>
<td>0.73</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Values rounded to 2 places.
Figure 39  Hemispherical spectral reflectance for black chrome heat treated in dry air over the 300 - 500°C range.
Figure 40  Hemispherical spectral reflectance for black chrome in vacuum, $1.3 \times 10^{-1}$ Pa with nitrogen background gas.
Figure 41 Hemispherical spectral reflectance for both black chrome annealed in dry air and vacuum (1.3 x 10^{-1} Pa) at 500, 600°C.
samples heat treated below 300°C the reflectance plots are fairly identical and resemble the reflectance shown in Figure 27 (Sample H4N). Black chrome whether heat treated in air or vacuum for short periods of time appears to exhibit the same characteristic reflectance. A major change in reflectance is noted between the 500°C and 600°C ranges and it appears to be accelerated by presence of oxygen (Figure 41). However, up to and including the 500°C range the basic reflectance only exhibits subtle variations.

All samples tested show a characteristic second maxima centered between 1-3 microns. It is fortunate that this maxima occurs close to the cutoff wavelength for the solar and blackbody spectra. That is, reflectance variations near the cutoff wavelength would have only a slight effect on the $a_1$ and $e_1$ values, as shown in Tables IV and V. This maxima becomes fairly pronounced at 300°C and subsequently grows in amplitude with increasing temperature. The presence of air accelerated its growth. The existence of this maxima might be partially explained as a thickness interference effect with its amplitude and position dictated by effective index of refraction and coating thickness, respectively. That is to say the coating appears more dielectric-like and thinner with higher temperature heat treatments. Also the metal-like interfacial region predominates, effectively lowering infrared emittance.

Another phenomena is observed from 300°C - 500°C. At 400°C a noticeable shift of the transition region occurs toward the infrared wavelengths. At 500°C this region shifts back towards the visible
region, the overall displacement being about 1 micron in wavelength. It is quite possible that structural changes are taking place within the coating to account for this.

Finally a minor infrared absorption, at about 20 microns, is noted commencing with the 400°C samples. This absorption is characteristic of crystalline Cr₂O₃.²⁹

To help explain these observed effects it is important to determine chemical and structural changes upon heating within the coating. This will be shown with the aid of both scanning and transmission electron microscopy.

2. Scanning Electron Microscopy

Typical surface microstructures are depicted in Figure 42 for all short term heat treatments ranging from as-plated to 600°C. By comparing the as-plated structure (Figure 42a) with the 400°C and 600°C samples (Figures 42b,c) an increase in surface roughness and particle size, including what appears to be a second phase oxide, has evolved at the higher temperatures. In all cases the surface structure exhibits a porous network of particles, like a sintered powder. From the as-prepared to 200°C range of samples the particle size varies from 0.05-0.30 microns in diameter, with the smaller particles comprising the peak distribution. Beginning at 300°C larger particles, probably an oxide phase (crystalline Cr₂O₃), become apparent. At 400°C particles as large as 1 micron are noticed although the average size is around 0.10-0.20 microns.
Figure 42 Black chrome examined by SEM at 20 kV after 1 hour annealing. (a) typical surface structure for 270 - 200°C heat treated samples (b) structure for 400°C heat treated specimens; notice the formation of white oxide particles (c) structure after 600°C anneal, showing the growth of oxide particles.
Finally, at $600^\circ C$ particle sizes in excess of 1 microns are observed, and the second phase now makes up a significant area of the surface structure. As this second phase grows, the surface tends to roughen. The presence of these second phase particles probably accounts for part of the complex reflectance at $600^\circ C$.

The effect of air upon the surface structure is not very noticeable until $600^\circ C$. Above $600^\circ C$ the coatings peeled off the samples heated in air, while samples heated in vacuum withstood $700^\circ C$ for one hour and $800^\circ C$ for 20 minutes. All coatings form erupted regions as shown in Figure 43 which are responsible for mechanical failure above $400^\circ C$, and which become very apparent at $600^\circ C$. These regions appear as glassy phases in the form of either black or white blotches as seen by the TEM (Figure 43a). Some areas appear as if gas has escaped (Figure 43c) while others appear unaffected (Figure 43d). EDAX analysis was performed on a peeled region, shown in Figure 44. Although the actual x-ray generation depth is unknown the top region appears to contain the bulk of the chromium. The interface region shows oxide particles and porosity along with high nickel content. This indicates that the chromium at the interface has migrated closer to the surface. It may be oxidized as well. For further analysis of the internal structure Transmission Electron Microscopy must be employed.

3. Transmission Electron Microscopy

Black chrome on nickel plated copper samples were ion thinned so each sample could be analyzed by conventional TEM techniques. Care
Figure 43 Black chrome on nickel heat treated at 500°C, 1 hour in air (revealed by SEM at 20 kV): (a) typical region white and dark degraded regions, (b) white erupted region, (c) dark erupted area, (d) unaffected area showing surface particles.
Figure 44  Heat treated peeled off black chrome coating (600°C in air, 1 hour) viewed by SEM at 20 kV: (a) top surface showing the presence of chromium and nickel (b) bottom surface (nickel interface) composed principally of nickel. White grains are an oxide phase.
was taken to ensure that the ion thinned samples were not altered or heated appreciably during thinning (see Appendix I).

The vacuum annealed structure is identical to the as-prepared structure up to 400°C; starting at 400°C-500°C the appearance of crystalline, Cr$_2$O$_3$ is noted, identified from the diffraction pattern in Figure 45. No appreciable decline in chromium content is noted; some agglomeration of chromium is apparent, however. At 600°C many lines of Cr$_2$O$_3$ can be identified from the diffraction pattern in Figure 46 along with a new phase NiCr$_2$O$_4$ or Cr$_3$O$_4$, a high temperature spinel. NiCr$_2$O$_4$ is the most probable phase since there is some doubt as to the existence of pure Cr$_3$O$_4$. At 600°C in air, only Cr$_2$O$_3$ is noted in the diffraction pattern as shown in Figure 47.

These conclusions are based on 6 identified lines of Cr$_2$O$_3$, 6 lines of the phase identified as NiCr$_2$O$_4$ and 1 faint line of chromium at 600°C vacuum heat treatments and 12 lines of Cr$_2$O$_3$ for air annealing. At even higher temperatures these phases predominate at the expense of metallic chromium which finally depletes. The oxygen deficient phase, NiCr$_2$O$_4$ must be favored thermodynamically to form in vacuum because for 600°C and 700°C, 1 hour heat treatments in air only Cr$_2$O$_3$ formed. However, this spinel phase is of minor consequence because for all practical purposes the coating has failed between 500-600°C when heated for short periods of time. Typical particle shapes and distributions are shown in Figure 48b for NiCr$_2$O$_4$ and Figure 48c for Cr$_2$O$_3$. This sample was heat treated at 600°C for 1 hour.
Figure 45  Typical diffraction pattern for 1 hour heat treatment at 400 and 500°C vacuum and air. Low order Cr$_2$O$_3$ and Cr rings are noted along with a diffuse halo region.
Figure 46 Diffraction pattern for vacuum (1.3 x 10^{-3} Pa) annealing at 600°C for 1 hour. Shown are low order NiCr$_2$O$_4$ and Cr$_2$O$_3$ with fair Cr lines. Experiment performed in microscope.
Figure 47  Diffraction pattern for 1 hour air annealed samples at 600°C upwards. Only Cr₂O₃ is present here.
Figure 48  Morphology of black chrome after 1 hour heat treatment at 600°C as viewed by TEM at 100 kV.

(a) Bright field showing particulate coating.
(b) Dark field of region (a) showing bright white spots as NiCr2O4.
(c) Dark field of region (a) showing Cr2O3.
All samples annealed in air up to 300°C exhibit similar morphology and composition to the as-plated structure. At 400°C and higher temperatures, the diffraction pattern for the coating revealed 4 lines of crystalline Cr₂O₃ along with crystalline chromium. These lines in general were more intense than those for vacuum annealed specimens. This may indicate that the amorphous to crystalline transformation of Cr₂O₃ is aided by the presence of air, essentially lowering the transformation temperature.

B. Hundred Hour Heat Treatments

Heat treatments ranging from 300-500°C were performed for 100 hours on both air exposed and vacuum encapsulated, 1.3x10⁻¹ Pa (10⁻³ Torr) samples. These experiments simulated the heating effects of a concentrating collector stagnation condition. In all cases an ion thinning technique was employed to produce microscope samples. Conventional electron microscopy was used to view the specimens.

During heat treatments various color changes were noted for the samples. The general color trend with heating was first black, becoming blue, then tan or brown and finally becoming a metallic greenish yellow. The corresponding temperatures at 100 hours for air are: 300°C (black), 400°C (bluish-tan), 500°C and above (metallic greenish-yellow). For vacuum the same sequence is observed, except at about 100°C higher in each case.
1. Spectral Reflectance

Data for integrated absorptance and total normal emittance are shown in Tables VI and VII. Spectral reflectance for the visible and infrared region is shown in Figure 49.

Several generalizations can be made from this data. With higher temperature heat treatments the emittance decreases corresponding to a more metal-like nature of the coating (from the substrate). The solar absorption is unstable and declines with time and increased with temperature. The presence of air accelerates degradation. It is assumed that the residual atmosphere of the encapsulated specimens contains some oxygen or the black chrome structure has trapped oxygen in it.

In terms of spectral reflectance the coating has degraded radically at 500°C in air and to a lesser extent in vacuum. Likewise, the 400°C vacuum data was so close to the 300°C air data they were plotted on the same curve. An interesting point here is that the reflectance response for the 500°C runs appear to be similar to the predictions for Maxwell Garnett modelling of a uniform distribution of particles in a matrix.

2. Electron Microscopy

Scanning electron microscopy reveals a surface structure for all samples much like those depicted in Figure 42, except that Figures 42, a, b and c would represent respectively, 300°C, 400°C, and 500°C, 100 hour treatments.
Table VI. Integrated Absorptance and Average Emittance (27°C) for Heat Treated Black Chrome in Dry Air.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>( e^+_tn )</th>
<th>( e_t )</th>
<th>( a_t )</th>
<th>( a_t/e^+_tn )</th>
<th>( a_t/e_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>None, as-plated</td>
<td>0.11</td>
<td>--</td>
<td>0.94</td>
<td>8.5</td>
<td>--</td>
</tr>
<tr>
<td>300°C, 100 hrs</td>
<td>0.08</td>
<td>0.08</td>
<td>0.89</td>
<td>11.1</td>
<td>11.1</td>
</tr>
<tr>
<td>400°C, 100 hrs</td>
<td>0.11</td>
<td>0.10</td>
<td>0.86</td>
<td>7.8</td>
<td>8.6</td>
</tr>
<tr>
<td>500°C, 100 hrs</td>
<td>0.09</td>
<td>0.09</td>
<td>0.74</td>
<td>8.2</td>
<td>8.2</td>
</tr>
</tbody>
</table>

*Total Normal Emittance

Values rounded to two places

Table VII. Integrated Absorptance and Average Emittance (27°C) for Heat Treated Black Chrome in Vacuum (10^-3 Torr), Evaporated**

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>( e^+_tn )</th>
<th>( e_t )</th>
<th>( a_t )</th>
<th>( a_t/e^+_tn )</th>
<th>( a_t/e_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>None, as-plated</td>
<td>0.11</td>
<td>--</td>
<td>0.94</td>
<td>8.5</td>
<td>--</td>
</tr>
<tr>
<td>300°C, 100 hrs</td>
<td>0.09</td>
<td>0.08</td>
<td>0.90</td>
<td>10.0</td>
<td>11.3</td>
</tr>
<tr>
<td>400°C, 100 hrs</td>
<td>0.08</td>
<td>0.08</td>
<td>0.87</td>
<td>10.9</td>
<td>10.9</td>
</tr>
<tr>
<td>500°C, 100 hrs</td>
<td>0.08</td>
<td>0.07</td>
<td>0.80</td>
<td>10.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

* Total Normal Emittance

** Residual gas is principally argon

Values rounded to two places
Figure 49 Spectral reflectance of black chrome annealed for 100 hours at various temperatures and conditions.
Transmission electron microscopy shows continuous $\text{Cr}_2\text{O}_3$ grain growth for progressively higher temperature treatments. A sequence of diffraction patterns is shown for various conditions in Figure 50. Notice that the diffraction patterns became more intense and spotty with higher heat treatments and air annealed samples. This signifies larger diameter $\text{Cr}_2\text{O}_3$ particles. In all experiments $\text{Cr}_2\text{O}_3$ was the principal phase noted (at least 15 lines identified); for some $300 - 400^\circ\text{C}$ treatments residual chromium was also identified.

Representative $\text{Cr}_2\text{O}_3$ particle sizes are shown in Figures 51 and 52. Contrasting cases are depicted for $400^\circ\text{C}$ heat treatments. In vacuum annealing the particles are smaller than shown for air annealed specimens. Finally, the most degraded specimen, $500^\circ\text{C}$ in air, is shown in Figure 53; here, very large particles of $\text{Cr}_2\text{O}_3$ can be noted.

The formation of crystalline $\text{Cr}_2\text{O}_3$ follows an interesting sequence of events according to diffraction pattern analysis and in situ heat treatments. First, only chromium rings and two amorphous halos are present. After heating for $300^\circ\text{C}$ for 100 hours or $400^\circ\text{C}$ for one hour, lines of $\text{Cr}_2\text{O}_3$ are noted. The prominent ones originate from the lowest order halo; they are $\text{Cr}_2\text{O}_3$ (104) and $\text{Cr}_2\text{O}_3$ (110) at 2.666Å and 2.480Å. At higher temperatures or times the other lines of $\text{Cr}_2\text{O}_3$ appear with no missing rings. The three faintest rings are, (006), (202) and (122) at 2.264, 2.048 and 1.579Å, respectively.
Figure 50 Diffraction patterns for heat treated black chrome. Intensity and spottiness of patterns increases with temperature.
(a) 300°C for 100 hours in either air or vacuum.
(b) 500°C for 100 hours in vacuum or 400°C for 100 hours in air.
(c) 500°C for 100 hours in air.
Figure 51 Transmission electron micrographs taken at 100 kV for 400°C 100 hour treatment in vacuum.
(a) Bright field.
(b) Dark field showing Cr_2O_3 particles.
Figure 52  Electron micrographs for 400°C samples annealed for 100 hours in air.
(a) Bright field.
(b) Dark field depicting Cr₂O₃ particles. Compare this to Figure 51b.
Figure 53 Dark field transmission electron micrograph with corresponding diffraction pattern for 500°C, 100 hour heat treated black chrome in vacuum.
To construct a model for black chrome degradation more extensive information is needed from depth profiles and supplementary experiments such as secondary ion mass spectroscopy.

3. Auger depth profile

Some Auger depth profile data is available for heat treated black chrome, but as yet no detailed study exists. What is required is a sequence of depth profiles for various annealing times and temperatures. This would certainly help to elucidate the electron microscopy studies.

Short term, 2 hour heat treatments were performed by Honeywell. They found that Harshaw black chrome does oxidize at $10^{-4}$ Pa and after annealing, about half of the carbon had left this coating, probably as CO or CO$_2$. They observed a linear increase of oxygen to chrome ratio up to $450^\circ C$ at the surface of the film. Internally, the film should show oxidation at $400^\circ C$ and above. Above $500^\circ C$ the nickel interface region also oxidizes. From their data it appears that metal ions start migrating to the surface at $500^\circ C$ and above.

Data for 70 hours in air also exist, obtained by investigators at Sandia. In Figure 54 their data is presented for comparison with Figure 31. Basically, the effect of air annealing at $350^\circ C$ is to increase oxidation throughout the coating and to redistribute chromium. Nickel diffusion is not noted for this relatively low temperature.
HEAT TREATED HARSHAW BLACK CHROME ON NICKEL.

350°C for 70 hrs in Air

Figure 54 Typical Auger depth profile for Harshaw black chrome heat treated at 350°C for 70 hours in air. Chromium is redistributed and further oxidation has occurred compared to the as-plated profile. (Data from Pettit at Sandia Labs)
C. Microstructural Model

From combined information about the microstructure and chemical depth profile, an artists model can be generated for the degradation of black chrome. Basically, the degradation mechanism appears to be the nucleation of oxide grains from an amorphous matrix or growth of grains from an ultrafine oxide. As this phase grows it consumes metallic chromium. Chromium diffuses at high temperatures, thereby reducing the grading effect. Also, the film appears to be densifying and outgassing CO and CO$_2$ and water vapor. It is unknown if black chrome outgasses heavy species such as chromium hydrides or oxides. Finally, at temperatures about 500$^\circ$C for long times, the coating appears as a crystalline oxide. A schematic is shown in Figure 55 of black chrome after heat treating in air at about 400$^\circ$C for 100 hours. Depicted here is the general degradation trend in black chrome.
Figure 55  Schematic of degraded black chrome at approximately 400°C in air or 500°C in vacuum for 100 hour heat treatment.
VII. CONCLUSIONS

The conclusions consist of two parts, the first summarizing the knowledge obtained from this study. The second half deals with recommendations for further work, along with problem areas which require further scrutiny.

A. Summary

Details of solar thermal energy utilization were discussed along with the virtues of using a selective absorber such as black chrome. Black chrome exhibits superior properties as an absorber and these were poorly understood in terms of what is known about selective absorbers in general, so a microstructural study was in order. Then, too, questions about its short term stability had to be answered. The starting point was the familiar electrodeposition process for metallic chromium. By comparing chromium deposition to that of black chrome, it was found that \( \text{Cr}_2\text{O}_3 \), an amorphous or very fine crystalline phase behaves as an impurity in chromium deposition. Frequently, an oxide is found in a hydrated form which is suspended in black chrome. Also, it was noted that black chrome can be deposited using a simple chromium deposition bath free of sulfate. After deposition of chromium, hydrides are known to exist but they are unstable and decompose to metallic chromium; this may happen also in black chrome.

To obtain a better understanding of the black chrome deposit electron microscopy was employed. As a result, it was found that the intermediate nickel layer exhibited a rough columnar structure with some macroscopic cracking. Black chrome appears as a partially
sintered powder overlayer, essentially replicating the nickel substructure. After a microscope sample making process was devised, transmission electron microscopy was employed to view the internal structure, necessary for theoretical modelling. The following information was revealed. The structure of black chrome on nickel consists of porosity and spherical particulate material resembling a sintered powder in the size range of 0.05 - 0.30 microns in diameter. These particles consist of even finer chromium grains with mean diameter of 139Å. The smaller particles are surrounded by an amorphous or very fine chromium oxide, Cr₂O₃. Also, large chromium particles appear as aggregates of finer particles. Spectral reflectance measurements show that the optical response of black chrome is dependent upon layer thickness, substrate roughness and somewhat upon substrate material. By incorporating Auger and XPS data a chemical profile of the black chrome coating is obtained, although sputtering effects cloud the exact profile. With this combined information the microstructural model is presented: black chrome consists of roughly three different regions, (1) a thin oxide, Cr₂O₃ top layer; (2) a graded intermediate Cr₂O₃-Cr cermet and; (3) a Cr - Cr₂O₃ cermet dominated with Cr and interfacial metal. In all layers Cr₂O₃ is in the amorphous or very fine crystalline form. Basically, the absorber operates as follows: the top layer serves an antireflective and protective oxide layer. The intermediate layer serves as the solar absorbing medium. The interfacial region appears metallic and provides the infrared reflector. It must be noted that these layers are
not ones with easily defined interfaces, but are graded regions with optically different characteristics. The absorber layer is best modelled, although not conclusively, using the metal rich Maxwell Garnett theory. Actually, the microstructure is too complex to be described adequately as a simple effective medium.

Procedures used in these experiments consisted of annealing in both air and medium vacuum to simulate operating conditions that the absorbers might experience. Also, by using high temperatures various degradation mechanisms could be suggested.

It was concluded that black chrome for 100 hour heat treatments shows minor instability below $300^\circ C$ in air and $400^\circ C$ in vacuum and degrades at $400^\circ C$ and above in air and $500^\circ C$ or above in vacuum. The major mode of degradation appears to be diffusion controlled oxidation in all cases including vacuum. Diffusion of oxygen may be enhanced by outgassing of CO and CO$_2$ at high temperatures. Their emanation acts to break up the coating, thereby providing paths for preferential diffusion. Metallic chromium is depleted in the process of nucleation and growth of Cr$_2$O$_3$ crystals. Crystallites of Cr$_2$O$_3$ have been observed growing on the surface of black chrome at high temperatures and this is to be expected, considering the porous nature of the coating. With time the coating appears to be densifying, giving the absorber a metallic like nature originating from the substrate.
B. Recommendations

It is first important to realize that this study pioneers an area of research, so many questions are raised as a result.

Demanding clarification, is the specific characterization of a-Cr$_2$O$_3$. Resistivity measurements during annealing could verify true amorphous to crystalline transformation. Optical characterizations in terms of n and k values of this semiconductor material is also necessary; of course, the current problem is making a pure amorphous Cr$_2$O$_3$. High resolution electron microscopy or synchrotron radiation analysis would also reveal the structure of the amorphous phase.

To determine the presence of water in Cr$_2$O$_3$, infrared absorption spectroscopy should be employed. Also, detection of CrOOH and Cr(OH)$_3$ might be possible by analysis of their bond stretching frequencies.

Mechanistic studies are also in order. An ultra-vacuum annealing study will help elucidate the importance of oxidation upon degradation. It is expected that under high vacuum conditions, this coating will not readily degrade except for outgassing and densification. The rate at which certain ionic species migrate and react should be correlated to optical property degradation. This would lead to an overall estimation of the degradation rate at various temperatures and conditions for a more in-depth study; a narrower temperature range should be used for the heat treating experiments. Combined Auger depth profile and electron microscopy are the utmost investigative
techniques for analysis. Rather than sputtering for depth profiling, a mechanical low angle thinning method should be employed or cross sections should be used so Auger spectroscopy can be utilized in the fashion for which it is best suited.

Other degradation effects should be researched, including humidity (currently pioneered by Tom Reitter), ultraviolet and concentrated light. Long term desert sunshine testing is recommended for longer term degradation effects.

Comparative analysis is necessary for different black chromes. The DuPont coating for example should be analyzed in the same manner as in this study.

A new black chrome coating is suggested as a result of this study. The elimination of carbon (restricting the formation of CO and CO$_2$) as an impurity may improve the lifetime of the coating. Also, a more oxidation resistant black chrome might be developed by adding alloying impurities such as TiO$_2$, which is known for reducing oxidation in similar systems. By using the black chrome model it appears that a whole range of cermet coatings can be designed as selective absorbers. Such systems as metal - SiO$_2$, Al$_2$O$_3$ and TiO$_2$ should be investigated.

Going a step further, a selective paint can be developed by use of small suspended particles in an oxide binder, as in black chrome's microstructure. The only drawback is that an infrared transparent binder must be formulated.
ACKNOWLEDGEMENTS

I am grateful to Professor Jack Washburn for his guidance and support throughout this study. I wish to thank my colleagues, Mr. Robert Drosd for his invaluable help with electron microscopy and Mr. George Cunnington of Lockheed for his advice and use of spectral reflectance equipment. I would like to express my appreciation to the entire staff of the Materials and Molecular Research Division along with the various people from outside the division for their continued support and interest.

Special thanks go to my understanding wife, Harue, and my parents Gwen and Gail for their helpful enthusiasm.

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APPENDIX

Beam Heating Effects During Ion Thinning

The influence of sample heating during argon ion thinning was investigated to characterize annealing that a typical specimen might have undergone. In general, this information can be applied to various conductive specimens while non-heat sunk samples can represent effects in thermally non-conductive samples. For black chrome the net result of these experiments verified that annealing damage was negligible for this study.

A. Experimental Procedure

A New Technics micro-ion milling machine (MIM) was used to perform this study. The system was thoroughly cleaned and allowed to pump down for 24 hours before the experiments were performed. Both new and worn (48 hour old) cathode plates were used to characterize the beam heating effect. In this manner the influence of cathode plate wear on beam heating can be determined.

Temperature measurements were accomplished by use of a calibrated thermocouple combined with a digital thermometer. The accuracy of the iron-constantan thermocouple was at least ±0.5°C over the 0 - 400°C. For the digital thermometer accuracy was also ±0.5°C with an absolute display reading to 1°C. Ion current was measured by a built-in probe. Both temperature and current readings were taken under steady state conditions after an appropriate settling-in period.
Special modifications of the stock MIM equipment included a custom entrance port to accommodate and thermocouple probe and an x-y translation sample stage. With this stage, very accurate and reproducible centering of the ion beam will result. The placement of the thermocouple was either 1 cm above the sample holder or directly attached to the holder using a highly conductive silicone heat transfer compound. The position of the sample holder also played an important role. Optimum sputtering occurs at 30° sample angle with respect to the plane of the beam (0° would be along the beam axis). The majority of the data was taken at 30°, however, 15° was also used for one experiment for comparison.

Results and Discussion

The data plots presented in this section were curve fit, using a statistical least squares technique for linear regions; non-linear areas were fit by simple averaging. Approximately 50 data points were used to generate the final curve shown (they have been omitted from the curves for simplicity). Only a minor difference between ion milling at 15° versus 30° for non-heat sunk samples was noted. In general, up to 2kV there was no noticeable difference, between 2-5 kV temperature increases amounted to 5-10°C and from 5-10kV a rise of 10-20°C was noted for 30° samples compared to 15° ones.

Scanning electron micrographs are shown in Figure A1 for the new and old cathode plates. Note the size difference and elliptical distortion of the worn plate. For the worn plate, higher ion currents are necessary to give the same beam heating effect of the new plate.
Figure A1 Ion thinner cathode plate hole
a. Before use
b. 48 hour worn plate
Of course this is due to the spreading of the beam through the larger cathode aperture.

Shown in Figure A2 is data for a new cathode plate and heat sunk sample. The beam heating effects are small compared to that of the non-heat sunk case shown in Figure A3. Beam heating for this case, which could represent a thermally insulating sample, is severe for higher accelerating voltages. For worn plates the beam heating follows a similar relationship as that of the new plates, which can be seen in Figure A4. Since in some investigations gun current is monitored, a graphic relationship with respect to ion current is shown for this apparatus in Figure A5. These curves are approximate.

The limitation of low ion currents for small accelerating voltages shown in these graphs is inherent to the ion thinner. The highest ion currents in each case are close to overload or discharge for this apparatus.

For black chrome, the effect of beam annealing during sample preparation was negligible according to these results.
Figure A2  Sample heating relationship in terms of ion beam current and accelerating voltage for a new cathode plate and 300 sample angle. Specimen is thermally conductive and well heat sunk.
Figure A3 Sample heating for a non-heat sunk sample (simulates a thermally insulating material). A 30° sample angle was used with a new cathode plate.
Figure A4 Beam heating for a non-heat sunk sample. A 30° sample angle was used with a 48 hour worn plate.
Figure A5 Approximate relationship between ion current and gun current for this study. Both new and worn cathodes are represented.
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