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To cite this version:

HAL Id: jpa-00220670
https://hal.archives-ouvertes.fr/jpa-00220670
Submitted on 1 Jan 1981

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THERMAL DEGRADATION OF CERMET SOLAR SELECTIVE ABSORBERS

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Résumé.- Plusieurs absorbeurs sélectifs de type cermet ont été élabo- 
rés soit par électrolyse, soit par des techniques de dépôt sous 
vide. Les principaux mécanismes de dégradation thermique de ces 
cerments ont été étudiés. Pour le chrome noir, une modification de 
la forme des particules semble être à l'origine de la dégradation. 
Pour les carburés et siliciures métalliques, on pense que la dégra-
dation provient d'interactions chimiques entre les divers compo-
sants du cermet. Cette étude permet de définir la structure idéale 
d'un absorbeur sélectif de type cermet.

Abstract.- Several different types of cermet selective absorbers 
have been produced by both electrochemical and vacuum deposition 
techniques. Their most important modes of thermal degradation have 
been studied. For electroplated chromium blacks, the change in the 
shape of the particles seems to be responsible for the degradation. 
For metallic carbides and silicides, degradation is presumed to be 
due to chemical reactions between the components of the cermet. Then, 
the structure of an ideal cermet selective absorber is given.

1. Introduction.- Solar selective absorbing surfaces are generally con-
idered to fall into three major categories, depending upon the mecha-
nism which is responsible for the selective absorption. An absorber may 
have an intrinsic spectral reflectance profile which leads to a high so-
lar absorptance \(a_s\) and low thermal emittance \(e_T\), have surface rough-
ness on such a scale that shorter wavelengths are absorbed and longer 
wavelengths reflected, or it may be a multilayer interference filter 
with the thicknesses and refractive indices of the layers chosen to pro-
duce the effect. Interference filters with excellent solar selective 
absorption properties can be produced by depositing a film which is ab-
sorbing in the solar spectral region but relatively transparent in the 
thermal infrared onto a highly reflecting metal underlayer. Metal-insu-
lator composites, in which metal particles are embedded in an insulating 
matrix (a cermet) are among the relatively few classes of materials 
which can be used as this absorbing layer, however due to their inhomoge-
neity they introduce a further degradation mechanism into the solar 
absorber.

In this article we shall discuss the thermal degradation of seve-
ral different types of cermet selective absorbers produced by both elec-
trochemical and vacuum deposition techniques to illustrate their most important modes of thermal degradation.

Single layer solar selective surfaces usually also employ additional effects to enhance their solar absorptance, such as surface roughness, or a gradient in refractive index through the layer; these effects may also cause a decrease in the absorber's performance after heat treatment and will also be discussed.

The degradation mechanisms of cermet materials may be divided into two classes: physical and chemical. However, although the physical or chemical nature of the cermet may change after heat treatment, significant degradation of the optical properties of the film may not occur. Consequently it is important to identify the parameters which affect solar selective performance.

Possible physical degradation modes in cermets are:
- Changes in metal particle shape
- Growth of particles
- Agglomeration of particles to give long chains
- Densification of the insulating matrix.

Chemical reactions can occur between the components of the cermet, or between the cermet and either the atmosphere or the substrate. These chemical changes may be facilitated if one of the components is metastable, which often occurs in non-equilibrium deposition processes.

Solar selective absorbers are of most interest in collectors which produce low or medium grade heat; consequently they must have a lifetime of at least several months at the stagnation temperature and several years at the operating temperature of the collector in which they are employed. In flat plate type collectors both these temperatures are below 200°C, but in evacuated or focussing collectors they may be as high as 400°C.

2. Cermet films.- Three cermet systems have been chosen for this study: electroplated chromium black films, which are characterized by their very high solar absorptance (> 0.95) and which have a structure which is probably fairly typical of such electroplated blacks, reactively sputtered metal carbide and silicide surfaces deposited in a manner which produces a particulate film, and films prepared by vacuum co-deposition of a metal and dielectric. The latter two selective surfaces have lower solar absorptances but when deposited onto suitable substrates show very low thermal emittances (< 0.05).

2.1. Electroplated chromium blacks.- The selective absorbers produced by electroplating chromium black are probably the most widely commercialized selective surface in use on flat plate type solar collectors. The chromium black film is deposited onto copper or electroplated nick-
el, to a thickness of 200-300 nm /1/ and typically has $a_s > 0.95$ and $0.15 < e_T < 0.25$.

Recent studies of these films have shown that they consist of needle-like particles of chromium oxide, oriented approximately normal to the substrate /2,3/, and that there is a high density of smaller chromium metal particles embedded in the chromium oxide particles. The film is more dense near the substrate than at the surface.

Chromium black films are stable up to about 300°C /1/, but show irreversible degradation (decreases in $a_s$ and $e_T$) at higher temperatures /1/. The principal degradation mechanism appears to be a transformation of the shape of the chromium oxide particles from needle-like to spherical.

**Fig. 1.** Scanning electron micrographs of a chromium black film; left, after preparation; right, after 134 hours at 350°C in air, are shown.

**Fig. 2.** Reflectance spectra as a function of wavelength of the two films in figure 1 are shown (—— as prepared: —— after annealing) together with calculated spectra (—— best fit to as prepared spectrum; —— similar model with spherical particles).

Figure 1 shows scanning electron micrographs of a chromium black film after preparation and after annealing in air at 350°C. The change in shape of the particles is clearly visible; no important chemical phase transitions were observed, nor was there any significant growth in par-
particle size. In figure 2 are shown the reflectance spectra of these two films, together with calculated spectra based on a model of the films /2/. The changes in the essential features of the experimental reflectance spectrum after annealing can be well reproduced in the model by altering the shape of the oxide particles.

This structural transformation occurs as the needle-like particles try to decrease their surface energy and thus become more spherical. A series of fifty, five minute heat cycles to 350°C did not produce any noticeable degradation, whereas an equivalent continuous treatment produces severe decreases in $a_s$ and $e_m$, which also indicates that the degradation mechanism has a physical, rather than chemical origin. The transformation is aided by the low density of the films ($\rho = 3.6 \text{ g/cm}^3$, $\rho_{\text{Cr}} = 7.2 \text{ g/cm}^3$, $\rho_{\text{Cr}_2\text{O}_3} = 5.1 \text{ g/cm}^3$); it is likely that a more dense film would show greater thermal stability, however such an increase in film density would increase the refractive index of the film and hence lower its solar absorptance.

2.2. Reactively sputtered films. Thin films of several of the transition metals, when sputtered in an atmosphere containing a suitable reactive gas (methane or silane) onto metal substrate, can produce solar absorbers with attractive selectivity and high thermal stability /4-7/. These films deposit as a cermetlike composite of the metal carbide or silicide in a porous matrix of carbon or silicon /6,8/, see figure 3.

![Fig. 3.- Transmission electron micrograph of a reactively sputtered Ti-Si film; the metallic particles in a Si matrix can be readily identified.](image)

The dielectric properties of these deposits may be altered considerably
by changing the pressure of the reactive gas in the discharge: low resistivity metallic films composed of small particles of the metallic phase are produced at low reactive gas pressures and high resistivity (∼ 50 Ωcm) dielectric films, where the metallic particles are embedded in the insulating matrix, are produced at high reactive gas pressures.

Consequently, the films may be graded in composition through their thickness by increasing the pressure of reactive gas in the sputter discharge. This has the effect of producing a coating which is more dielectric near the surface than near the substrate, increasing the solar absorbance of the film /9/. Uniform films on copper substrates are stable above 400°C /4,5/ and have $a_s \sim 0.80$ and $e_T \sim 0.03$ whilst graded films are stable up to 400°C /6,7/ and have $a_s > 0.90$ and $e_T \sim 0.05$.

The structure of this class of films was revealed by electron microscopy, and no change in the films', structure could be observed after annealing for a sufficiently long time to cause significant changes in their optical properties. However, the resistivities of the films increased significantly after annealing. Since transition metal carbides and silicides exist over a large range of stoichiometries, it is presumed that heat treatment causes some of the dielectric component of the metallic particles to precipitate out into the insulating matrix, which will result in the observed increase in resistance. Films which are more stable could presumably be manufactured by performing a post-deposition anneal on films which were initially too metallic to produce this precipitation under controlled conditions.

The influence of operating environment is also illustrated by the behaviour of these films; whilst metal silicide films can be produced which are stable in both air and vacuum, metal carbides are only stable in vacuum, degrading rapidly when annealed in air. This degradation is presumably due to the formation of CO$_2$ on the carbide films and the subsequent depletion of carbon from the film, whereas the oxidation or silicon would produce a relatively stable layer on the metal silicide absorbers.

2.3. Vacuum co-deposited cermets.- In an effort to avoid several of the difficulties mentioned above, associated with films having a cermet structure inherent in the deposition method, several workers have produced cermet films by vacuum co-deposition of a metal and a dielectric from separate sources onto a metal substrate /10-13/. The noble metals (Au, Ag, Cu) mainly have been employed, together with either MgO or Al$_2$O$_3$ as dielectric, and these cermet films are often graded in composition to be dielectric near the surface and metallic near the substrate, by changing the relative deposition rates of metal and dielectric during the deposit.

Although these absorbers are more complicated to produce than the
selective surfaces discussed above, the two components can be chosen
to be immiscible, and thus films which are stable up to 500°C /12,13/
have been produced. The volume fraction of the metallic phase in these
cermets can be sufficiently high to lead to particles which are almost
touching and at these temperatures significant agglomeration of the me-
tallic particles can occur /14/ , especially if the film is graded in
composition so that it is metallic near the substrate. Agglomeration of
the metallic particles in a cermet causes it to become more metallic,
as long conducting chains are formed.

Certain metal particles such as those of W or Mo, remain uniformly
dispersed within the dielectric phase even after prolonged annealing
/15/ (although some particle growth does occur) and so cermets such as
these may be sufficiently stable to be used as high temperature absor-
bbers. McKenzie /13/ has suggested that the relative stability of Cr-Al₂
O₃ cermets is due to the reaction of the metal particles with the oxide
matrix to form a stable oxide coating which prevents coalescence and
subsequent degradation of the solar absorption properties of these
films. Unfortunately, little systematic work has been done on solar se-
lective properties of cermet films composed of these more refractory
metals.

3. Conclusion.– From the above examples of the types of thermal degra-
dation which can occur in cermet films, the structure of an ideal cermet
selective absorber emerges. The film would consist of small isolated
spherical metallic particles, sufficiently refractory to resist agglome-
ration, in a dielectric matrix of low refractive index which is immis-
cible with the metallic material. Such a composite would be the most
likely to withstand thermal degradation by the three most common mecha-
nisms: particle shape changes (or densification), precipitation (che-
mmical reaction between the two phases) and particle agglomeration or
growth. Additionally, the film should be deposited by a technique which
is readily and economically adapted to the large area production of
optical-quality films; though the shape of the absorber, either flat-
plate or tubular, may limit this choice.

However it must be recognized that several unstable structures
can increase the solar selective absorptance of cermet films; ellip-
soidal particles and porous matrices are examples. Consequently, a tho-
rough thermal characterization of any cermet selective absorber should
be performed to determine its suitability for a given temperature appli-
cation and collector design.

In conclusion, cermet films deposited onto metal substrates show
attractive solar selective absorption properties but their composite
structure introduces another thermal degradation mechanism. The surfa-
ces should be carefully defined so that this thermal degradation does
not limit the lifetime of the solar collector in which it is used.
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