LBL-8857 C. 2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA, BERKELEY, CA

Materials & Molecular Research Division

Presented at the International Solar Energy Society Meeting, Atlanta, GA, May 28 - June 1, 1979

THERMAL DEGRADATION OF A BLACK CHROME SOLAR SELECTIVE ABSORBER COATING: SHORT TERM

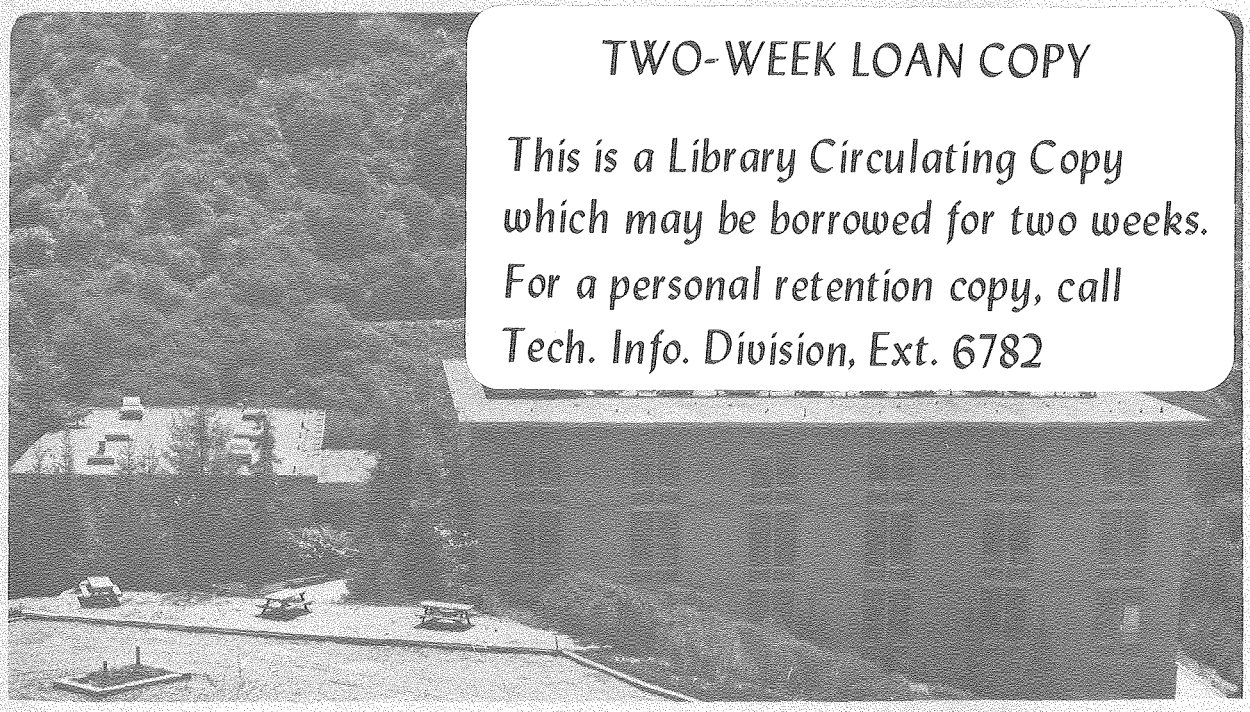
RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUL 9 1979

LIBRARY AND
DOCUMENTS SECTION

Carl M. Lampert

May 1979



TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

LBL-8857 c. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THERMAL DEGRADATION OF A BLACK CHROME SOLAR SELECTIVE ABSORBER COATING: SHORT TERM

by Carl M. Lampert

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Materials Science and Mineral Engineering
College of Engineering; University of California
Berkeley, California 94720 USA

ABSTRACT

Both the energy absorption properties and chemical microstructure of CHROM-ONYX were investigated using electron microscopy and X-ray diffraction techniques. Different temperatures for short annealing times were used to evaluate this coating's temperature resistance limitations along with possible degradation mechanisms for various stagnation situations. Samples were tested in both air and vacuum. As a result, each sample regardless of atmosphere was characteristically similar, with air acting to mildly accelerate optical degradation at higher temperatures. Below 300-400°C black chrome exhibited a structural transformation precipitating Cr_2O_3. Above 500°C this phase grew considerably, while chromium was depleted. At 600°C and above, a new dominant phase developed corresponding to $NiCr_2O_4$, a cubic spinel. However, for all practical purposes black chrome optically degraded between 500-600°C during short exposure times.

1. INTRODUCTION

Black chrome not only is one of the leading selective surface candidates for use in solar collector absorber coatings, but its absorption mechanism is of theoretical importance, also. The commercial coating "CHROM-ONYX", a jet black finish produced by the Harshaw Chemical Company, has been the subject of interest to various investigators and commercial solar collector manufacturers. Although the basic solar selective properties of this material have been investigated (1,2) and life tested relative to other coatings (3-5), very little as yet is known about the relationship between the microstructure and physics of black chrome. However, a simplified absorption mechanism for this coating has been suggested (6) and modeled (7,8), according to modified Maxwell-Garnet theory. Consequently, there is need to clearly identify the actual absorption mechanism and it is necessary to understand the effect of stagnation events, thermal aging, humidity, air and vacuum atmospheres upon solar selectivity and the stability of black chrome. The following study focuses upon the character of as-plated black chrome and the effects of short term heat treatments upon its microstructural and optical properties.

2. EXPERIMENTAL PROCEDURES

In this study copper test panels were electroplated with black chrome by the Harshaw Chemical Company, according to a conventional procedure (9). Throughout this investigation identical samples, consisting of 1.0 micron of black chrome on dull nickel plated copper, were used.

Hemispherical integrated spectral reflectance measurements were used to investigate the optical selectivity of each sample. All reflectance measurements were taken near normal (20°) incidence. Surface morphology was analyzed with the aid of a scanning electron microscope (SEM). Qualitative elemental analysis was determined by energy dispersive X-ray analysis (EDAX). Both conventional and transmission electron microscopy (TEM) and high voltage electron microscopy (HVEM) were employed to analyze the internal structure and chemical makeup of the coating. By use of a heating stage attachment to the TEM it was possible to view the effects of heating upon the morphology and chemistry of black chrome.

Heat treating experiments were performed by one of three methods. Samples heat treated in air were annealed in dry air at 1 atmosphere in a tube furnace. Continuous temperature monitoring and melting point standards were used to assure the accuracy of the heat treatment. Vacuum annealing was carried out either in situ within the TEM hot stage at 10^{-4}-10^{-5} Torr or by vacuum encapsulation. Samples used for spectral reflectance measurements were encapsulated in long quartz ampules. The encapsulation process consisted of pumping the ampules below 10^{-3} Torr, backfilling with argon and resuming pumping. This process was repeated twice and the ampules were sealed off under vacuum.

3. RESULTS AND DISCUSSION

The following treatment is divided into three major categories. The first deals with spectral reflectance measurements; the second, scanning electron microscopy and last, transmission electron microscopy including in situ heat treating. These results will be correlated to form a microstructural and chemical model of the black chrome surface to show how it transforms and degrades during short term heat treatments.

3.1 Spectral Reflectance Measurements

Hemispherical reflectance measurements are used to calculate integrated absorptance, a_i and emittance, e_i.

Table 1

Integrated Absorptance and Emittance (27°) for Heat Treated Black Chrome (Values Rounded).

Heat Treatment	Vacuum		Air	
	a_i	e_i	a_i	e_i
none, as plated	0.93	0.12	0.93	0.12
200°C, 1 hour	0.93	0.11	0.93	0.11
300°C, 1 hour	0.93	0.11	0.93	0.09
400°C, 1 hour	0.94	0.12	0.93	0.10
500°C, 1 hour	0.92	0.08	0.90	0.07
600°C, 1 hour	0.80	0.08	0.73	0.10

In Table 1, values for a_i and e_i are tabulated for 1 hour heat treatments. Corresponding spectral reflectance plots are shown in Figs. 1-3. For samples heat treated below 300°C the reflectance plots are fairly identical.

Black chrome whether heat treated in air or vacuum for short periods of time exhibits 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 slightly by presence of air as shown in Fig. 3. However, up to and including the 500° 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 cut-off wavelength for the solar and black body spectra. That is, reflectance variations near the cut-off wavelength have only slight effect on the a_i and e_i values. 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 explained partially as a thickness interference effect with its amplitude and position dictated by effective index of refraction and coating thickness, respectively.

Another phenomenon is observed between 300°-500°C. At 400°C a noticeable shift of the transition region (2-10 microns) occurs toward the infrared wavelengths. At 500°C this region shifts back towards the visible region; the overall shift equals 1 micron in wavelength. It is quite possible that structural transformations are taking place within the coating to account for this.

Finally, an infrared absorption, at about 20 microns, is noted commencing with the 400°C samples. This absorption is characteristic of crystalline Cr_2O_3.

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.

3.2 Scanning Electron Microscopy

Typical surface microstructure is depicted in Fig. 4 for all short term heat treatments at 600°C. By comparing the as-plated structure with the 600 C sample (Fig. 4) an increase in particle size and surface roughness, including what appears to be a second phase, has evolved at higher temperatures. In all cases the surface structure exhibits a porous network of particles, like a sintered powder. From the as-plated 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, become apparent. At 400°C particles as large as 1 micron are noticed although the average size is around 0.10-0.20 microns for both phases. Finally, at 600°C particle sizes in excess of 1 micron are observed, and the second phase now makes up a significant fraction of the surface structure. As this second phase grows the surface tends to roughen. The presence of these second phase particles may account for part of the complex reflectance at 600°C.

The effect of air upon the surface structure is not very noticeable until 600°C. Above 600°C the coatings peeled off the samples heated in air, while samples heated in vacuum withstood 700°C for one hour and 800°C for 20 minutes. All coatings form erupted regions which are responsible for mechanical failure above 400°C, which becomes very apparent at 600°C. These regions appear as glassy phases either in the form of black or white blotches as seen by the SEM. Energy Dispersive X-ray Analysis was performed on all samples. From this analysis the presence of chromium and nickel (from the substrate) was detected.

3.3 Transmission Electron Microscopy

Black chrome on nickel plated copper samples were ion thinned so each sample could be analyzed by conventional TEM techniques. Care was taken to ensure that the ion thinned samples were not greatly altered or heated appreciably during thinning. Ion thinned samples were compared to chemically etched ones to verify this.

The as-plated structure consisted of a graded mixture of crystalline chromium particles imbedded in an amorphous matrix, presumed to be α-Cr_2O_3, see (9). The presence of the amorphous phase and crystalline chromium was also noted by both TEM and HVEM for chemically and ion milled samples.

The vacuum and air annealed structure is identical to the as-plated structure up to 400° C. Starting at 400-500° C the appearance of crystalline Cr_2O_3 is noted, identified in Fig. 5a; the presence of air promoting growth of these crystallites at a slightly lower temperature than in vacuum. No appreciable decline in chromium content is noted signifying that an amorphous to crystalline transformation is taking place in the matrix oxide.

At 600° -800° C, a new dominant phase forms in vacuum corresponding to $NiCr_2O_4$, previously thought to be Cr_3O_4, shown in Fig. 5b and b. The actual existence and stability of Cr_3O_4 is in doubt. However, the presence of $NiCr_2O_4$ is of little consequence, since for all practical purposes the coating has failed between 500-600° C. The effects of longer periods of time and higher temperatures in both air and vacuum, remain as a current research project.

4. CONCLUSIONS

From this research the following conclusions appear to be valid for short term high temperature heat treatments of CHROM-ONYX.

1. After being heated for a short period of time in air or vacuum, black chrome does not show appreciable degradation optically, chemically or mechanically up to 300° C.

2. The effect of air upon black chrome appears only to mildly accelerate degradation at temperatures above 300° C, when compared to that in vacuum. However, it may be possible that the coating contains trapped oxygen or water.

3. At and above 400° C black chrome exhibits a structural transformation within the matrix material, Cr_2O_3. The metallic chromium distribution appears to be unaffected.

4. Above 500° C after 1 hour heat treatments, this coating shows growth of Cr_2O_3 particles at the expense of the chromium concentration. At even higher temperatures of 600° C in vacuum a new phase $NiCr_2O_4$ predominates.

5. The coating, for practical purposes, optically degrades between 500-600° C after being heated for one hour. In terms of reflectance only minor changes take place above 300° C, although at 400° C infrared absorption can be noted corresponding to Cr_2O_3. All of these transformations appear to be permanent and irreversible.

5. ACKNOWLEDGMENTS

The author wishes to thank Professor J. Washburn, R. M. Drosd, and G. R. Cunnington (Lockheed) for their invaluable assistance during this investigation.

This work was performed at the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory and supported by the Division of Material Sciences Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. W-7405-ENG-48.

6. REFERENCES

(1) McDonald, G. E., Solar Energy 17, 119 (1975).

(2) Lampert, C. M. and Washburn, J., Solar Energy Materials, 1-1, 82 (1979).

(3) Masterson, K. D. and Seraphin, B. O., University of Az. Report, NSF/RANN/SE/FI-36731X/TR/75/1 (May 1975).

(4) Pettit, R. B. and Sowell, R. R., J. Vac. Sci Tech. 13-2, 596 (1976).

(5) Lowery, J. R., Marshal SFC Report, NASA, TMX-3509, (March 1977).

(6) Hogg, S. W. and Smith, G. B., J. of Physics, D 10, 1863 (1977).

(7) Granquist, C. G. and Niklasson, G. A., J. Applied Physics 49-6, 3512 (1978).

(8) Ignatiev, A., Appl. Phys. Lett., 34, 42 (1979).

(9) Lampert, C. M., Proc. of SPIE, Vol 161, SPIE, Bellingham, Wash. (Sept. 1978).

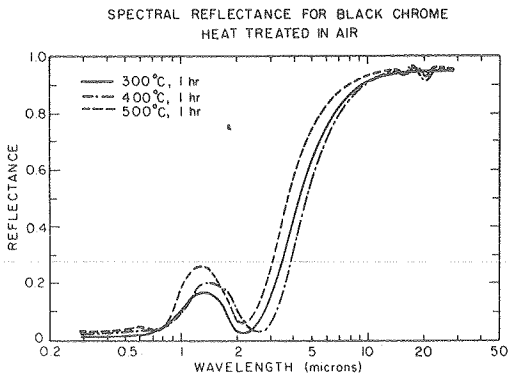


Fig. 1. Spectral reflectance for black chrome heat treated in dry air over the 300-500° C range.

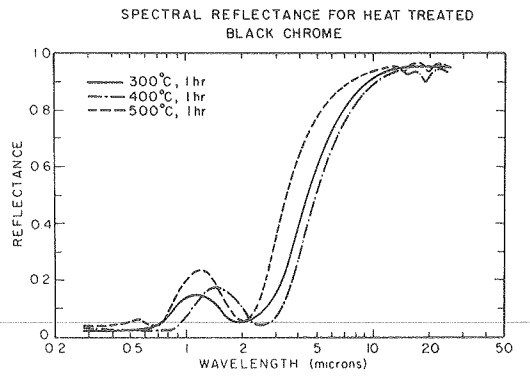


Fig. 2. Spectral reflectance for black chrome heat treated in vacuum over the 300-500 C° range.

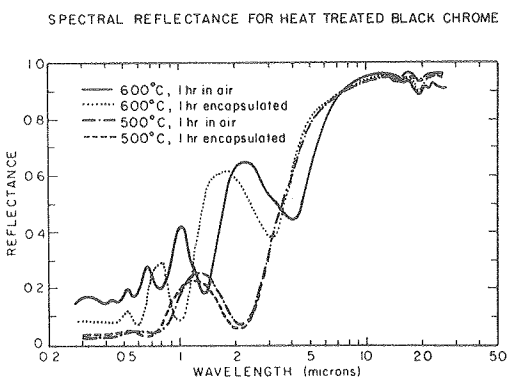
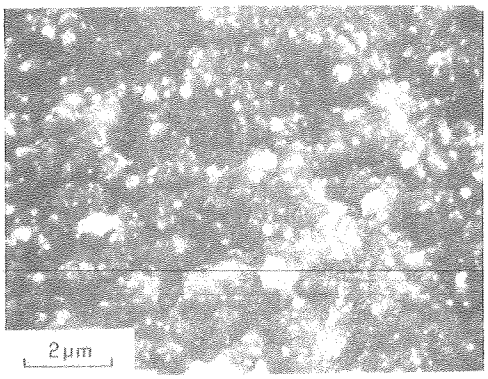
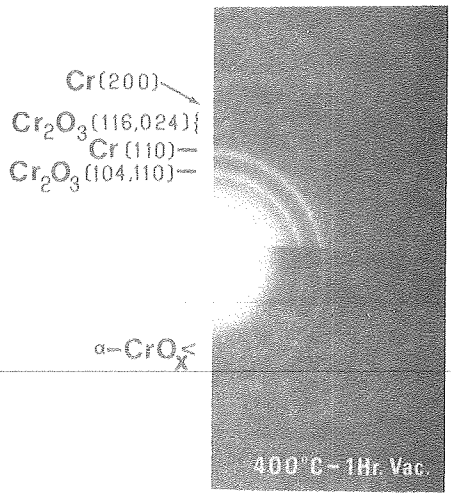


Fig. 3. Spectral reflectance for both black chrome annealed in dry air and vacuum at 500, 600°C.

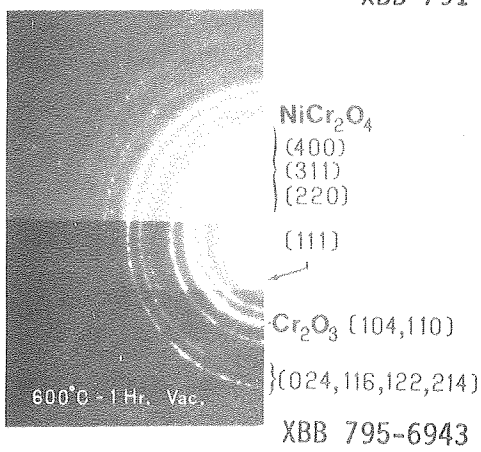


XBB 791-496 C

Fig. 4. Black chrome examined by SEM at 20 kV, 20° tilt after 1 hour, 600°C heat treatment.

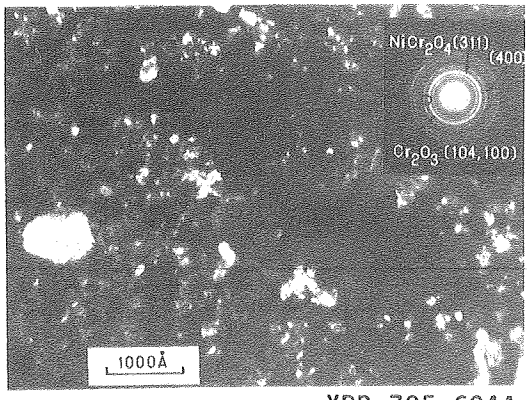


XBB 791-4941



XBB 795-6943

Fig. 5. Typical diffraction pattern for 1 hour heat treatment.
(a) at 400 and 500° C. Low order Cr_2O_3 and chromium rings are noted along with a diffuse halo region.
(b) annealed at 600° C. $NiCr_2O_4$ lines are shown.



XBB 795-6944

Fig. 6. Morphology of black chrome after 1 hour heat treatment at 600° C, viewed by TEM at 100 kV. This dark field shows Cr_2O_3 and $NiCr_2O_4$ particles.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720