10/15/79
3 week

LBL-8632 Rev. c2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

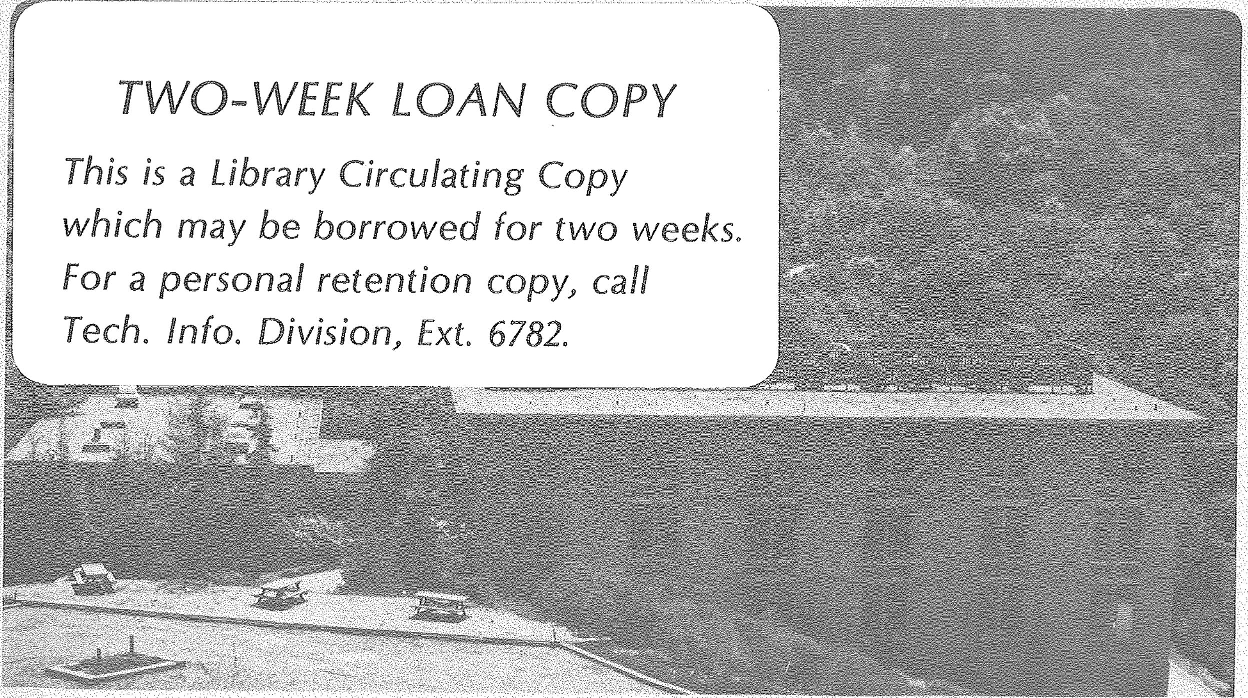
Materials & Molecular
Research Division

To be presented at the Second Annual Conference on
Absorber Surfaces for Solar Receivers, Boulder, CO,
January 24-25, 1979

MICROSTRUCTURE AND OPTICAL PROPERTIES OF BLACK CHROME BEFORE AND AFTER EXPOSURE TO HIGH TEMPERATURES

Carl M. Lampert and Jack Washburn

January 1979



LBL-8632 c2

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

MICROSTRUCTURE AND OPTICAL PROPERTIES OF BLACK CHROME BEFORE AND AFTER EXPOSURE TO HIGH TEMPERATURES

Carl M. Lampert
and
Jack Washburn

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

ABSTRACT

The chemical and microstructural stability of the CHROM-ONYX type of black chrome solar coating was investigated at different temperatures and atmospheres. This was done to give a better understanding of the mechanism of solar energy selectivity and its variability when subjected to short term heat treatments. The as-plated structure was found to consist of a suspension of metallic chromium particles within the size range of 100Å in an amorphous oxide matrix. This assembly was in turn formed into larger particles within the size range of 0.05-0.30 microns. Short term high temperature heat treatments were used to simulate stagnation conditions. Samples were annealed in both air and vacuum, which resulted in similar characteristics. Annealing in air appeared to mildly accelerate optical degradation at high temperatures. For short term heat treatments below 300°C the reflective and microstructural properties appeared to be unchanged. By in situ vacuum annealing of the coating above 400°C microcrystalline Cr_2O_3 was identified. By observation of diffraction patterns it was concluded that a-Cr_2O_3 was transformed into crystalline Cr_2O_3. The Cr_2O_3 phase continued to grow at higher temperatures at the expense of chromium content. At temperatures above 500°C in vacuum, a new phase identified as $NiCr_2O_4$ formed. It was found that black chrome failed optically between 500-600°C for 1 hour heat treatments in both air and vacuum; also the coating heated in air failed mechanically by peeling at 600°C.

INTRODUCTION

Black chrome is one of the major selective surface candidates for use as solar collector absorber coatings. Of the different types of black chrome, the commercial coating "CHROM-ONYX," a jet black finish manufactured by the Harshaw Chemical Company, has been 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 [3-6], very little as yet is known about the physics and microstructure of black chrome. Three major areas remain as fields of current research on black chrome. They are: the investigation of the physical mechanisms of selectivity, its stability upon heating and humidity (both short and long term), and the atmospheric corrosion effects upon black chrome.

However, a simplified absorption mechanism for this coating has been suggested [7] and modeled [8,9] according to Maxwell Garnet theory. Accordingly, there is need to clearly identify the actual absorption mechanism and how it is affected by various operating conditions experienced by solar collectors. It is necessary to understand the effect of stagnation events, humidity, thermal aging, vacuum and air atmospheres upon solar selectivity and stability of black chrome. The following study focuses upon two areas of research, namely the character of as-plated black chrome and the effect of short term heat treatments upon its microstructural and optical properties.

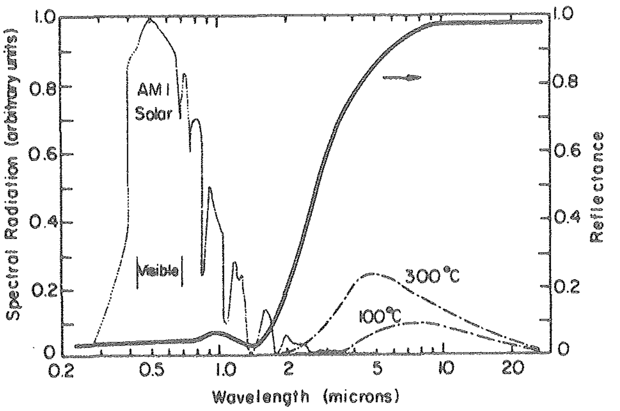
EXPERIMENTAL PROCEDURES

In this study copper test panels were electroplated with black chrome by the Harshaw Chemical Company, according to a conventional procedure. Further details of the as-plated structure and plating parameters are discussed in related research [10]. Throughout this investigation identical samples, consisting of 1.0 micron of black chrome on dull nickel plated copper, were used.

Hemispherical spectral reflectance measurements were used to investigate the optical selectivity of each sample. All reflectance measurements were performed on a Cary 14 integrating spectrophotometer for wavelength range of 0.28-1.8 microns. The measurements for the wavelength range 2.0-2.5 microns (infrared) were done on a Gier Dunkle Model HC 300 heated cavity reflectometer with a directional integrating sphere. All reflectance measurements were taken near normal (20°) incidence.

Both surface and cross sectional morphology were analyzed with the aid of an AMR 1000 scanning electron microscope (SEM). Qualitative elemental analysis was determined by energy dispersive X-ray analysis (EDAX).

Transmission electron microscopy (TEM) was employed to analyze the internal structure and chemical makeup of the coating. A Philips EM 301 research electron microscope was used for this investigation. 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



XBL 775-5462A

Figure 1. Wavelength correlation between black chrome spectral reflectance, the solar spectrum and black body spectrum (100°C, 300°C).

chrome. Metallic chromium and oxide particle distributions were revealed by use of gun tilt dark field techniques. A Zeiss particle size analyzer was used to determine the size distribution of these particles.

Heat treating experiments were carried out by one of three methods. Samples heat treated in air were annealed in dry air at 1 atmosphere in a Lindberg tube furnace. Melting point standards and continuous temperature monitoring 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. For purely mechanical strength reasons a partial pressure of argon was allowed to remain in the final encapsulated sample tubes.

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.

Spectral Reflectance Measurements

Hemispherical reflectance measurements are used to derive both absorptance, a(w,s,t) and emittance e(w,s,t) where w is a given wavelength of incident energy at a position (s,t) of the material. An example of a typical reflectance plot and its relationship to the solar spectrum and black body spectra is shown in Figure 1.

In general practice integrated values of absorptance and emittance are useful for solar collector designers. Integrated absorptance (a_i) is

TABLE 1

Integrated Absorptance and Emittance (27°)
for Heat Treated Black Chrome in Vacuum**

Heat Treatment	e_i	a_i	a_i/e_i
None, As-plated	0.12	0.93	7.75
200°C, 1 hr.	0.11	0.93	8.45
300°C, 1 hr.	0.11	0.93	8.45
400°C, 1 hr.	0.12	0.94	7.83
500°C, 1 hr.	0.08	0.92	11.5
600°C, 1 hr.	0.08	0.8	10.0

Values rounded to 2 places. **Residual atmosphere is inert gas.

TABLE 2

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

Heat Treatment	e_i	a_i	a_i/e_i
None, As-plated	0.12	0.93	7.75
200°C, 1 hr.	0.11	0.93	8.45
300°C, 1 hr.	0.09	0.93	10.3
400°C, 1 hr.	0.10	0.93	9.3
500°C, 1 hr.	0.07	0.90	12.86
600°C, 1 hr.	0.10	0.73	7.3

Values rounded to 2 places.

the average absorptance at each wavelength weighted according to the solar energy intensity distribution. Integrated emittance (e_i) is computed by taking the average emittance at each wavelength weighted according to the blackbody intensity distribution.

In Tables 1 and 2 values for a_i and e_i are tabulated for various short term heat treatments. One hour heat treatments are used for each sample. The data shown in Tables 1 and 2 is derived in part from the curves shown in Figures 2-4. For samples heat treated below 300°C the reflectance plots are fairly identical and resemble the reflectance shown in Figure 1.

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

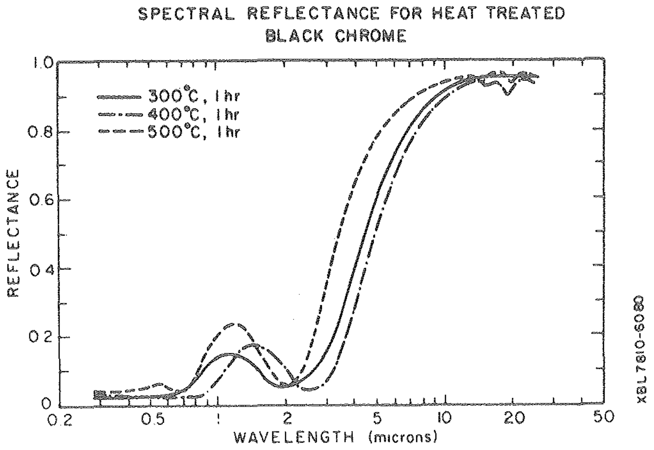


Figure 2. Spectral reflectance for black chrome heat treated in vacuum over the 300-500°C range.

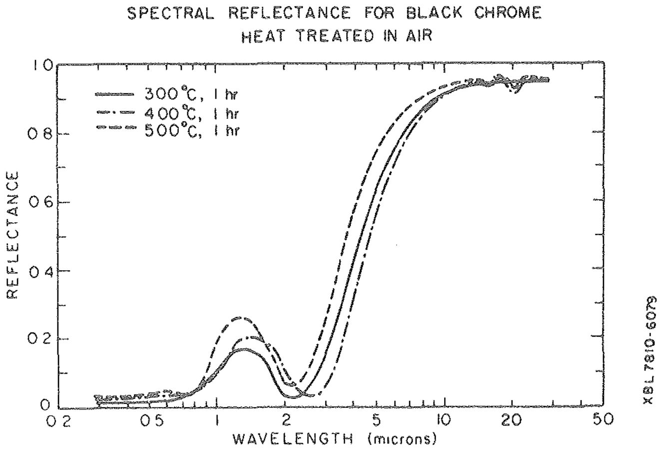


Figure 3. Spectral reflectance for black chrome heat treated in dry air over the 300-500°C range.

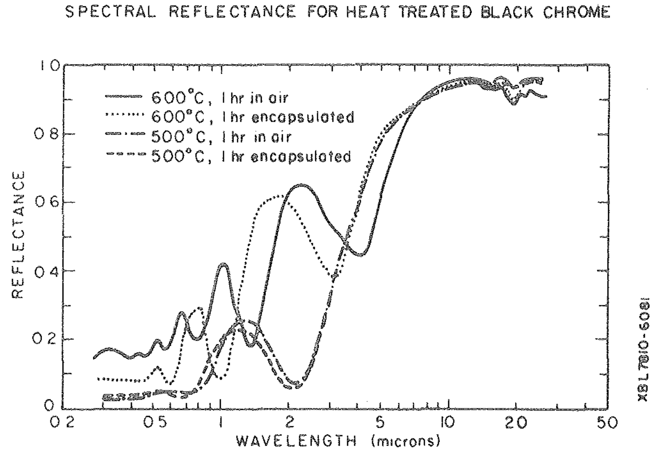


Figure 4. Spectral reflectance for both black chrome annealed in dry air and vacuum at 500, 600°C.

appears to be accelerated slightly by presence of air (Figure 4). 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 would have only a slight effect on the a_i and e_i values, as shown in Tables 1 and 2. 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.

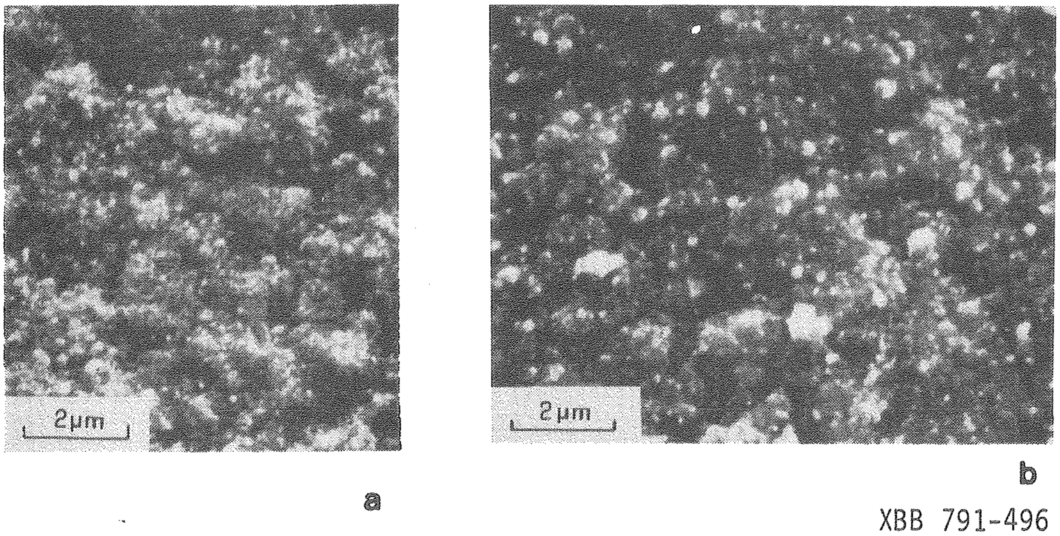
Another phenomena is observed from 300°-500°C. At 400°C a noticeable shift of the transition region (2-10 microns) occurs toward the infrared wavelengths. At 500°C this region shifts back towards the visible region, the overall shift being about 1 micron in wavelength. It is quite possible that structural 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 Cr_2O_3 [11].

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.

Scanning Electron Microscopy

Typical surface microstructures are depicted in Figure 5 for all short term heat treatments ranging from as-plated to 600°C. By comparing the as-plated structure (Figure 5a) with the 600°C sample (Figure 5b) an increase in surface roughness and particle size, including what appears to be a second phase, 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-plated to 200°C range of samples



XBB 791-496

Figure 5. Black chrome examined by SEM at 20 kV, 20° tilt after 1 hour heat treatments. (a) typical surface structure for 27°-200°C heat treated samples. (b) surface structure for 600°C heat treatment, showing formation of bright white particles.

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 Cr_2O_3), 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 significant areas 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°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 become very apparent at 600°C. These regions appear as glassy phases either in the form of black or white blotches as seen by the TEM. This failure mode will be discussed in detail elsewhere [12]. Energy Dispersive X-ray Analysis (EDAX) was performed on all samples. From this analysis the presence of chromium and nickel (from the substrate) was detected. This method does not specify whether chromium is metallic or part of a compound, or what its structural forms might be. For further analysis of the internal structure Transmission Electron Microscopy must be employed.

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 altered or heated appreciably during thinning.

As-Plated and Low Temperature Structure

A dark field photograph depicting large agglomerated composite particles containing metallic chromium particles is shown in Figure 6. The diffraction pattern reveals crystalline chromium embedded in an amorphous (a) oxide matrix, presumed to be a-Cr_2O_3. This analysis is detailed elsewhere [13]. The peak chromium particle size occurred at 72Å with a mean size of 139Å.

In Situ Vacuum Annealed Structure

The vacuum annealed structure is identical to the as-plated structure up to 400°C; starting at 400°C-500°C the appearance of crystalline, Cr_2O_3 is noted, identified from diffraction patterns in Figure 7a. No appreciable decline in chromium content is noted; some agglomeration of chromium is apparent, however. At 600°C many lines of Cr_2O_3 can be identified from the diffraction pattern (Figure 7b) along with a new phase $NiCr_2O_4$ or Cr_3O_4, a high temperature spinel. $NiCr_2O_4$ is the most probable phase since there is some doubt as to the existence of pure Cr_3O_4 [14]. These conclusions are based on 6 identified lines of Cr_2O_3, 4-6 lines of the phase identified as $NiCr_2O_4$ and 1 faint line of chrom-

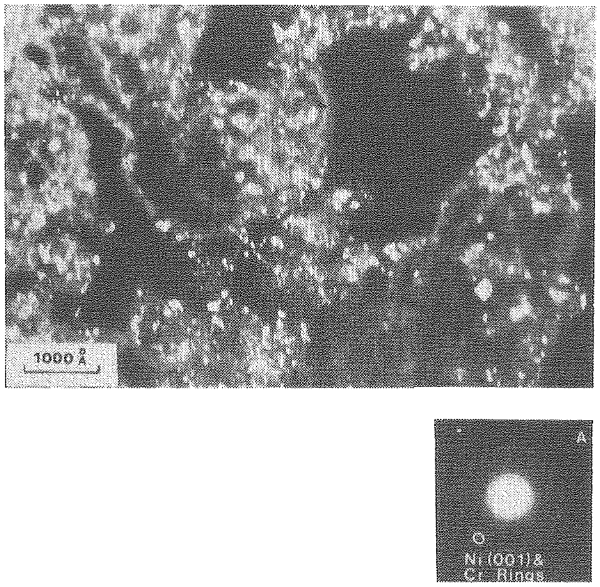


Figure 6. Agglomeration of chromium particles with matrix material viewed by TEM at 100 kV. The dark field shows metallic chromium particles as white spots. The dense black regions are holes produced by ion thinning.

XBB 774-3545C

ium at 600°C heat treatments. At even higher temperatures both phases predominate at the expense of metallic chromium which finally depletes. It is uncertain if $NiCr_2O_4$, an oxygen deficient phase, forms because it is favored thermodynamically to form in vacuum or whether Cr_2O_3 in air would be favored at high temperatures. However, this 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 8b for $NiCr_2O_4$ and Figure 8c for Cr_2O_3. This sample was heat treated at 600°C for 30 minutes. The bright field for this pair is shown in Figure 8a and diffraction pattern in Figure 7b.

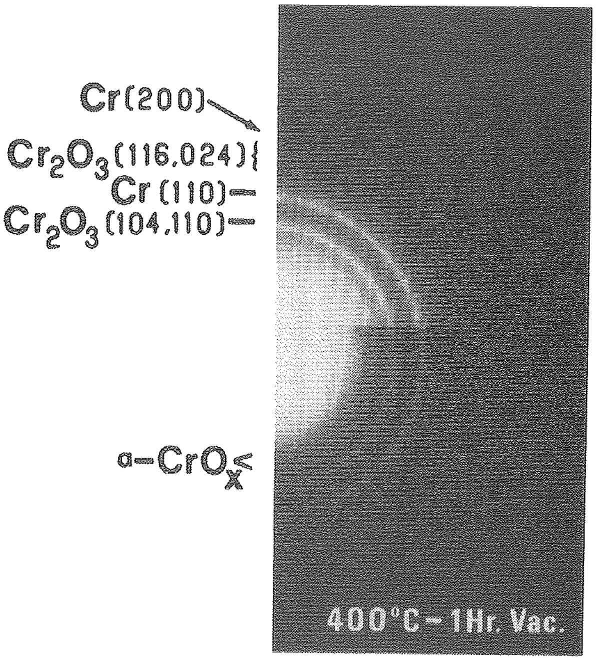
Annealing in Air

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 Cr_2O_3 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 Cr_2O_3 is aided by the presence of air, essentially lowering the transformation temperature. Effects of higher temperatures remain as a current research effort for samples annealed in air.

CONCLUSIONS

From this research the following conclusions appear to be valid for the solar selective absorber, known as CHROM-ONYX.

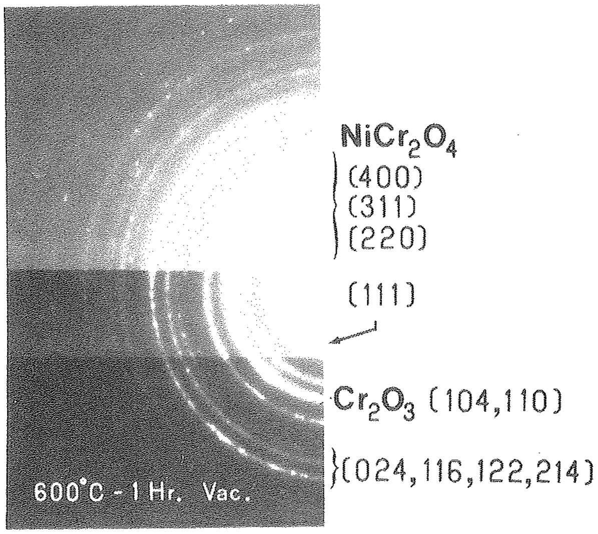
1. The as-plated structure of black chrome on dull nickel consists of voids and particulate masses within the size range of 0.05-0.30 microns in diameter. These particles are in turn composed of fine chromium



XBB 791-494

Figure 7. 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.



XBB 795-6943

(b) Annealed at 600°C. Low order $NiCr_2O_4$, Cr_2O_3 and faint Cr lines are shown.

particles (mean dia. 139Å) suspended within a matrix of amorphous Cr_2O_3.

2. After heating for a short period of time (e.g., 1 hr.) in air or vacuum, black chrome does not show appreciable degradation optically, chemically or mechanically up to 300°C.

3. 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.

4. 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.

10. C.M. Lampert and J. Washburn, Microstructure of a Black Chrome Solar Selective Absorber, Sol. Energy Mat. 1-1 (1979).

11. C.G. Granquist and G.A. Niklasson, Selective Absorption of Solar Energy in Ultrafine Chromium Particles, Appl. Phys. Lett. 31-10 (1977) 666.

12. C.M. Lampert, J. Mat. Energy Sys. (to be published).

13. C.M. Lampert, Proceedings of SPIE, vol. 161, SPIE, Bellingham, Wash. Sept. 1978.

14. H. Goldschmidt, Interstitial Alloys, Butterworths, London, 1967.

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